Quantum Gases

lectures

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October 6, 2019

Preface

When I was scheduled to give an introductory course on the physics of quantum gases I was full of ideas about what to teach. The research in this field had flourished for more than a decade and many experimental results and theoretical insights had become available. An enormous body of literature had emerged with in its wake excellent review papers, summer school lectures and books, not to mention the relation with a hand full of related Nobel prizes. So I drew my plan to teach about a selection of the wonderful advances in this field. However, already during the first lecture it became clear that at the bachelor level - even with excellent students - the common language was lacking to bring across what I wanted to teach. So, rather than pushing my own program and becoming a story teller, I decided to adapt my own ambitions to the level of the students, in particular to assure a good contact with their level of understanding of quantum mechanics and statistical physics. This resulted in a course allowing the students to digest parts of quantum mechanics and statistical physics by analyzing various aspects of the physics of the quantum gases. The course was first given in the form of 8 lectures of 1.5 hours to bachelor students at honors level in their third year of education at the University of Amsterdam. Condensed into 5 lectures and presented within a single week, the course was also given a number of times since the summer of 2006 for a group of 60 graduate students at an international predoc school organized together with Dr. Philippe Verkerk and Dr. Hélène Perrin at the *Centre de Physique des Houches* in the French Alps. In 2012 part of the course was given at the *First African Winter School* in Chlef Algeria organized by Prof. Georgi Shlyapnikov and Prof. Mohamed Benarous. A special opportunity to improve the text arose when I was invited by Prof. Markus Arndt to teach the summer semester of 2013 at the University of Vienna for an audience of mostly graduate students.

A feature of the physics education is that quantum mechanics and statistical physics are taught in "vertical courses" emphasizing the depth of the formalisms rather than the phenomenology of particular systems. The idea behind the present course is to emphasize the "horizontal" structure, maintaining the cohesion of the topic without sacrificing the contact with the elementary ingredients essential for a proper introduction. As the subject has become enormous, severe choices have to be made in the material to be covered. Thus, the entire atomic physics side of the subject, including the interaction with the electromagnetic field, is simply skipped, giving preference to aspects of the gaseous state. In this way the main goal of the course became to reach the point where the students have a good physical understanding of the nature of the ground state of a trapped quantum gas in the presence of binary interactions, including Feshbach resonances. The feedback of the students turned out to be invaluable in this respect. Rather than presuming existing knowledge I found it to be more efficient to simply reintroduce well-known concepts in the context of the discussion of specific aspects of the quantum gases. In this way a firmly based understanding and a common language developed quite naturally and prepared the students to read advanced textbooks like the one by Pitaevskii and Stringari on *Bose-Einstein Condensation* as well as many papers from the research and review literature. In its present form the course is taught in 14 oral lectures of 1.5 hours with a parallel set of exercise meetings and homework, together representing a work load of 6 EC. In this format typically a choice of 6 out of 10 chapters are covered depending on the interest of the students.

The starting point is the quasi-classical gas at low densities (Chapter 1). Emphasis is put on the presence of a trapping potential and interatomic interactions. The density and momentum distributions are derived along with some thermodynamic and collisional properties. All these aspects meet in a discussion of the principles of evaporative cooling. The limitations of the classical description is discussed by introducing the quantum resolution limit in the classical phase space. The notion of a quantum gas is introduced by comparing the thermal de Broglie wavelength with characteristic length scales of the gas: the range of the interatomic interaction, the interatomic spacing and the size of a gas cloud.

Chapter 2 is included in preparation for treating interactions. We review the quantum mechanical motion of particles in a central field potential. After deriving the radial wave equation we put it in the form of the 1D Schrödinger equation. As this is part of the standard quantum mechanics curriculum it is briefly summarized during the lectures and acts as a reference chapter for the rest of the course.

The underlying idea of Chapter 3 is that a lot can be learned about quantum gases by considering no more than two atoms confined to a finite volume. The discussion is fully quantum mechanical. It is restricted to elastic interactions and short-range potentials as well as to the low-energy limit. Particular attention is paid to the analytically solvable cases: free atoms, hard spheres and the square well and arbitrary short range potentials. The central quantities are the asymptotic phase shift and the s-wave scattering length. It is shown how the phase shift in combination with the boundary condition of the confinement volume suffices to calculate the energy of interaction between the atoms. Once this is digested the concept of pseudo potential is introduced enabling the calculation of the interaction energy by first-order perturbation theory. More importantly it enables insight in how the symmetry of the wavefunction affects the interaction energy.

Of course no introduction into the quantum gases is complete without a discussion of the relation between interatomic interactions and collisions. Therefore, we discuss in Chapter 4 the concept of the scattering amplitude as well as of the differential and total cross sections, including their relation to the scattering length. Particular attention is paid to the quantum statistics of colliding pairs demonstrating how collisions between identical particles differs from those between unlike particles. All examples are given for collisions involving only a single interatomic potential and atomic species without hyperfine interaction.

In Chapter 5 we turn to ground state atoms with more than one interaction potential. It is demonstrated how the hyperfine interaction can give rise to a coupling between these channels and thus shift the energy levels of bound states. It allows the students to understand one of the marvels of the quantum gases: the *in situ* tunability of the interatomic interaction by a field-induced Feshbach resonance. This chapter as inspired by a collaboration with Dr. Tobias Tiecke and Dr. Servaas Kokkelmans. The chapter is concluded with a simple case of coupled channels. Although one may argue that this section is a bit technical there are good reasons to include it. Weak coupling between two channels is an important problem in elementary quantum mechanics and therefore a valuable component in a course at bachelor level.

In Chapter 6 the knowledge of collisional properties is used in a simple application of the Boltzmann equation showing how to obtain the time scale on which equilibrium is reached in a dilute quasi-classical gas. Using the kinetic equation we discuss how binary quantum collisions affect the phase space distribution of a dilute gas of neutral atoms in the presence of an external potential.

Chapter 7 is included in the same spirit as Chapter 2 as an introduction into the quantum mechanics of many-body systems. We start by quantizing the single-atom states. Then, we look at pair states and introduce the concept of distinguishable and indistinguishable atoms, showing the impact of indistinguishability on the probability of occupation of already occupied states. We emphasize that even in the absence of interactions we should account for the quantum correlations between all atoms to describe a quantum gas. To handle these many-body states we introduce the occupation number representation.

At this point we turn to the quantum gases, first in the absence of interactions (Chapter 8).

Using the grand canonical ensemble we derive the Bose-Einstein and Fermi-Dirac distributions and the link to thermodynamics. In Chapter 9 we specialize to the case of Bose gases in different kinds of trapping potentials. We show how the quantum statistics gives rise to a distortion of the density profile and ultimately to the phenomenon of Bose-Einstein condensation.

In the last chapter we study the weakly-interacting Bose gas. In this chapter most of the lecture material comes together in the derivation of the Gross-Pitaevskii equation. We discuss the order parameter of the condensate and its decomposition in amplitude and phase. By studying the fluctuations of the order parameter around the stationary value we obtain the Bogoliubov excitation spectrum. We conclude with a discussion of superfluidity and topological excitations, in particular vorticity and solitons.

I thank the students who inspired me to write up this course and Dr. Mikhail Baranov who was invaluable as a sparring partner in testing my own understanding of the material and who shared with me valuable insights that appear in the text. The same holds for Dr. Li Yun who joint me in giving the course in Singapore and gave valuable feedback after critically reading the lecture notes. Special thanks go to Prof. Kai Dieckmann at the National University of Singapore for his hospitality and for offering me the opportunity to teach the full course in Singapore during the winter semester of 2014. The winter and spring of 2015 I was in Innsbruck, where in particular the interaction with Dr. Marko Cetina was valuable and enjoyable for me and helped me to include the section on narrow s-wave resonances. I thank Prof. Rudolf Grimm for the generous hospitality during my stimulating stay in his group. The text was actualized for the *School on Interaction of Light with Cold Atoms* in Sao Paolo. Being back in Innsbruck in 2017, I used the opportunity to improve Chapter 7. The present version was created during the Les Houches predoc school in 2019.

Les Houches, October 6, 2019, *Jook Walraven.*

Fundamental constants

The values given below for the fundamental physical constants correspond to the recommended values (CODATA-2018).

$\Delta\nu_{\mathrm{Cs}}$	$9\,192\,631\,770$	Hz	^{133}Cs hyperfine frequency	def
c	$299\,792\,458$	$\mathrm{m\,s^{-1}}$	speed of light in vacuum	def
h	$6.626\,070\,15 \times 10^{-34}$	$\mathrm{J\,Hz^{-1}}$	Planck constant	def
$\hbar$	$1.054\,571\,817 \cdots \times 10^{-34}$	$\mathrm{J\,s}$	Planck constant (reduced)	$\hbar = h/2\pi$
e	$1.602\,176\,634 \times 10^{-19}$	C	elementary charge	def
N_{A}	$6.022\,140\,76 \times 10^{23}$	$\mathrm{mol^{-1}}$	Avogadro constant	def
k_B	$1.380\,649 \times 10^{-23}$	$\mathrm{J\,K^{-1}}$	Boltzmann constant	def
K_{cd}	683	$\mathrm{lm\,W^{-1}}$	Luninous efficacy	def
K_J	$483\,597.8484 \cdots \times 10^{9}$	$\mathrm{Hz\,V^{-1}}$	Josephson constant	$K_J = 2e/\hbar$
R_K	$25\,812\,807\,45 \cdots$	Ω	Von Klitzing constant	$R_K = 2\pi\hbar/e^2$
R	$8.314\,464\,618 \cdots$	$\mathrm{J\,mol^{-1}K^{-1}}$	Molar gas constant	
σ	$5.670\,374\,419 \cdots \times 10^{-8}$	$\mathrm{W\,m^{-2}K^{-4}}$	Stephan-Boltzmann constant	
μ_0	$1.256\,637\,062\,12(19) \times 10^{-7}$	$\mathrm{N\,A^{-2}}$	vacuum magnetic permeability	$\mu_0 = 4\pi\alpha\hbar/e^2c$
ε_0	$8.854\,187\,8128(13). \times 10^{-12}$	$\mathrm{F\,m^{-1}}$	vacuum electric permitivity	$\varepsilon_0 = 1/\mu_0 c^2$
α	$7.297\,352\,5693(11) \times 10^{-3}$		fine-structure constant	$\alpha = e^2/4\pi\varepsilon_0\hbar c$
α^{-1}	$137.035\,999\,084(21)$		inverse fine-structure constant	$\alpha^{-1} = 4\pi\varepsilon_0\hbar c/e^2$
a_0	$0.529\,177\,210\,92(17) \times 10^{-10}$	m	Bohr radius	$a_0 = \hbar/\alpha m_e c$
m_e	$9.109\,383\,7015(28) \times 10^{-31}$	kg	electron mass	
m_p	$1.007\,276\,466\,621(53)$	m_u	proton mass	
m_p/m_e	$1836.152\,673\,43(11)$		proton-electron mass ratio	
R_∞	$1.097\,373\,156\,8160(21) \times 10^{7}$	$\mathrm{m^{-1}}$	Rydberg constant	$R_\infty = \alpha^2 m_e c/2h$
Ry	$3.289\,841\,960\,2508(64) \times 10^{15}$	Hz	Rydberg frequency	$R_\infty c$
λ_C	$3.861\,592\,6796(12) \times 10^{-13}$	m	Compton wavelength (reduced)	$\lambda_C = \hbar/m_e c = \alpha a_0$
μ_B	$9.274\,010\,0783(28) \times 10^{-24}$	$\mathrm{J\,T^{-1}}$	Bohr magneton	$\mu_B = e\hbar/2m_e$
g_e	$2.002\,319\,304\,362\,56(35)$		electron g factor [1]	$g_e = 2(1 + a_e)$
a_e	$1.159\,652\,181\,28(18) \times 10^{-3}$		electron anomaly	$a_e = \lvert\mu_e\rvert/\mu_B - 1$
m_d	$2.013\,553\,212\,745(40)$	m_u	deuteron mass	
μ_N	$5.050\,783\,699(31) \times 10^{-27}$	$\mathrm{J\,T^{-1}}$	nuclear magneton	$\mu_N = e\hbar/2m_p$
g_p	$5.585\,694\,689\,3(16)$		proton g factor	$g_p = 2\mu_p/\mu_N$
g_d	$0.857\,438\,233\,8(22)$		deuteron g factor	$g_d = 2\mu_d/\mu_N$
r_p	$0.87\,51(61) \times 10^{-15}$	m	proton rms charge radius	
m_u	$1.660\,539\,066\,60(50) \times 10^{-27}$	kg	atomic mass constant	$m_u = \frac{1}{12}m(^{12}\mathrm{C})$

[1] Here we deviate from the CODATA recommendation in which g_e is defined as a negative number.

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The quasi-classical gas at low densities

1.1 Introduction

Let us visualize a gas as a system of N atoms moving around in some volume V. Experimentally we can measure its density n and temperature T and sometimes even count the number of atoms. In a classical description we assign to each atom a position $\mathbf{r}$ as a point in *configuration space* and a momentum $\mathbf{p} = m\mathbf{v}$ as a point in *momentum space*, denoting by $\mathbf{v}$ the velocity of the atoms and by m their mass. In this way we establish the *kinetic state* of each atom as a point $s = (\mathbf{r}, \mathbf{p})$ in the 6-dimensional (product) space known as the *phase space* of the atoms. The kinetic state of the entire gas is defined as the set $\{\mathbf{r}_i, \mathbf{p}_i\}$ of points in phase space, where $i \in \{1, \cdots N\}$ is the particle index.

In any real gas the atoms interact mutually through some *interatomic potential* $\mathcal{V}(\mathbf{r}_i - \mathbf{r}_j)$. For *neutral* atoms in their electronic ground state this interaction is typically *isotropic* and *short-range.* By isotropic we mean that the interaction potential has *central symmetry*; i.e., does not depend on the relative orientation of the atoms but only on their relative distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$; short-range means that beyond a certain distance r_0 the interaction is negligible. This distance r_0 is called the *radius of action* or *range* of the potential. Isotropic potentials are also known as *central potentials.* A typical example of a short-range isotropic interaction is the *Van der Waals* interaction between inert gas atoms like helium. The interactions affect the *thermodynamics* of the gas as well as its *collisional properties.* For example they affect the relation between pressure and temperature; i.e., the thermodynamic *equation of state.* On the collisional side the interactions determine the time scale on which *thermal equilibrium* is reached.

For sufficiently low densities the behavior of the gas is governed by *binary interactions*; i.e., the probability to find three atoms simultaneously within a sphere of radius r_0 is much smaller than the probability to find only two atoms within this distance. In practice this condition is met when the mean particle separation $n^{-1/3}$ is much larger than the range r_0; i.e.,

$$nr_0^3 \ll 1. \tag{1.1}$$

In this low-density regime the atoms are said to interact *pairwise* and the gas is referred to as *dilute*.

A dilute gas is said to be *nearly ideal* or *weakly interacting* if the *collisional size* a is small[1],

$$na^3 \ll 1. \tag{1.2}$$

It is important to emphasize - right from the start - that at ultra-low temperature the length a depends strongly on the details of the interatomic potential and can differ dramatically for minor changes of this potential. Further it may or may not show a strong dependence on the collisional

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[1] Note that weakly interacting does not mean that that the potential is “shallow”. Any gas can be made weakly interacting by making the density sufficiently small.

energy. To calculate the *collision rate* as well as the *mean-free-path* traveled by an atom in between two collisions we need expressions for the *collision cross section*

$$\sigma \simeq 4\pi a^2. \tag{1.3}$$

In terms of this cross section the *mean-free-path* is given by

$$\ell = 1/n\sigma \tag{1.4}$$

and the *collision rate* is

$$\tau_c^{-1} = n\bar{v}_r\sigma. \tag{1.5}$$

Here $\bar{v}_r = \sqrt{16k_BT/\pi m}$ is the average relative atomic *speed.* In many cases estimates based on the approximation $a \simeq r_0$ are not at all bad but there are notable exceptions. For instance in the case of the low-temperature gas of hydrogen the cross section was found to be anomalously small, in the case of cesium anomalously large. Understanding of such anomalies has led to experimental methods by which, for some gases, the cross section can be tuned to essentially any value with the aid of external fields.

For any practical experiment one has to rely on methods of confinement. This necessarily limits the volume of the gas and has consequences for its behavior. Traditionally confinement is done by the walls of some vessel. This approach typically results in a gas with a density distribution which is constant throughout the volume. Such a gas is called *homogeneous.* Unfortunately, the presence of surfaces can seriously affect the behavior of a gas. Therefore, it was an enormous breakthrough when the invention of *atom traps* made it possible to arrange *wall-free confinement*. Atom traps are based on *levitation* of atoms or microscopic gas clouds in vacuum with the aid of an external potential $\mathcal{U}(\mathbf{r})$. Such potentials can be created by applying *inhomogeneous* static or dynamic electromagnetic fields, for instance a focused laser beam. Trapped atomic gases are typically strongly *inhomogeneous* as the density has to drop from its maximum value in the center of the cloud to zero (vacuum) at the "edges" of the trap. Comparing the atomic mean-free-path with the size of the cloud two density regimes are distinguished: a low-density regime where the mean-free-path exceeds the size of the cloud $\left(\ell \gg V^{1/3}\right)$ and a high density regime where $\ell \ll V^{1/3}$. In the low-density regime the gas is referred to as *free-molecular* or *collisionless.* In the opposite limit the gas is called *collisionally hydrodynamic.* Even under "collisionless" conditions collisions are essential to establish thermal equilibrium. Collisionless conditions yield the best experimental approximation to the hypothetical *ideal gas* of theoretical physics. If collisions are absent even on the time scale of an experiment we are dealing with a non-interacting assembly of atoms which may be referred to as a *non-thermal gas.*

1.2 Basic concepts

1.2.1 Hamiltonian of trapped gas with binary interactions

We consider a classical gas of N atoms in the same internal state, interacting *pairwise* through a short-range central potential $\mathcal{V}(r)$ and trapped in an external potential $\mathcal{U}(\mathbf{r})$. In accordance with the common convention the potential energies are defined such that $\mathcal{V}(r \to \infty) = 0$ and $\mathcal{U}(r_{\min}) = 0$, where $r_{\min}$ is the position of the minimum of the trapping potential. The total energy of this *single-component* gas is given by the classical hamiltonian obtained by adding all kinetic and potential energy contributions in summations over the individual atoms and interacting pairs,

$$H = \sum_i \left(\frac{p_i^2}{2m} + \mathcal{U}(\mathbf{r}_i) \right) + \frac{1}{2} {\sum_{i,j}}' \mathcal{V}(r_{ij}), \tag{1.6}$$

where the prime on the summation indicates that coinciding particle indices like $i = j$ are excluded. Here $p_i^2/2m$ is the kinetic energy of atom i with $p_i = |\mathbf{p}_i|$, $\mathcal{U}(\mathbf{r}_i)$ its potential energy in the trapping field and $\mathcal{V}(r_{ij})$ the potential energy of interaction *shared* between atoms i and j, with $i, j \in \{1, \cdots N\}$. The contributions of the internal states, chosen the same for all atoms, are not included in this expression.

Because the kinetic state $\{\mathbf{r}_i, \mathbf{p}_i\}$ of a gas cannot be determined in detail[1] we have to rely on statistical methods to calculate the properties of the gas. The best we can do experimentally is to measure the density and velocity distributions of the atoms and the fluctuations in these properties. Therefore, it suffices to have a theory describing the *probability* of finding the gas in state $\{\mathbf{r}_i, \mathbf{p}_i\}$. This is done by presuming states of equal total energy to be equally probable, a conjecture known as the *statistical principle.* The idea is plausible because for kinetic states of equal energy there is no energetic advantage to prefer one microscopic realization (*microstate*) over the other. However, the kinetic path to transform one microstate into the other may be highly unlikely, if not absent. For so-called *ergodic* systems such paths are always present. Unfortunately, in important experimental situations the assumption of *ergodicity* is questionable. In particular for trapped gases, where we are dealing with situations of quasi-equilibrium, we have to watch out for the implicit assumption of ergodicity in situations where this is not justified. This being said the statistical principle is an excellent starting point for calculating many properties of trapped gases.

1.2.2 Ideal gas limit

We may ask ourselves the question under what conditions it is possible to single out *one* atom to determine the properties of the gas. In general this will not be possible because each atom interacts with all other atoms of the gas. Clearly, in the presence of interactions it is impossible to calculate the total energy ε_i of atom i just by specifying its kinetic state $s_i = (\mathbf{r}_i, \mathbf{p}_i)$. The best we can do is write down a hamiltonian $H^{(i)}$, satisfying the condition $H = \sum_i H^{(i)}$, in which we account for the potential energy by equal sharing with the atoms of the surrounding gas,

$$H^{(i)} = H_0\left(\mathbf{r}_i, \mathbf{p}_i\right) + \frac{1}{2}\sum_j{}' \mathcal{V}(r_{ij}) \qquad \text{with } H_0\left(\mathbf{r}_i, \mathbf{p}_i\right) = \frac{p_i^2}{2m} + \mathcal{U}(\mathbf{r}_i). \tag{1.7}$$

The hamiltonian $H^{(i)}$ not only depends on the state s_i but also on the configuration $\{\mathbf{r}_j\}$ of *all atoms* of the gas. Actually, the same total energy $H^{(i)}$ of atom i can be obtained for many different configurations of the gas but knowledge of only the state s_i is not sufficient.

Importantly, because the potential has a short range, for decreasing density the energy of the probe atom $H^{(i)}$ becomes less and less dependent on the configuration of the gas. Ultimately the interactions may be neglected except for establishing thermal equilibrium. This is called the *ideal gas regime*. From a practical point of view this regime is reached if the energy of interaction ε_{int} is much smaller than the kinetic energy, $\varepsilon_{int} \ll \varepsilon_{kin} < H_0$. In Section 1.4.3 we shall derive an expression for ε_{int} showing a linear dependence on the density.

1.2.3 Quasi-classical behavior

In discussing the properties of classical gases we are well aware of the underlying quantum mechanical structure of any realistic gas. Therefore, when speaking of classical gases we actually mean *quasi-classical* gaseous behavior of a quantum mechanical system. Rather than using the classical hamiltonian and the classical equations of motion the proper description is based on the Hamilton operator and the Schrödinger equation. However, in many cases the quantization of the states of the system is of little consequence because gas clouds are typically macroscopically large and the spacing of the energy levels extremely small. In such cases gaseous systems can be accurately described by replacing the spectrum of states by a *quasi-classical continuum.*

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[1] Position and momentum cannot be determined to infinite accuracy, the states are quantized. Moreover, from any point of view the task is humbling when dealing with a large number of atoms.

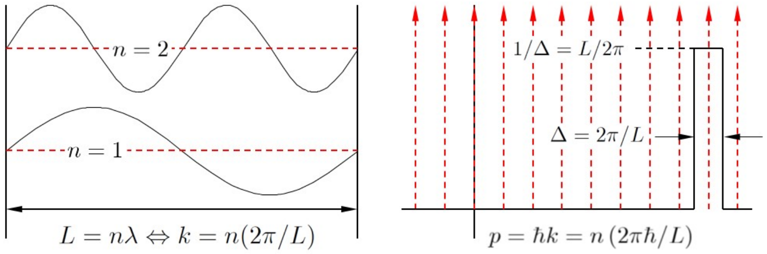

Figure 1.1: *Left*: Periodic boundary conditions illustrated for the one-dimensional case. *Right*: Periodic boundary conditions give rise to a discrete spectrum of momentum states, which may be represented by a quasi-continuous distribution if we approximate the delta function by a distribution of finite width $\Delta = 2\pi\hbar/L$ and height $1/\Delta = L/2\pi\hbar$. Note that the latter represents the density of momentum states.

Let us have a look how this continuum transition is realized. We consider an external potential $\mathcal{U}(\mathbf{r})$ representing a cubic box of length L and volume $V = L^3$ (see Fig. 1.1). Introducing periodic boundary conditions, $\psi\,(x+L, y+L, z+L) = \psi\,(x, y, z)$, the Schrödinger equation for a single atom in the box can be written as

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}\,(\mathbf{r}) = \varepsilon_k\psi_{\mathbf{k}}\,(\mathbf{r})\,, \tag{1.8}$$

where the eigenfunctions and corresponding eigenvalues are given by

$$\psi_{\mathbf{k}}\,(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}} \text{ and } \varepsilon_k = \frac{\hbar^2k^2}{2m}. \tag{1.9}$$

The $\psi_{\mathbf{k}}\,(\mathbf{r})$ represent *plane wave solutions*, normalized to the volume of the box, with $\mathbf{k}$ the *wave vector* of the atom and $k = |\mathbf{k}| = 2\pi/\lambda$ its *wave number*. The periodic boundary conditions give rise to a discrete set of wavenumbers, $k_\alpha = (2\pi/L)\,n_\alpha$ with $n_\alpha \in \{0, \pm1, \pm2, \cdots\}$ and $\alpha \in \{x, y, z\}$. The corresponding wavelength λ is the *De Broglie wavelength* of the atom. For large values of L the allowed $\mathbf{k}$ values form the quasi continuum we are looking for.

We write the momentum states of the individual atoms in the Dirac notation as $|\mathbf{p}\rangle$ and normalize the wavefunction $\psi_{\mathbf{p}}(\mathbf{r}) = \langle\mathbf{r}|\mathbf{p}\rangle$ on the quantization volume $V = L^3$,

$$\langle\mathbf{p}|\mathbf{p}\rangle = \int d\mathbf{r}|\langle\mathbf{r}|\mathbf{p}\rangle|^2 = 1. \tag{1.10}$$

For the free particle this corresponds to a discrete set of plane wave eigenstates,

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{1.11}$$

with $\mathbf{p} = \hbar\mathbf{k}$. The complete set of eigenstates $\{|\mathbf{p}\rangle\}$ satisfies the orthogonality and closure relations

$$\langle\mathbf{p}'|\mathbf{p}\rangle = \frac{1}{V}\int_V e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}/\hbar}d\mathbf{r} = \delta_{\mathbf{p},\mathbf{p}'} \qquad \text{and} \qquad \underline{1} = \sum_{\mathbf{p}}|\mathbf{p}\rangle\langle\mathbf{p}|, \tag{1.12}$$

where $\underline{1}$ is the unit operator. In the limit $L \to \infty$ the momentum $\mathbf{p}$ becomes a quasi-continuous variable and the orthogonality relation and closure relations can be written in the form

$$\langle\mathbf{p}'|\mathbf{p}\rangle = (2\pi\hbar/L)^3\,f_L(\mathbf{p}-\mathbf{p}') \qquad \text{and} \qquad \underline{1} = (L/2\pi\hbar)^3\int d\mathbf{p}\,|\mathbf{p}\rangle\langle\mathbf{p}|, \tag{1.13}$$

where $f_L(0) = (L/2\pi\hbar)^3$ is the density of momentum states and

$$\lim_{L\to\infty} f_L(\mathbf{p}-\mathbf{p}') = (2\pi\hbar)^{-3}\int e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}/\hbar}d\mathbf{r} = \delta(\mathbf{p}-\mathbf{p}'). \tag{1.14}$$

Note that the delta function has the dimension of inverse cubic momentum; the elementary volume of phase space $d\mathbf{r}d\mathbf{p}$ has the same dimension as the cubic Planck constant. Thus the continuum transition does not affect the dimension. For finite L the Eqs. (1.12) remain valid to good approximation and can be used to replace discrete state summation by the mathematically often more convenient phase-space integration

$$\sum_s \to \frac{1}{(2\pi\hbar)^3}\int d\mathbf{r}d\mathbf{p}. \tag{1.15}$$

Importantly, for finite L the distribution $f_L(\mathbf{p}-\mathbf{p}')$ does not diverge for $\mathbf{p}=\mathbf{p}'$ like a true delta function but has the finite value $(L/2\pi\hbar)^3$, which corresponds to the density of momentum states. Its width scales like $2\pi\hbar/L$ as follows by applying periodic boundary conditions to a cubic quantization volume (see Fig. 1.1).

1.2.4 Canonical distribution

In search for the properties of trapped dilute gases we ask for the probability P_s of finding an atom in a given quasi-classical state s for a trap loaded with a single-component gas of a large number of atoms ($N_{tot} \ggg 1$) at temperature T. The total energy E_{tot} of this system is given by the classical hamiltonian (1.6); i.e., $E_{tot} = H$. According to the statistical principle, the probability $P_0(\varepsilon)$ of finding the atom with energy between ε and $\varepsilon + \delta\varepsilon$ is proportional to the number $\Omega^{(0)}(\varepsilon)$ of microstates accessible to the *total* system in which the atom has such an energy,

$$P_0(\varepsilon) = C_0\Omega^{(0)}(\varepsilon), \tag{1.16}$$

with C_0 being the normalization constant. Being aware of the actual quantization of the states the number of microstates $\Omega^{(0)}(\varepsilon)$ will be a large but finite number because a trapped gas is a finite system. In accordance we shall presume the existence of a *discrete set of states* rather than the classical phase space continuum.

Restricting ourselves to the ideal gas limit, the interactions between the atom and the surrounding gas may be neglected and the number of microstates $\Omega^{(0)}(\varepsilon)$ accessible to the total system under the constraint that the atom has energy near ε must equal the *product* of the number of microstates $\Omega_1(\varepsilon)$ with energy near ε accessible to the atom with the number of microstates $\Omega(E^*)$ with energy near $E^* = E_{tot} - \varepsilon$ accessible to the rest of the gas:

$$P_0(\varepsilon) = C_0\Omega_1(\varepsilon)\,\Omega(E_{tot}-\varepsilon). \tag{1.17}$$

This expression shows that the distribution $P_0(\varepsilon)$ can be calculated by only considering the exchange of *heat* with the surrounding gas. Since the number of trapped atoms is large ($N_{tot} \ggg 1$) the heat exchanged is always small as compared to the total energy of the remaining gas, $\varepsilon \lll E^* < E_{tot}$. In this sense the remaining gas of $N^* = N_{tot} - 1$ atoms acts as a *heat reservoir* for the selected atom. The ensemble $\{s_i\}$ of microstates in which the selected atom i has energy near ε is called the *canonical ensemble.*

As we are dealing with the ideal gas limit the total energy of the atom is fully defined by its kinetic state s, $\varepsilon = \varepsilon_s$. Note that $P_0(\varepsilon_s)$ can be expressed as

$$P_0(\varepsilon_s) = \Omega_1(\varepsilon_s)\,P_s, \tag{1.18}$$

because the statistical principle requires $P_{s'} = P_s$ for all states s' with $\varepsilon_{s'} = \varepsilon_s$. Therefore, comparing Eqs. (1.18) and (1.17) we find that the probability P_s for the atom to be in a specific *state* s is given by

$$P_s = C_0 \Omega \left(E_{tot} - \varepsilon_s\right) = C_0 \Omega \left(E^*\right). \tag{1.19}$$

In general P_s will depend on E^*, N^* and the trap volume but for the case of a fixed number of atoms in a fixed trapping potential $\mathcal{U}(\mathbf{r})$ only the dependence on E^* needs to be addressed.

As is often useful when dealing with large numbers we turn to a logarithmic scale by introducing the function, $S^* = k_B \ln \Omega(E^*)$, where k_B is the *Boltzmann constant.*[1] Because $\varepsilon_s \lll E^*$ we may approximate $\ln \Omega(E^*)$ with a Taylor expansion to first order in ε_s,

$$\ln \Omega(E^*) = \ln \Omega \left(E_{tot}\right) - \varepsilon_s \left(\partial \ln \Omega(E^*)/\partial E^*\right)_{\mathcal{U},N^*}. \tag{1.20}$$

Introducing the constant $\beta \equiv \left(\partial \ln \Omega \left(E^*\right)/\partial E^*\right)_{\mathcal{U},N^*}$ we have $k_B \beta = \left(\partial S^*/\partial E^*\right)_{\mathcal{U},N^*}$ and the probability to find the atom in a specific kinetic state s of energy ε_s takes the form

$$P_s = C_0 \Omega \left(E_{tot}\right) e^{-\beta \varepsilon_s} = \frac{1}{Z_1} e^{-\beta \varepsilon_s}. \tag{1.21}$$

This is called the single-particle *canonical distribution* with normalization $\sum_s P_s = 1$. The normalization constant Z_1 is known as the single-particle *canonical partition function*

$$Z_1 = \textstyle\sum_s e^{-\beta \varepsilon_s}. \tag{1.22}$$

Note that for a truly classical system the partition sum has to be replaced by a partition integral over the phase space.

Importantly, in view of the above derivation the canonical distribution applies to *any* small subsystem (including subsystems of interacting atoms) in contact with a heat reservoir as long as it is justified to split the probability (1.16) into a product of the form of Eq. (1.17). For such a subsystem the canonical partition function is written as

$$Z = \textstyle\sum_s e^{-\beta E_s}, \tag{1.23}$$

where the summation runs over all physically different states s of energy E_s of the subsystem.

If the subsystem consists of more than one atom an important subtlety has to be addressed. For a subsystem of N identical trapped atoms one may distinguish $\Omega_N \left(E_s, s\right) = N!$ permutations yielding the same state $s = \{s_1, \cdots, s_N\}$ in the classical phase space. In quasi-classical treatments it is customary to correct for this degeneracy by dividing the probabilities P_s by the number of permutations leaving the hamiltonian (1.6) invariant.[2] This yields for the N-particle canonical distribution

$$P_s = C_0 \Omega \left(E_{tot}\right) e^{-\beta E_s} = \frac{1}{N! Z_N} e^{-\beta E_s}, \tag{1.24}$$

with the N-particle canonical partition function given by

$$Z_N = \frac{1}{N!} \textstyle\sum_s e^{-\beta E_s}. \tag{1.25}$$

where the summation runs over all physically different states s of energy E_s of the N-body subsystem. This approach may be justified in quantum mechanics as long as multiple occupation of the same

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[1] The appearance of the logarithm in the definition $S^* = k_B \ln \Omega(E)$ can be motivated as resulting from the wish to connect the statistical quantity $\Omega(E)$, which may be regarded as a *product* of single particle probabilities, to the thermodynamic quantity entropy, which is an extensive (i.e., *additive*) property. Attractively, it implies that the zero of the entropy scale is obtained for the smallest system; i.e., as system with only a single microstate.

[2] Omission of this correction gives rise to the paradox of Gibbs - see e.g. the book by Frederick Reif [60]. Arguably this famous paradox can be regarded - in hindsight - as pointing towards the modern concept of indistinguishability of identical particles [41].

single-particle state is negligible. In Section 1.4.4 we show that for a weakly interacting gas $Z_N = \left(Z_1^N/N!\right)\mathcal{J}$, with $\mathcal{J} \to 1$ in the ideal gas limit.

Interestingly, as the role of the reservoir is purely restricted to allow the exchange of heat of the small system with its surroundings, the reservoir may be replaced by any object that can serve this purpose. Therefore, in cases where a gas is confined by the walls of a vessel the expressions for the small system apply to the entire of the confined gas.

Problem 1.1. Show that for a small system of N atoms within a trapped ideal gas the rms energy fluctuation relative to the total average total energy $\overline{E}$

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{\overline{E}} = \frac{A}{\sqrt{N}}$$

decreases with the square root of the total number of atoms. Here A is a constant and $\Delta E = E - \overline{E}$ is the deviation from equilibrium. What is the physical meaning of the constant A? Hint: for an ideal gas $Z_N = \left(Z_1^N/N!\right)$.

Solution. The average energy $\overline{E} = \langle E \rangle$ and average squared energy $\left\langle E^2 \right\rangle$ of a small system of N atoms are given by

$$\begin{aligned}\langle E \rangle &= \textstyle\sum_s E_s P_s = (N! Z_N)^{-1} \sum_s E_s e^{-\beta E_s} = -\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta} = -\frac{\partial \ln Z_N}{\partial \beta} \\ \left\langle E^2 \right\rangle &= \textstyle\sum_s E_s^2 P_s = (N! Z_N)^{-1} \sum_s E_s^2 e^{-\beta E_s} = \frac{1}{Z_N}\frac{\partial^2 Z_N}{\partial^2 \beta}.\end{aligned}$$

The $\left\langle E^2 \right\rangle$ can be related to $\langle E \rangle^2$ using the expression

$$\frac{1}{Z_N}\frac{\partial^2 Z_N}{\partial^2 \beta} = \frac{\partial}{\partial \beta}\left(\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta}\right) + \frac{1}{Z_N^2}\left(\frac{\partial Z_N}{\partial \beta}\right)^2.$$

Combining the above relations we obtain for the variance of the energy of the small system

$$\left\langle \Delta E^2 \right\rangle \equiv \langle \left(E - \overline{E}\right)^2 \rangle = \left\langle E^2 \right\rangle - \langle E \rangle^2 = \partial^2 \ln Z_N / \partial^2 \beta.$$

Because the gas is ideal we may use the relation $Z_N = \left(Z_1^N/N!\right)$ to relate the average energy $\overline{E}$ and the variance $\left\langle \Delta E^2 \right\rangle$ to the single atom values,

$$\begin{aligned}\overline{E} &= -\partial N \ln Z_1 / \partial \beta = N\overline{\varepsilon} \\ \left\langle \Delta E^2 \right\rangle &= \partial^2 N \ln Z_1 / \partial^2 \beta = N \left\langle \Delta \varepsilon^2 \right\rangle.\end{aligned}$$

Taking the ratio we obtain

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{\overline{E}} = \frac{1}{\sqrt{N}}\frac{\sqrt{\langle \Delta \varepsilon^2 \rangle}}{\overline{\varepsilon}}.$$

Hence, although the rms fluctuations grow proportional to the square root of number of atoms of the small system, relative to the average total energy these fluctuations decrease with $\sqrt{N}$. The constant mentioned in the problem represents the fluctuations experienced by a single atom in the gas, $A = \sqrt{\langle \Delta \varepsilon^2 \rangle}/\overline{\varepsilon}$. In view of the derivation of the canonical distribution this analysis is only correct for $N \lll N_{tot}$ and $\overline{E} \lll E_{tot}$. □

1.2.5 Link to thermodynamic properties - Boltzmann factor

Recognizing $S^* = k_B \ln \Omega(E^*)$ as a function of $E^*, N^*, \mathcal{U}$ in which N and $\mathcal{U}$ are kept constant, we identify S^* with the *entropy* of the reservoir because the thermodynamic function also depends on the total energy, the number of atoms and the confinement volume. Thus, the most probable state of the total system is seen to correspond to the state of maximum entropy, $S^* + S = \max$, where S is the entropy of the small system. Next we recall the thermodynamic relation

$$dS = \frac{1}{T}dU - \frac{1}{T}đW - \frac{\mu}{T}dN, \tag{1.26}$$

where $đW$ is the *mechanical work* done on the small system, U its *internal energy* and μ the *chemical potential.* For homogeneous systems $đW = -pdV$ with p the *pressure* and V the volume. Since $dS = -dS^*$, $dN = -dN^*$ and $dU = -dE^*$ for conditions of maximum entropy, we identify $k_B\beta = (\partial S^*/\partial E^*)_{\mathcal{U},N^*} = (\partial S/\partial U)_{\mathcal{U},N}$ and $\beta = 1/k_BT$, where T is the temperature of the reservoir (see also problem 1.2). The subscript $\mathcal{U}$ indicates that the external potential is kept constant; i.e., no mechanical work is done on the system. For homogeneous systems it corresponds to the case of constant volume.

Comparing two kinetic states s_1 and s_2 having energies ε_1 and ε_2 and using $\beta = 1/k_BT$ we find that the ratio of probabilities of occupation is given by the *Boltzmann factor*

$$P_{s_2}/P_{s_1} = e^{-\Delta\varepsilon/k_BT}, \tag{1.27}$$

with $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$. Similarly, the N-particle canonical distribution takes the form

$$P_s = (N!Z_N)^{-1} e^{-E_s/k_BT} \tag{1.28}$$

where

$$Z_N = (N!)^{-1} \textstyle\sum_s e^{-E_s/k_BT} \tag{1.29}$$

is the N-particle canonical partition function. With Eq. (1.28) the average energy of the small N-body system can be expressed as

$$\overline{E} = \textstyle\sum_s E_s P_s = (N!Z_N)^{-1} \sum_s E_s e^{-E_s/k_BT} = k_BT^2 (\partial \ln Z_N/\partial T)_{\mathcal{U},N}. \tag{1.30}$$

Identifying $\overline{E}$ with the internal energy U of the small system we have

$$U = k_BT^2 (\partial \ln Z_N/\partial T)_{\mathcal{U},N} = T\left[\partial (k_BT \ln Z_N)/\partial T\right]_{\mathcal{U},N} - k_BT\ln Z_N. \tag{1.31}$$

Introducing the energy

$$F = -k_BT\ln Z_N \quad \Leftrightarrow \quad Z_N = e^{-F/k_BT} \tag{1.32}$$

we note that $F = U + T(\partial F/\partial T)_{\mathcal{U},N}$. Comparing this expression with the thermodynamic relation $F = U - TS$ we recognize in F the Helmholtz free energy F, which is a function of T, N and V (for inhomogeneous systems $\mathcal{U}$). Once F is known the thermodynamic properties of the small system can be obtained by combining the thermodynamic relations for changes of the free energy $dF = dU - TdS - SdT$ and internal energy $dU = đW + TdS + \mu dN$ into $dF = đW - SdT + \mu dN$,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{\mathcal{U},N} \quad \text{and} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{\mathcal{U},T}. \tag{1.33}$$

Like above, the subscript $\mathcal{U}$ indicates the absence of mechanical work done on the system. Note that the usual expression for the pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{1.34}$$

is only valid for the homogeneous gas but cannot be applied more generally before the expression for the mechanical work $đW = -pdV$ has been generalized to deal with the general case of an inhomogeneous gas. We return to this issue in Section 1.3.1.

Problem 1.2. Show that the entropy $S_{tot} = S + S^*$ of the total system of N_{tot} particles is maximum when the temperature of the small system equals the temperature of the reservoir ($\beta = \beta^*$).

Solution. With Eq. (1.17) we have for the entropy of the total system

$$S_{tot}/k_B = \ln \Omega_N(E) + \ln \Omega(E^*) = \ln P_0(E) - \ln C_0.$$

Differentiating this equation with respect to E we obtain

$$\frac{\partial S_{tot}}{k_B \partial E} = \frac{\partial \ln P_0(E)}{\partial E} = \frac{\partial \ln \Omega_N(E)}{\partial E} + \frac{\partial \ln \Omega(E^*)}{\partial E^*}\left(\frac{\partial E^*}{\partial E}\right) = \beta - \beta^*.$$

Hence $\ln P_0(E)$ and therefore also S_{tot} reaches a maximum when $\beta = \beta^*$. □

1.3 Equilibrium properties in the ideal gas limit

1.3.1 Phase-space distributions

In this Section we apply the canonical distribution (1.28) to calculate the density and momentum distributions of a classical ideal gas confined at temperature T in an atom trap characterized by the trapping potential $\mathcal{U}(\mathbf{r})$, where $\mathcal{U}(0) = 0$ corresponds to the trap minimum. In the ideal gas limit the energy of the individual atoms may be approximated by the non-interacting one-body hamiltonian

$$\varepsilon = H_0(\mathbf{r}, \mathbf{p}) = \frac{p^2}{2m} + \mathcal{U}(\mathbf{r}). \tag{1.35}$$

Note that the lowest single particle energy is $\varepsilon = 0$ and corresponds to the kinetic state $(\mathbf{r}, \mathbf{p}) = (0, 0)$ of an atom which is classically localized in the trap center. In the ideal gas limit the individual atoms can be considered as small systems in thermal contact with the rest of the gas. Therefore, the probability of finding an atom in a specific state s of energy ε_s is given by the canonical distribution (1.28), which with $N = 1$ and Z_1 takes the form $P_s = Z_1^{-1} e^{-\varepsilon_s/k_BT}$. As the classical hamiltonian (1.35) is a continuous function of $\mathbf{r}$ and $\mathbf{p}$ we obtain the expression for the quasi-classical limit by turning from the *probability* P_s of finding the atom in state s, with normalization $\sum_s P_s = 1$, to the *probability density*

$$P(\mathbf{r}, \mathbf{p}) = (2\pi\hbar)^{-3} Z_1^{-1} e^{-H_0(\mathbf{r},\mathbf{p})/k_BT} \tag{1.36}$$

of finding the atom with momentum $\mathbf{p}$ at position $\mathbf{r}$, with normalization $\int P(\mathbf{r}, \mathbf{p}) d\mathbf{p} d\mathbf{r} = 1$. Here we used the continuum transition (1.15). In this quasi-classical limit the single-particle canonical partition function takes the form

$$Z_1 = \frac{1}{(2\pi\hbar)^3} \int e^{-H_0(\mathbf{r},\mathbf{p})/k_BT} d\mathbf{p} d\mathbf{r}. \tag{1.37}$$

Note that (for a given trap) Z_1 *depends only on temperature.*

The significance of the factor $(2\pi\hbar)^{-3}$ in the context of a classical gas deserves some discussion. For this we turn to a quantity closely related to $P(\mathbf{r}, \mathbf{p})$ known as the *phase-space density*

$$n(\mathbf{r}, \mathbf{p}) = NP(\mathbf{r}, \mathbf{p}) = (2\pi\hbar)^{-3} f(\mathbf{r}, \mathbf{p}). \tag{1.38}$$

This is the number of single-atom phase points per unit volume of phase space at the location $(\mathbf{r}, \mathbf{p})$. In dimensionless form the phase-space distribution function is denoted by $f(\mathbf{r}, \mathbf{p})$. This quantity represents the *phase-space occupation* at point $(\mathbf{r}, \mathbf{p})$; i.e., the number of atoms at time t present within an elementary phase space volume $(2\pi\hbar)^3$ near the phase point $(\mathbf{r}, \mathbf{p})$. Integrating over phase space we obtain the total number of particles under the distribution

$$N = \frac{1}{(2\pi\hbar)^3} \int f(\mathbf{r}, \mathbf{p}) d\mathbf{p} d\mathbf{r}. \tag{1.39}$$

Thus, in the center of phase space we have

$$f\left(0,0\right)=\left(2\pi\hbar\right)^{3}NP\left(0,0\right)=N/Z_{1}\equiv D \tag{1.40}$$

the quantity $D\equiv N/Z_1$ is seen to be a dimensionless number representing the number of single-atom phase points per unit cubic Planck constant. Obviously, except for its dimension, the use of the Planck constant in this context is a completely arbitrary choice. It has absolutely no physical significance in the classical limit. However, from quantum mechanics we know that when D approaches unity the average distance between the phase points reaches the *quantum resolution limit* expressed by the *Heisenberg uncertainty relation.*[1] Under these conditions the gas will display deviations from classical behavior known as *quantum degeneracy* effects. The dimensionless constant D is called the *degeneracy parameter.* Note that the presence of the quantum resolution limit implies that only a finite number Ω of microstates of a given energy can be distinguished, whereas at low phase-space density the gas behaves *quasi-classically.*

Integrating the phase-space density over momentum space we find for the probability of finding an atom at position $\mathbf{r}$

$$n(\mathbf{r})=\frac{1}{(2\pi\hbar)^{3}}\int f(\mathbf{r},\mathbf{p})d\mathbf{p}=f\left(0,0\right)e^{-\mathcal{U}(\mathbf{r})/k_{B}T}\frac{1}{(2\pi\hbar)^{3}}\int_{0}^{\infty}e^{-(p/\alpha)^{2}}4\pi p^{2}dp \tag{1.41}$$

with $\alpha=\sqrt{2mk_BT}$ the *most probable momentum* in the gas. Not surprisingly, $n(\mathbf{r})$ is just the density distribution of the gas in configuration space. Rewriting Eq. (1.41) in the form

$$n(\mathbf{r})=n_{0}e^{-\mathcal{U}(\mathbf{r})/k_{B}T} \tag{1.42}$$

and using the definition (1.40) we may identify

$$n_{0}=n(0)=D/(2\pi\hbar)^{3}\int_{0}^{\infty}e^{-(p/\alpha)^{2}}4\pi p^{2}dp \tag{1.43}$$

with the density in the trap center. This density is usually referred to as the *central density*, the *maximum density* or simply the density of a trapped gas. Note that the result (1.42) is valid for both collisionless and hydrodynamic conditions as long as the ideal gas approximation is valid. Evaluating the momentum integral using (C.12) we obtain

$$\int_{0}^{\infty}e^{-(p/\alpha)^{2}}4\pi p^{2}dp=\pi^{3/2}\alpha^{3}=\left(2\pi\hbar/\Lambda\right)^{3}, \tag{1.44}$$

where

$$\Lambda\equiv[2\pi\hbar^{2}/(mk_{B}T)]^{1/2} \tag{1.45}$$

is called the *thermal De Broglie wavelength.* The interpretation of Λ as a De Broglie wavelength and the relation to spatial resolution in quantum mechanics is further discussed in Section 1.5. Substituting Eq. (1.44) into (1.43) we find that the degeneracy parameter is given by

$$D=n_{0}\Lambda^{3}. \tag{1.46}$$

The total number of atoms N in a trapped cloud is obtained by integrating the density distribution $n(\mathbf{r})$ over configuration space

$$N=\int n(\mathbf{r})d\mathbf{r}=n_{0}\int e^{-\mathcal{U}(\mathbf{r})/k_{B}T}d\mathbf{r}. \tag{1.47}$$

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[1] $\Delta x\Delta p_x\geq\frac{1}{2}\hbar$ with similar expressions for the y and z directions.

Noting that the ratio N/n_0 has the dimension of a volume we can introduce the concept of the *effective volume* of an atom cloud,

$$V_e \equiv N/n_0 = \int e^{-\mathcal{U}(\mathbf{r})/k_BT} d\mathbf{r}. \tag{1.48}$$

The effective volume of an inhomogeneous gas equals the volume of a homogeneous gas with the same number of atoms and density. Experimentally, the central density n_0 of a trapped gas is often determined with the aid of Eq. (1.48) after measuring the total number of atoms and the effective volume. Note that V_e *depends only on temperature*, whereas n_0 depends on both N and T. Recalling that also Z_1 depends only on T we look for a relation between Z_1 and V_e. Rewriting Eq. (1.40) we have

$$N = n_0 \Lambda^3 Z_1. \tag{1.49}$$

Eliminating N using Eq. (1.48) the mentioned relation is found to be

$$Z_1 = V_e \Lambda^{-3}. \tag{1.50}$$

Having defined the effective volume we can also calculate the mechanical work done when the effective volume is changed,

$$đW = -p_0 dV_e, \tag{1.51}$$

where p_0 is the pressure in the center of the trap.

Similar to the density distribution $n(\mathbf{r})$ in configuration space we can introduce a distribution $n(\mathbf{p}) = (2\pi\hbar)^{-3} \int f(\mathbf{r},\mathbf{p}) d\mathbf{r}$ in momentum space. It is more customary to introduce a distribution $P_{\mathrm{M}}(\mathbf{p})$ by integrating $P(\mathbf{r},\mathbf{p})$ over configuration space,

$$P_{\mathrm{M}}(\mathbf{p}) = \int P(\mathbf{r},\mathbf{p}) d\mathbf{r} = Z_1^{-1} \frac{e^{-(p/\alpha)^2}}{(2\pi\hbar)^3} \int e^{-\mathcal{U}(\mathbf{r})/k_BT} d\mathbf{r} = (\Lambda/2\pi\hbar)^3 e^{-(p/\alpha)^2} = \frac{e^{-(p/\alpha)^2}}{\pi^{3/2}\alpha^3}, \tag{1.52}$$

which is again a distribution with unit normalization. This distribution is known as the Maxwellian momentum distribution.

Problem 1.3. Show that the average thermal speed in an ideal gas is given by $\bar{v}_{th} = \sqrt{8k_BT/\pi m}$, where m is the mass of the atoms and T the temperature of the gas.

Solution. By definition the average thermal speed $\bar{v}_{th} = \bar{p}/m$ is related to the *first moment* of the momentum distribution,

$$\bar{p} = \frac{1}{m} \int p \, P_{\mathrm{M}}(\mathbf{p}) d\mathbf{p}.$$

Substituting Eq. (1.52) we obtain using the definite integral (C.13)

$$\bar{p} = \frac{1}{\pi^{3/2}\alpha^3} \int e^{-(p/\alpha)^2} 4\pi p^3 dp = \frac{4\alpha}{\pi^{1/2}} \int e^{-x^2} x^3 dx = \sqrt{8mk_BT/\pi}\,, \tag{1.53}$$

which is the desired result. □

Problem 1.4. Show that the average kinetic energy in an ideal gas is given by $\bar{E}_K = \frac{3}{2}k_BT$.

Solution. By definition the kinetic energy $\bar{E}_K = \overline{p^2}/2m$ is related to the *second moment* of the momentum distribution,

$$\overline{p^2} = \int p^2 P_{\mathrm{M}}(\mathbf{p}) d\mathbf{p}.$$

Substituting Eq. (1.52) we obtain using the definite integral (C.13)

$$\overline{p^2} = \frac{1}{\pi^{3/2}\alpha^3} \int e^{-(p/\alpha)^2} 4\pi p^4 dp = \frac{4\alpha^2}{\pi^{1/2}} \int e^{-x^2} x^4 dx = 3mk_BT\,, \tag{1.54}$$

which implies the desired result. □

Problem 1.5. Show that the variance in the atomic momentum around its average value in a thermal quasi-classical gas is given by

$$\left\langle (p-\bar{p})^2 \right\rangle = (3-8/\pi)\, mk_BT \simeq mk_BT/2,$$

where m is the mass of the atoms and T the temperature of the gas.

Solution. The variance in the atomic momentum around its average value can be written as

$$\left\langle (p-\bar{p})^2 \right\rangle = \left\langle p^2 \right\rangle - 2\left\langle p \right\rangle \bar{p} + \bar{p}^2 = \overline{p^2} - \bar{p}^2, \tag{1.55}$$

where $\bar{p}$ and $\overline{p^2}$ are the first and second moments of the momentum distribution. Substituting Eqs. (1.53) and (1.54) we obtain the desired result. □

1.3.2 Example: the harmonically trapped gas

As an important example we analyze some properties of a dilute gas in an isotropic *harmonic trap*. For magnetic atoms this can be realized by applying an inhomogeneous magnetic field $\mathbf{B}(\mathbf{r})$. For atoms with a magnetic moment μ this gives rise to a position-dependent Zeeman energy

$$E_Z(\mathbf{r}) = -\boldsymbol{\mu}\cdot\mathbf{B}(\mathbf{r}) \tag{1.56}$$

which acts as an effective potential $\mathcal{U}(\mathbf{r})$. For gases at low temperature, the magnetic moment experienced by a moving atom will generally follow the local field adiabatically. A well-known exception occurs near field zeros. For vanishing fields the precession frequency drops to zero and *any* change in field direction due to the atomic motion will cause in depolarization, a phenomenon known as *Majorana depolarization.* For hydrogen-like atoms, neglecting the nuclear spin, $\boldsymbol{\mu} = -2\mu_B\mathbf{S}$ and

$$E_Z(\mathbf{r}) = 2\mu_B m_s B(\mathbf{r}), \tag{1.57}$$

where $m_s = \pm 1/2$ is the *magnetic quantum number*, μ_B the *Bohr magneton* and $B(\mathbf{r})$ the modulus of the magnetic field. Hence, spin-up atoms in a harmonic magnetic field with non-zero minimum in the origin given by $B(\mathbf{r}) = B_0 + \frac{1}{2}B''(0)r^2$ will experience a trapping potential of the form

$$\mathcal{U}(r) = \tfrac{1}{2}\mu_B B''(0)r^2 = \tfrac{1}{2}m\omega^2r^2, \tag{1.58}$$

where m is the mass of the trapped atoms, $\omega/2\pi$ their oscillation frequency and r the distance to the trap center. Similarly, spin-down atoms will experience anti-trapping near the origin. For harmonically trapped gases it is useful to introduce the *thermal radius* R of the cloud, which is the distance from the trap center at which the density has dropped to $1/e$ of its maximum value,

$$n(r) = n_0 e^{-(r/R)^2}. \tag{1.59}$$

Note that for harmonic traps the density distribution of a classical gas has a *gaussian shape* in the ideal-gas limit. Comparing with Eq. (1.42) we find for the *thermal radius*

$$R = \sqrt{\frac{2k_BT}{m\omega^2}}. \tag{1.60}$$

Substituting Eq. (1.58) into Eq. (1.48) we obtain after integration for the *effective volume* of the gas

$$V_e = \int e^{-(r/R)^2} 4\pi r^2 dr = \pi^{3/2}R^3 = \left(\frac{2\pi k_BT}{m\omega^2}\right)^{3/2}. \tag{1.61}$$

Note that for a given harmonic magnetic trapping field and a given magnetic moment we have $m\omega^2 = \mu B''(0)$ and the cloud size is *independent* of the atomic mass.

Next we calculate explicitly the total energy of the harmonically trapped gas. First we consider the potential energy and calculate with the aid of Eq. (C.12)

$$E_P = \int \mathcal{U}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} = n_0 k_B T \int_0^{\infty} (r/R)^2 \, e^{-(r/R)^2} 4\pi r^2 dr = \frac{3}{2} N k_B T. \tag{1.62}$$

Similarly we calculate for the kinetic energy

$$E_K = \int \left(p^2/2m\right) n(\mathbf{p}) d\mathbf{p} = \frac{N k_B T}{\pi^{3/2} \alpha^3} \int_0^{\infty} (p/\alpha)^2 \, e^{-(p/\alpha)^2} 4\pi p^2 dp = \frac{3}{2} N k_B T. \tag{1.63}$$

Hence, the total energy is given by

$$E = 3 N k_B T. \tag{1.64}$$

Problem 1.6. An isotropic harmonic trap has the same potential energy curvature of $m\omega^2/k_B = 2000\ \mathrm{K/m^2}$ for ideal classical gases of ^{7}Li and ^{39}K.
a. Calculate the trap frequencies for these two gases.
b. Calculate the harmonic radii for these gases at the temperature $T = 10\ \mu\mathrm{K}$.

Problem 1.7. Consider a thermal cloud of atoms in a harmonic trap and in the classical ideal gas limit.
a. Is there a difference between the average speed of the atoms in the center of the cloud (where the potential energy is zero) and in the far tail of the density distribution (where the potential energy is high?
b. Is there a difference in this respect between collisionless and hydrodynamic conditions?

Problem 1.8. Derive an expression for the effective volume of an ideal classical gas in an isotropic linear trap described by the potential $\mathcal{U}(r) = u_0 r$. How does the linear trap compare with the harmonic trap for given temperature and number of atoms when aiming for high-density gas clouds?

Problem 1.9. Consider the imaging of a harmonically trapped cloud of ^{87}Rb atoms in the hyperfine state $|F = 2, m_F = 2\rangle$ immediately after switching off of the trap. If a small (1 Gauss) homogeneous field is applied along the imaging direction (z direction) the attenuation of circularly polarized laser light at the resonant wavelength $\lambda = 780$ nm is described by the Lambert-Beer relation

$$\frac{1}{I(\mathbf{r})} \frac{\partial}{\partial z} I(\mathbf{r}) = -\sigma n\left(\mathbf{r}\right),$$

where $I(\mathbf{r})$ is the intensity of the light at position $\mathbf{r}$, $\sigma = 3\lambda^2/2\pi$ is the resonant optical absorption cross section and $n\left(\mathbf{r}\right)$ the density of the cloud.
a. Show that for homogeneously illuminated low density clouds the image is described by

$$I(x, y) = I_0 \left[1 - \sigma n_2(x, y)\right],$$

where I_0 is the illumination intensity, $n_2(x, y) = \int n\left(\mathbf{r}\right) dz$. The image magnification is taken to be unity.
b. Derive an expression for $n_2(x, y)$ normalized to the total number of atoms.
c. How can we extract the gaussian $1/e$ size (R) of the cloud from the image?
d. Derive an expression for the central density n_0 of the atom cloud in terms of the absorbed fraction $A(x, y)$ in the center of the image $A_0 = \left[I_0 - I(0, 0)\right]/I_0$ and the $R_{1/e}$ radius defined by $A(0, R_{1/e})/A_0 = 1/e$.

1.3.3 Density of states

Many properties of trapped gases do not depend on the distribution of the gas in configuration space or in momentum space separately but only on the distribution of the total energy, represented by the ergodic distribution function $f(\varepsilon)$. This quantity is related to the phase-space distribution function $f(\mathbf{r},\mathbf{p})$ through the relation

$$f(\mathbf{r},\mathbf{p}) = \int d\varepsilon' \, f(\varepsilon') \, \delta[\varepsilon' - H_0(\mathbf{r},\mathbf{p})]. \tag{1.65}$$

To obtain the inverse relation we note that there are many microstates $(\mathbf{r},\mathbf{p})$ with the same energy ε and introduce the concept of the *density of states*

$$\rho(\varepsilon) \equiv (2\pi\hbar)^{-3} \int d\mathbf{r} d\mathbf{p} \, \delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})], \tag{1.66}$$

which is the number of classical states $(\mathbf{r},\mathbf{p})$ per unit phase space at a given energy ε and $H_0(\mathbf{r},\mathbf{p}) = p^2/2m + \mathcal{U}(\mathbf{r})$ is the single particle hamiltonian; note that $\rho(0) = (2\pi\hbar)^{-3}$. After integrating Eq. (1.66) over $\mathbf{p}$ the density of states takes the form[1]

$$\rho(\varepsilon) = \frac{2\pi(2m)^{3/2}}{(2\pi\hbar)^3} \int_{\mathcal{U}(\mathbf{r})\leq\varepsilon} \sqrt{\varepsilon - \mathcal{U}(\mathbf{r})} d\mathbf{r}, \tag{1.67}$$

which expresses the dependence on the potential shape. In the homogeneous case, $\mathcal{U}(\mathbf{r}) = 0$, the density of states takes the well-known form

$$\rho(\varepsilon) = \frac{4\pi m V}{(2\pi\hbar)^3} \sqrt{2m\varepsilon}, \tag{1.68}$$

where V is the volume of the system. As a second example we consider the harmonically trapped gas. Substituting Eq. (1.58) into Eq. (1.67) we find after a straightforward integration for the density of states

$$\rho(\varepsilon) = \tfrac{1}{2}(1/\hbar\omega)^3 \varepsilon^2. \tag{1.69}$$

Problem 1.10. Show the relation

$$\int d\mathbf{r} d\mathbf{p} \, f(\mathbf{r},\mathbf{p}) \delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})] = f(\varepsilon)\rho(\varepsilon) = f(\varepsilon) \int d\mathbf{r} d\mathbf{p} \, \delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})]. \tag{1.70}$$

Solution. Substituting Eq. (1.65) into the left hand side of Eq. (1.70) we obtain using the definition for the density of states

$$(2\pi\hbar)^{-3} \int d\varepsilon' \, f(\varepsilon') \int d\mathbf{r} d\mathbf{p} \, \delta[\varepsilon' - H_0(\mathbf{r},\mathbf{p})] \, \delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})] = \int d\varepsilon' \, f(\varepsilon') \, \rho(\varepsilon') \, \delta(\varepsilon - \varepsilon') = f(\varepsilon)\rho(\varepsilon).$$

□

1.3.4 Power-law traps

Let us analyze *isotropic power-law traps*. These are traps for which the potential can be written in the form

$$\mathcal{U}(\mathbf{r}) = \mathcal{U}_0 \, (r/l_{tr})^{3/\gamma} \equiv w_0 r^{3/\gamma}, \tag{1.71}$$

where γ is known as the *trap parameter*. For instance, for $\gamma = 3/2$ and $w_0 = \frac{1}{2}m\omega^2$ we have the *harmonic trap*; for $\gamma = 3$ and $w_0 = \nabla\mathcal{U}$ the *spherical linear trap*. Note that the trap coefficient can be written as $w_0 = \mathcal{U}_0 l_{tr}^{-3/\gamma}$, where $\mathcal{U}_0$ is the *trap strength* and l_{tr} the *characteristic trap size*. In the

Table 1.1: Properties of isotropic power-law traps of the type $\mathcal{U}(\mathbf{r}) = \mathcal{U}_0(r/l_{tr})^{3/\gamma}$.

	square well	harmonic trap	linear trap	square root dimple trap
w_0	$\mathcal{U}_0 l_{tr}^{-3/\gamma}$ with $\gamma \to 0$	$\frac{1}{2}m\omega^2$	$\mathcal{U}_0 l_{tr}^{-1}$	$\mathcal{U}_0 l_{tr}^{-1/2}$
γ	0	3/2	3	6
α_{PL}	$\frac{4}{3}\pi l_{tr}^3$	$\left(2\pi/m\omega^2\right)^{3/2}$	$\frac{4}{3}\pi l_{tr}^3\, 3!/\mathcal{U}_0^3$	$\frac{4}{3}\pi l_{tr}^3\, 6!/\mathcal{U}_0^6$
A_{PL}	$(m/2\pi\hbar^2)^{3/2}\alpha_{PL}/\Gamma(3/2)$	$\frac{1}{2}(1/\hbar\omega)^3$	$(m/2\pi\hbar^2)^{3/2}\alpha_{PL}/\Gamma(9/2)$	$(m/2\pi\hbar^2)^{3/2}\alpha_{PL}/\Gamma(15/2)$

limit $\gamma \to 0$ we obtain the *spherical square well.* Traps with $\gamma > 3$ are known as *spherical dimple traps.* A summary of properties of isotropic traps is given in Table 1.1.

More generally one distinguishes *orthogonal power-law traps* [4], which are represented by potentials of the type

$$\mathcal{U}(x,y,z) = w_1 |x|^{1/\gamma_1} + w_2 |y|^{1/\gamma_2} + w_3 |z|^{1/\gamma_3} \quad \text{with } \gamma = \sum_i \gamma_i, \tag{1.72}$$

where γ is again the *trap parameter.* Substituting the power-law potential (1.71) into Eq. (1.48) we calculate (see problem 1.11) for the volume

$$V_e(T) = \alpha_{PL} (k_B T)^\gamma, \tag{1.73}$$

where the coefficients α_{PL} are included in Table 1.1 for some typical cases of γ. Similarly, substituting Eq. (1.71) into Eq. (1.67) we find (see problem 1.12) for the density of states

$$\rho(\varepsilon) = A_{PL}\varepsilon^{1/2+\gamma} \text{ with } A_{PL} = \alpha_{PL}\frac{(m/2\pi\hbar^2)^{3/2}}{\Gamma(\gamma+3/2)}. \tag{1.74}$$

Also some A_{PL} coefficients are given in Table 1.1.

Problem 1.11. Show that the effective volume of an isotropic power-law trap is given by

$$V_e = \tfrac{4}{3}\pi l_{tr}^3 \Gamma(\gamma+1) (k_B T/\mathcal{U}_0)^\gamma,$$

where γ is the trap parameter and $\Gamma(z)$ is de Euler gamma function.

Solution. The effective volume is defined as $V_e = \int e^{-\mathcal{U}(r)/k_B T} d\mathbf{r}$. Substituting $\mathcal{U}(\mathbf{r}) = w_0 r^{3/\gamma}$ for the potential of an isotropic power-law trap we find with $w_0 = \mathcal{U}_0 l_{tr}^{-3/\gamma}$

$$V_e = \int e^{-w_0 r^{3/\gamma}/k_B T} 4\pi r^2 dr = \tfrac{4}{3}\pi l_{tr}^3 \gamma (k_B T/\mathcal{U}_0)^\gamma \int e^{-x} x^{\gamma-1} dx,$$

where $x = (\mathcal{U}_0/k_B T)(r/l_{tr})^{3/\gamma}$ is a dummy variable. Evaluating the integral yields the Euler gamma function $\Gamma(\gamma)$ and with $\gamma\Gamma(\gamma) = \Gamma(\gamma+1)$ provides the desired result. □

Problem 1.12. Show that the density of states of an isotropic power-law trap is given by (compare with Eq. (1.68))

$$\rho(\varepsilon) = \frac{4\pi m V_e}{(2\pi\hbar)^3}\sqrt{2m\varepsilon}\frac{\sqrt{\pi}(\varepsilon/k_B T)^\gamma}{2\,\Gamma(\gamma+3/2)}.$$

Solution. Substituting into Eq. (1.67) for the density of states the expression $\mathcal{U}(\mathbf{r}) = w_0 r^{3/\gamma}$, with $w_0 = \mathcal{U}_0 l_{tr}^{-3/\gamma}$, and introducing the dummy variable $x = \varepsilon - w_0 r^{3/\gamma}$ we find

$$\rho(\varepsilon) = \frac{2\pi(2m)^{3/2}}{(2\pi\hbar)^3}\frac{4}{3}\pi w_0^{-\gamma}\gamma \int_0^\varepsilon \sqrt{x}\,(\varepsilon - x)^{\gamma-1} dx.$$

Using the integral (C.26) this leads to the desired result. □

---

[1] Note that for isotropic momentum distributions $\int d\mathbf{p} = 4\pi \int dp\, p^2 = 2\pi(2m)^{3/2} \int d\left(p^2/2m\right)\sqrt{p^2/2m}$.

1.3.5 The harmonically trapped gas - a special case

In harmonic traps the restoring force acting on the atoms is *linear* in the distance to the trap center *irrespective* of the direction of oscillation. For this reason *harmonic oscillators* are called *linear oscillators*. As the force is linear in all directions the oscillations along the three principal axes decouple, which places the harmonic trap on a special position among the trapping potentials. Here we analyze the consequence for the effective volume and the density of states of the *anisotropic* harmonic trapping potential

$$\mathcal{U}(x,y,z) = \tfrac{1}{2}m(\omega_x^2x^2 + \omega_y^2y^2 + \omega_z^2z^2). \tag{1.75}$$

The energy levels are well known and given by

$$\varepsilon(n_x,n_y,n_z) = (n_x + \tfrac{1}{2})\hbar\omega_x + (n_y + \tfrac{1}{2})\hbar\omega_y + (n_z + \tfrac{1}{2})\hbar\omega_z. \tag{1.76}$$

(a) The effective volume is given by

$$V_e = R_xR_yR_z \int e^{-(X^2+Y^2+Z^2)}dXdYdZ, \tag{1.77}$$

where $X = \left(m\omega_x^2/2k_BT\right)^{1/2}x = x/R_x$ with similar expressions for the y and z direction. The integral is evaluated by introducing the variable R, where $R^2 = X^2 + Y^2 + Z^2$. Note that with our transformation we reduced the problem to that of the isotropic harmonic oscillator,

$$V_e = \bar{R}^3 \int_0^\infty e^{-R^2}4\pi R^2dR = \pi^{\frac{3}{2}}\bar{R}^3 = \left(2\pi k_BT/m\bar{\omega}^2\right)^{3/2}, \tag{1.78}$$

where $\bar{R} = \left(2k_BT/m\bar{\omega}^2\right)^{1/2}$ with $\bar{\omega} = (\omega_x\omega_y\omega_z)^{1/3}$. Thus we obtained the result for the isotropic harmonic oscillator with the oscillator frequency ω replaced by the geometric mean $\bar{\omega}$. Alternatively we can integrate the X, Y and Z directions explicitly,

$$V_e = \bar{R}^3 \int dR \int_0^R e^{-X^2}dX \int_0^{R-} e^{-Y^2}dY \int e^{-Z^2}dZ$$

(b) The density of states is given by

$$\rho(\varepsilon) = \frac{2\pi(2m)^{3/2}}{(2\pi\hbar)^3}\bar{R}^3 \int_{R^2\leq\varepsilon} \sqrt{\varepsilon - (X^2+Y^2+Z^2)}dXdYdZ, \tag{1.79}$$

where $X = \left(m\omega_x^2/2\right)^{1/2}x = x/U_x$ with similar expressions for the y and z direction. The integral is evaluated by introducing the variable U, where $U^2 = X^2 + Y^2 + Z^2$. Note that with our transformation we reduced the problem to that of the isotropic harmonic oscillator,

$$\rho(\varepsilon) = \frac{2\pi(2m)^{3/2}}{(2\pi\hbar)^3}\bar{U}^3 \int_{R^2\leq\varepsilon} \sqrt{\varepsilon - U^2}4\pi U^2dU, \tag{1.80}$$

In fact it is better to transform once more to the variable $u = U^2 \to du = 2UdU$,

$$\rho(\varepsilon) = \frac{4\pi^2(2m)^{3/2}}{(2\pi\hbar)^3}\bar{U}^3 \int_0^\varepsilon \sqrt{\varepsilon - u}\sqrt{u}du = \frac{4\pi^2(2m)^{3/2}}{(2\pi\hbar)^3}\bar{R}^3\frac{\pi}{4\Gamma(3)}\varepsilon^2 = \left(\frac{1}{\hbar\bar{\omega}}\right)^3 \tfrac{1}{2}\varepsilon^2, \tag{1.81}$$

where $\bar{U} = \left(2/m\bar{\omega}^2\right)^{1/2}$ with $\bar{\omega} = (\omega_x\omega_y\omega_z)^{1/3}$. Thus we obtained also in this case the result for the isotropic harmonic oscillator with the oscillator frequency ω replaced by the geometric mean $\bar{\omega}$.

1.3.6 Thermodynamic properties of a trapped gas in the ideal gas limit

The concept of the density of states is ideally suited to derive general expressions for the thermodynamic properties of an ideal classical gas confined in an arbitrary power-law potential $\mathcal{U}(\mathbf{r})$ of the type (1.72). Taking the approach of Section 1.2.5 we start by writing down the canonical partition function, which for a Boltzmann gas of N atoms is given by

$$Z_N = \frac{1}{N!}(2\pi\hbar)^{-3N}\int e^{-H(\mathbf{p}_1,\mathbf{r}_1;\cdots;\mathbf{p}_N,\mathbf{r}_N)/k_BT}d\mathbf{p}_1\cdots d\mathbf{p}_N d\mathbf{r}_1\cdots d\mathbf{r}_N. \tag{1.82}$$

In the ideal gas limit the hamiltonian is the simple sum of the single-particle hamiltonians of the individual atoms, $H_0(\mathbf{r},\mathbf{p}) = p^2/2m+\mathcal{U}(\mathbf{r})$, and the canonical partition function reduces to the form

$$Z_N = \frac{Z_1^N}{N!}. \tag{1.83}$$

Here Z_1 is the single-particle canonical partition function given by Eq. (1.37). In terms of the density of states it takes the form[1]

$$Z_1 = (2\pi\hbar)^{-3}\int\{\int e^{-\varepsilon/k_BT}\delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})]d\varepsilon\}d\mathbf{p}d\mathbf{r} = \int e^{-\varepsilon/k_BT}\rho(\varepsilon)d\varepsilon. \tag{1.84}$$

Substituting the power-law expression Eq. (1.74) for the density of states we find for power-law traps

$$Z_1 = A_{PL}\,(k_BT)^{(\gamma+3/2)}\int e^{-x}x^{(\gamma+1/2)}dx = A_{PL}\Gamma(\gamma+3/2)\,(k_BT)^{(\gamma+3/2)}\,, \tag{1.85}$$

where $\Gamma(z)$ is the Euler gamma function. For the special case of harmonic traps this corresponds to

$$Z_1 = (k_BT/\hbar\omega)^3\,. \tag{1.86}$$

First we calculate the total energy. Substituting Eq. (1.83) into Eq. (1.31) we find

$$E = Nk_BT^2\,(\partial\ln Z_1/\partial T)_{\mathcal{U},N} = (3/2+\gamma)\,Nk_BT, \tag{1.87}$$

where γ is the trap parameter defined in Eq. (1.72). For harmonic traps ($\gamma = 3/2$) we regain the result $E = 3Nk_BT$ derived previously in Section 1.3.2. Identifying the term $\frac{3}{2}k_BT$ in Eq. (1.87) with the average kinetic energy per atom we notice that the potential energy per atom in a power-law potential with trap parameter γ is given by

$$E_P = \gamma Nk_BT. \tag{1.88}$$

To obtain the thermodynamic quantities of the gas we look for the relation between Z_1 and the Helmholtz free energy F. For this we note that for a large number of atoms we may apply Stirling's approximation $N! \simeq (N/e)^N$ and Eq. (1.83) can be written in the form

$$Z_N \simeq \left(\frac{Z_1e}{N}\right)^N \quad \text{for } N \ggg 1. \tag{1.89}$$

Substituting this result into expression (1.32) we find for the Helmholtz free energy

$$F = -Nk_BT[1+\ln(Z_1/N)] \quad \Leftrightarrow \quad Z_1 = Ne^{-(1+F/Nk_BT)}. \tag{1.90}$$

As an example we derive a thermodynamic expression for the degeneracy parameter. First we recall Eq. (1.49), which relates D to the single-particle partition function,

$$D = n_0\Lambda^3 = N/Z_1. \tag{1.91}$$

---

[1] Note that $e^{-H_0(\mathbf{r},\mathbf{p})/k_BT} = \int e^{-\varepsilon/k_BT}\delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})]d\varepsilon$.

Substituting Eq. (1.90) we obtain

$$n_0\Lambda^3 = e^{1+F/Nk_BT}, \tag{1.92}$$

or, substituting $F = E - TS$, we obtain

$$n_0\Lambda^3 = \exp\left[E/Nk_BT - S/Nk_B + 1\right]. \tag{1.93}$$

Hence, we found that for *fixed* E/Nk_BT increase of the degeneracy parameter expresses the removal of entropy from the gas.

To calculate the pressure in the trap center we use Eq. (1.51),

$$p_0 = -\left(\partial F/\partial V_e\right)_{T,N}. \tag{1.94}$$

Substituting Eq. (1.50) into Eq. (1.90) the free energy can be written as

$$F = -Nk_BT[1 + \ln V_e - 3\ln\Lambda - \ln N]. \tag{1.95}$$

Thus, combining (1.94) and (1.95), we obtain for the *central pressure* the well-known expression,

$$p_0 = (N/V_e)\,k_BT = n_0k_BT. \tag{1.96}$$

Problem 1.13. Show that the chemical potential of an ideal classical gas is given by

$$\mu = -k_BT\ln(Z_1/N) \Leftrightarrow \mu = k_BT\ln(n_0\Lambda^3). \tag{1.97}$$

Solution. Starting from Eq. (1.33) we evaluate the chemical potential as a partial derivative of the Helmholtz free energy,

$$\mu = \left(\partial F/\partial N\right)_{\mathcal{U},T} = -k_BT[1 + \ln(Z_1/N)] - Nk_BT[\partial\ln(Z_1/N)/\partial N]_{\mathcal{U},T}.$$

Recalling $Z_1 = V_e\Lambda^{-3}$ we note that Z_1 does not depend on N. Evaluating the partial derivative we obtain

$$\mu = -k_BT[1 + \ln(Z_1/N)] - Nk_BT[\partial\ln(N)/\partial N]_{\mathcal{U},T} = -k_BT\ln(Z_1/N),$$

which is the requested result. □

1.3.7 Adiabatic variations of the trapping potential - adiabatic cooling

In many experiments the trapping potential is varied in time. This may be necessary to increase the density of the trapped cloud to promote collisions or just the opposite, to avoid inelastic collisions, as this results in spurious heating or in loss of atoms from the trap.

In changing the trapping potential mechanical work is done on a trapped cloud ($đW \neq 0$) changing its volume and possibly its shape but there is no exchange of *heat* between the cloud and its surroundings; i.e., the process proceeds *adiabatically* ($đQ = 0$). If, in addition, the change proceeds sufficiently slowly the temperature and pressure will change *quasi-statically* and reversing the process the gas returns to its original state; i.e., the process is *reversible*. Reversible adiabatic changes are called *isentropic* as they conserve the entropy of the gas ($đQ = TdS = 0$).[1]

In practice slow means that the changes in the thermodynamic quantities occur on a time scale long as compared to the time to randomize the atomic motion; i.e., times long in comparison to the collision time or - in the collisionless limit - the oscillation time in the trap.

---

[1] Paul Ehrenfest extended the concept of adiabatic change to the quantum mechanical case, showing that a system stays in the same energy level when the levels shift as a result of slow variations of an external potential. Note that also in this case only *mechanical* energy is exchanged between the system and its surroundings.

An important consequence of entropy conservation under slow adiabatic changes may be derived for the degeneracy parameter. We illustrate this for power-law potentials. Using Eq. (1.87) the degeneracy parameter can be written for this case as

$$n_0\Lambda^3 = \exp\left[5/2 + \gamma - S/Nk_B\right], \tag{1.98}$$

implying that $n_0\Lambda^3$ is conserved provided the cloud shape remains constant ($\gamma = $ constant). Recalling Eq. (1.45) this implies that the temperature changes with central density according to

$$T(t) = T_0\left[n_0(t)/n_0\right]^{2/3}. \tag{1.99}$$

Let us analyze what happens if we adiabatically change the power-law potential (1.71) by varying the trap strength $\mathcal{U}_0(t)$ as a function of time,

$$\mathcal{U}(\mathbf{r}) = \mathcal{U}_0(t)\left(r/l_{tr}\right)^{3/\gamma}. \tag{1.100}$$

Using Eq. (1.48) we find that in this case also the central density n_0 and the effective volume V_e become functions of time (see Problem 1.11),

$$\frac{n_0}{n_0(t)} = \frac{V_e(t)}{V_0} = \left(\frac{T(t)/T_0}{\mathcal{U}_0(t)/\mathcal{U}_0}\right)^{\gamma}. \tag{1.101}$$

Substituting this expression into Equation (1.99) we obtain

$$T(t) = T_0\left[\mathcal{U}_0(t)/\mathcal{U}_0\right]^{\gamma/(\gamma+3/2)}, \tag{1.102}$$

which shows that a trapped gas cools by reducing the trap strength in time, a process known as adiabatic cooling. Reversely, adiabatic compression gives rise to heating. Similarly we find using Eq. (1.99) that the central density will change like

$$n_0\,(t) = n_0\left[\mathcal{U}_0(t)/\mathcal{U}_0\right]^{\gamma/(1+2\gamma/3)}. \tag{1.103}$$

Using Table 1.1 we find for harmonic traps $T \sim \mathcal{U}_0^{1/2} \sim \omega$ and $n_0 \sim \mathcal{U}_0^{3/4} \sim \omega^{3/2}$; for spherical quadrupole traps $T \sim \mathcal{U}_0^{2/3}$ and $n_0 \sim \mathcal{U}_0$; for square root dimple traps $T \sim \mathcal{U}_0^{4/5}$ and $n_0 \sim \mathcal{U}_0^{6/5}$.

Interestingly, the degeneracy parameter is *not* conserved under slow adiabatic variation of the trap parameter γ. From Eq. (1.98) we see that transforming a harmonic trap ($\gamma = 3/2$) into a square root dimple trap ($\gamma = 6$) the degeneracy parameter increases by a factor $e^{9/2} \approx 90$.

Hence, increasing the trap depth $\mathcal{U}_0$ for a given trap geometry (constant l_{tr} and γ) typically results in an increase of the density. This increase is linear for the case of a spherical quadrupole trap. For harmonic traps the density increases slower than linear whereas for dimple traps the increases is faster. In the limiting case of the square well potential ($\gamma = 0$) the density is not affected as long as the gas remains trapped. The increase in density is accompanied by and increase of the temperature, leaving the degeneracy parameter D unaffected. To change D the trap *shape* (i.e., γ) has to be varied. Although in this way the degeneracy may be changed significantly [57] or even substantially [64], adiabatic variation will typically not allow to change D by more than two orders of magnitude in trapped gases.

1.4 Nearly ideal gases with binary interactions

1.4.1 Evaporative cooling and run-away evaporation

An enormous advantage of trapped gases is that one can *selectively* remove the atoms with the largest total energy. The atoms in the low-density tail of the density distribution necessarily have

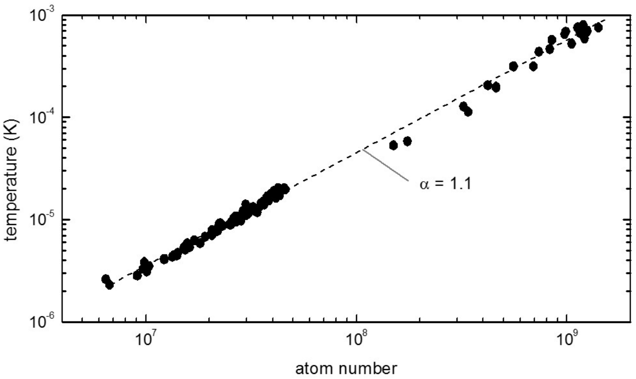

Figure 1.2: Measurement of evaporative cooling of a ^{87}Rb cloud in a Ioffe-Pritchard trap. In this example the efficiency parameter was observed to be slightly larger than unity ($\alpha = 1.1$). See further K. Dieckmann, *Thesis*, University of Amsterdam (2001).

the highest potential energy. As, in thermal equilibrium, the average momentum of the atoms is independent of the position also the average total energy of the atoms in the low-density tail is largest. This feature allows an incredibly simple and powerful cooling mechanism known as *evaporative cooling* [30, 31]. By this method the most energetic atoms are continuously removed by "evaporating off" the low-density tail of the atom cloud on a time scale slow in comparison to the *thermalization time* τ_{th}, which is the time required to achieve thermal equilibrium in the cloud. Because only a few collisions are sufficient to thermalize the atomic motion in the gas we may approximate

$$\tau_{th} \simeq \tau_c = (n_0 \bar{v}_r \sigma)^{-1}, \tag{1.104}$$

where $\bar{v}_r$ is the average relative speed given by Eq. (1.121). The finite trap depth by itself gives rise to evaporation. However in many experiments the evaporation is forced by a radio-frequency field inducing spin-flips at the edges of a spin-polarized cloud. In such cases the effective trap depth ε_{tr} can be varied without changing the shape of the trapping potential. For temperatures $k_BT \ll \varepsilon_{tr}$ the probability per thermalization time to produce an atom of energy equal to the trap depth is given by the Boltzmann factor $e^{-\eta}$, where $\eta \equiv \varepsilon_{tr}/k_BT$. Hence, the evaporation rate is approximately given by

$$-\dot{N}/N = \tau_{ev}^{-1} \simeq n_0 \bar{v}_r \sigma e^{-\eta}. \tag{1.105}$$

Not surprisingly, the evaporation rate *decreases exponentially* with η.

Let us analyze evaporative cooling for the case of a harmonic trap[1], where the total energy is given by Eq. (1.64). As the total energy can be changed by either reducing the temperature or the number of trapped atoms, the rate of change of total energy should satisfy the relation

$$\dot{E} = 3\dot{N}k_BT + 3Nk_B\dot{T}. \tag{1.106}$$

Suppose next that we continuously remove the tail of atoms of potential energy $\varepsilon_{tr} = \eta k_BT$ with $\eta \gg 1$. Under such conditions the loss rate of total energy is given by[2]

$$\dot{E} = (\eta + 1)\dot{N}k_BT. \tag{1.107}$$

---

[1] In this course we only emphasize the essential aspects of evaporative cooling. More information can be found in the reviews by W. Ketterle and N.J. van Druten [38]; C. Cohen Tannoudji, *Course 96/97 at College de France*; J.T.M. Walraven [70].

[2] Naively one might expect $\dot{E} = (\eta + 3/2)\dot{N}k_BT$. However, in the presence of evaporation the gas is out of equilibrium. The expression given here results from a kinetic analysis of evaporative cooling in the limit $\eta \to \infty$ [45].

As the energy removal is largest for large η we should evaporate as slow as possible but obviously not slower than the vacuum loss rate τ_{vac}^{-1} of the gas. Equating Eqs. (1.106) and (1.107) we obtain the relation

$$\dot{T}/T = \tfrac{1}{3}(\eta - 2)\dot{N}/N. \tag{1.108}$$

This relation shows that the temperature decreases with the number of atoms provided $\eta > 2$, which is easily arranged. The solution of Eq. (1.108) can be written as[1]

$$T/T_0 = (N/N_0)^{\alpha} \text{ with } \alpha = \tfrac{1}{3}(\eta - 2),$$

demonstrating that the temperature drops linearly with the number of atoms for $\eta = 5$ and even faster for $\eta > 5$ (see Fig.1.2).

Amazingly, although the number of atoms drops dramatically, typically by a factor 1000, the density n_0 of the gas increases! To analyze this behavior we note that $N = n_0 V_e$ and the atom loss rate should satisfy the relation $\dot{N} = \dot{n}_0 V_e + n_0 \dot{V}_e$, which can be rewritten in the form

$$\dot{n}_0/n_0 = \dot{N}/N - \dot{V}_e/V_e. \tag{1.109}$$

Substituting Eq. (1.61) for the effective volume in a harmonic trap Eq. (1.109) takes the form

$$\dot{n}_0/n_0 = \dot{N}/N - \tfrac{3}{2}\dot{T}/T, \tag{1.110}$$

and after substitution of Eq. (1.108)

$$\dot{n}_0/n_0 = \tfrac{1}{2}(4 - \eta)\,\dot{N}/N. \tag{1.111}$$

Hence, for evaporation at constant η, the density *increases* with *decreasing* number of atoms for $\eta > 4$.

The phase-space density grows even more dramatically. Using the same approach as before we write for the rate of change of the degeneracy parameter $\dot{D} = \dot{n}_0\Lambda^3 + 3n_0\Lambda^2\dot{\Lambda}$ and arrive at

$$\dot{D}/D = (3 - \eta)\,\dot{N}/N \tag{1.112}$$

This shows that the degeneracy parameter D increases with decreasing number of atoms already for $\eta > 3$.

The spectacular growth of phase-space density is illustrated in Fig.1.3.

Further, with increasing density the evaporation rate

$$\dot{N}/N = -\tau_{ev}^{-1} \simeq -n_0\bar{v}_r\sigma e^{-\eta}, \tag{1.113}$$

becomes faster and faster because the loss in thermal speed is compensated by the increase in density. We are dealing with a run-away process known as *run-away evaporative cooling*, in which the evaporation speeds up until the gas density is so high that the interactions between the atoms give rise to heating and loss processes and put a halt to the cooling. This typically happens at densities where the gas has become hydrodynamic but long before the thermodynamic properties deviate significantly from ideal gas behavior.

Interestingly, the underlying assumption of forced evaporation at *constant* η turns out to be satisfied *automatically* if the initial density n_0 is sufficiently high, which is extremely convenient from the experimental point of view. To understand this phenomenon, let us presume that the trap is ramped down exponentially at the rate

$$\dot{\varepsilon}_{tr}/\varepsilon_{tr} = -\tau_R^{-1}. \tag{1.114}$$

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[1] Eq.(1.108) is an expression between *logarithmic derivatives* ($y'/y = d\ln y/dx$) and corresponds to a straight line of slope α on a log-log plot.

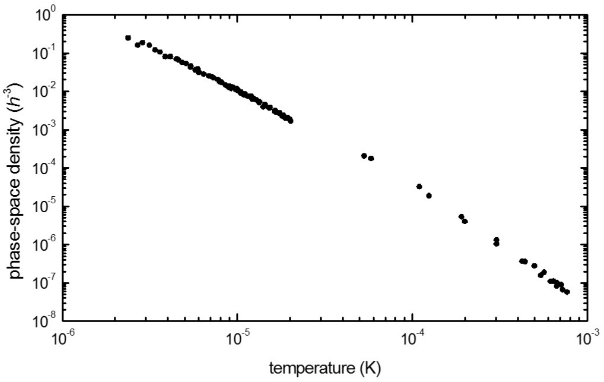

Figure 1.3: Example of the increase in phase-space density with decreasing temperature as observed with a cloud of ^{87}Rb atoms in a Ioffe-Pritchard trap. In this example the gas reaches a temperature of 2.4 μK and a phase-space density of 0.24. Further cooling results in Bose-Einstein condensation. See further K. Dieckmann, *Thesis*, University of Amsterdam (2001).

The condition for η to remain constant is

$$\dot{\eta}/\eta = \dot{\varepsilon}_{tr}/\varepsilon_{tr} - \dot{T}/T = 0. \tag{1.115}$$

For constant η we may substitute Eq. (1.108) and find

$$\dot{\eta}/\eta = -\tau_R^{-1} - \tfrac{1}{3}(\eta - 2)\,\dot{N}/N = -\tau_R^{-1} + \tfrac{1}{3}(\eta - 2)\,\tau_{ev}^{-1}, \tag{1.116}$$

which means that $\dot{\eta}/\eta = 0$ is obtained for

$$\eta = 2 + 3\,(\tau_c/\tau_R)\,e^{\eta}. \tag{1.117}$$

The second term becomes negligible if n_0 is sufficiently high. For $\tau_c = \tau_R e^{-\eta}$ the forced evaporation proceeds at constant η for $\eta = 5$. For $\tau_R = 15$ s this requires 10 collisions per second. If this collision rate is not reached the stable point shifts to larger η until the evaporation rate drops below the vacuum loss rate, which means that the gas lacks the time to rethermalize and forced evaporation turns into to spilling of trapped atoms without increase in phase-space density.

Problem 1.14. What is the minimum value for the evaporation parameter η to observe run-away evaporation in a harmonic trap?

Problem 1.15. The lifetime of ultracold gases is limited by the quality of the vacuum system and amounts to typically 1 minute in the collisionless regime. This means that evaporative cooling to the desired temperature should be completed within typically 15 seconds. Let us consider the case of ^{87}Rb in an isotropic harmonic trap of curvature $m\omega^2/k_B = 1000$ K/m^2. For $T \leq 500$ μK the cross section is given by $\sigma = 8\pi a^2$, with $a \simeq 100a_0$ ($a_0 = 0.529 \times 10^{-10}$ m is the Bohr radius).
a. Calculate the density n_0 for which the evaporation rate is $\dot{N}/N = -1$ s^{-1} at $T = 0.5$ mK and evaporation parameter $\eta = 5$.
b. What is the thermalization time under the conditions of question a?
c. Is the gas collisionless or hydrodynamic under the conditions of question a?

1.4.2 Canonical distribution for pairs of atoms

Just as in the case of a single atom we can write down the canonical distribution for pairs of atoms in a single-component classical gas of N trapped atoms. In analogy with Section 1.2.4 we argue that for $N \ggg 1$ we can split off one pair without affecting the energy E of the remaining gas significantly, $E_{tot} = E + \varepsilon$ with $\varepsilon \ll E < E_{tot}$. In view of the central symmetry of the interaction potential, the hamiltonian for the pair is best expressed in center of mass and relative coordinates (see Appendix A.7),

$$\varepsilon = H(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) = \frac{P^2}{2M} + \frac{p^2}{2\mu} + \mathcal{U}_2(\mathbf{R}, \mathbf{r}) + \mathcal{V}(r), \tag{1.118}$$

with $P^2/2M = P^2/4m$ the kinetic energy of the center of mass of the pair, $p^2/2\mu = p^2/m$ the kinetic energy of its relative motion,

$$\mathcal{U}_2(\mathbf{R}, \mathbf{r}) = \mathcal{U}(\mathbf{R} + \tfrac{1}{2}\mathbf{r}) + \mathcal{U}(\mathbf{R} - \tfrac{1}{2}\mathbf{r}) = \mathcal{U}(\mathbf{r}_1) + \mathcal{U}(\mathbf{r}_2) \tag{1.119}$$

the potential energy of trapping and $\mathcal{V}(r)$ the potential energy of interaction.

In the ideal gas limit introduced in Section 1.2.2 the pair may be regarded as a small system in thermal contact with the heat reservoir embodied by the surrounding gas. In this limit the probability to find the pair in the kinetic state $(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) \Leftrightarrow (\mathbf{p}_1, \mathbf{r}_1; \mathbf{p}_2, \mathbf{r}_2)$ is given by the canonical distribution

$$P(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) = \tfrac{1}{2}(2\pi\hbar)^{-6} Z_2^{-1} e^{-H(\mathbf{P},\mathbf{R};\mathbf{p},\mathbf{r})/k_BT}, \tag{1.120}$$

with normalization $\int P(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) d\mathbf{P} d\mathbf{R} d\mathbf{p} d\mathbf{r} = 1$. Hence the partition function for the pair is given by

$$Z_2 = \tfrac{1}{2}(2\pi\hbar)^{-6} \int e^{-H(\mathbf{P},\mathbf{R};\mathbf{p},\mathbf{r})/k_BT} d\mathbf{P} d\mathbf{R} d\mathbf{p} d\mathbf{r}.$$

The pair hamiltonian shows complete separation of the variables $\mathbf{P}$ and $\mathbf{p}$. This allows us to write in analogy with the procedure of Section 1.3.1 a unit-normalized distribution for the relative momentum

$$P_{\mathrm{M}}(\mathbf{p}) = \int P(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) d\mathbf{P} d\mathbf{R} d\mathbf{r}.$$

As an example we calculate the average relative speed between the atoms

$$\bar{v}_r = \int_0^\infty \frac{p}{\mu} P_{\mathrm{M}}(\mathbf{p}) d\mathbf{p} = \frac{1}{\mu} \frac{\int_0^\infty p e^{-(p/\alpha)^2} 4\pi p^2 dp}{\int_0^\infty e^{-(p/\alpha)^2} 4\pi p^2 dp} = \sqrt{8k_BT/\pi\mu}, \tag{1.121}$$

where where $\alpha = \sqrt{2\mu k_BT}$. Here we used the definite integrals (C.12) and (C.13) with dummy variable $x = p/\alpha$. As for a single component gas $\mu = m/2$ and we obtain $\bar{v}_r = \sqrt{2}\bar{v}_{th}$ (compare with problem 1.3)

1.4.3 Pair-interaction energy

In this section we estimate the correction to the total energy caused by the interatomic interactions in a single-component classical gas of N atoms interacting pairwise through a short-range central potential $\mathcal{V}(r)$ and trapped in an external potential $\mathcal{U}(\mathbf{r})$. In thermal equilibrium, the probability to find a pair of atoms at position $\mathbf{R}$ with the two atoms at relative position $\mathbf{r}$ is obtained by integrating the canonical distribution (1.120) over $\mathbf{P}$ and $\mathbf{p}$,

$$P(\mathbf{R}, \mathbf{r}) = \int P(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) d\mathbf{P} d\mathbf{p}, \tag{1.122}$$

normalization $\int P(\mathbf{R}, \mathbf{r}) d\mathbf{r} d\mathbf{R} = 1$. The function $P(\mathbf{R}, \mathbf{r})$ is the *two-body distribution function*,

$$P(\mathbf{R}, \mathbf{r}) = \tfrac{1}{2}(2\pi\hbar)^{-6} \int Z_2^{-1} e^{-H(\mathbf{P},\mathbf{R};\mathbf{p},\mathbf{r})/k_BT} d\mathbf{P} d\mathbf{p} = J_{12}^{-1} V_e^{-2} e^{-[\mathcal{U}_2(\mathbf{R},\mathbf{r}) + \mathcal{V}(r)]/k_BT}, \tag{1.123}$$

and V_e the effective volume of the gas as defined by Eq. (1.48). Further, we introduced the normalization integral

$$J_{12} \equiv V_e^{-2} \int e^{-[\mathcal{U}_2(\mathbf{R},\mathbf{r})+\mathcal{V}(r)]/k_BT} d\mathbf{r}d\mathbf{R} \tag{1.124}$$

as an integral over the pair configuration. The integration of Eq. (1.123) over momentum space is straightforward because the pair hamiltonian (1.118) shows complete separation of the momentum variables $\mathbf{P}$ and $\mathbf{p}$.

To evaluate the integral J_{12} we note that the short-range potential $\mathcal{V}(r)$ is everywhere zero except for short relative distances $r \lesssim r_0$. This suggests to split the configuration space for the relative position into a long-range and a short-range part by writing $e^{-\mathcal{V}(r)/k_BT} = 1 + [e^{-\mathcal{V}(r)/k_BT} - 1]$, bringing the configuration integral in the form

$$J_{12} = V_e^{-2} \int e^{-\mathcal{U}_2(\mathbf{R},\mathbf{r})/k_BT} d\mathbf{r}d\mathbf{R} + V_e^{-2} \int e^{-\mathcal{U}_2(\mathbf{R},\mathbf{r})/k_BT} \left[e^{-\mathcal{V}(r)/k_BT} - 1\right] d\mathbf{r}d\mathbf{R}. \tag{1.125}$$

The first term on the r.h.s. is a free-space integration yielding unity.[1] The argument of the second integral is only non-vanishing for $r \lesssim r_0$, where $\mathcal{U}_2(\mathbf{R},\mathbf{r}) \simeq \mathcal{U}_2(\mathbf{R},0) = 2\mathcal{U}(\mathbf{R})$. This allows us to separate the configuration integral into a product of integrals over the relative and the center of mass coordinates. Comparing with Eq. (1.47) we note that $\int e^{-2\mathcal{U}(\mathbf{R})/k_BT}\mathbf{dR} = V_e(T/2) \equiv V_{2e}$ is the effective volume for the distribution of pairs; hence, the configuration integral can be written as

$$J_{12} = 1 + v_{int} V_{2e}/V_e^2, \tag{1.126}$$

where

$$v_{int} \equiv \int \left[e^{-\mathcal{V}(r)/k_BT} - 1\right] 4\pi r^2 dr \equiv \int [g(r) - 1]\, 4\pi r^2 dr \tag{1.127}$$

is the *interaction volume.* The function $f(r) = [g(r) - 1]$ is called the *pair correlation function* and $g(r) = e^{-\mathcal{V}(r)/k_BT}$ the classical *radial distribution function* of the pair.

The trap-averaged interaction energy of the pair is given by

$$\bar{\mathcal{V}} \equiv \int \mathcal{V}(r) P(\mathbf{R},\mathbf{r}) d\mathbf{r}d\mathbf{R} = J_{12}^{-1} V_e^{-2} \int \mathcal{V}(r) e^{-[\mathcal{U}_2(\mathbf{R},\mathbf{r})+\mathcal{V}(r)]/k_BT} d\mathbf{r}d\mathbf{R}. \tag{1.128}$$

In the numerator the integrals over $\mathbf{R}$ and $\mathbf{r}$ separate because the argument of the integral is only non-vanishing for $r \lesssim r_0$ and like above we may approximate $\mathcal{U}_2(\mathbf{R},\mathbf{r}) \simeq 2\mathcal{U}(\mathbf{R})$. As a result Eq. (1.128) reduces to

$$\bar{\mathcal{V}} = V_e^{-2} \int e^{-2\mathcal{U}(\mathbf{R})/k_BT} d\mathbf{R}\, J_{12}^{-1} \int \mathcal{V}(r) e^{-\mathcal{V}(r)/k_BT} d\mathbf{r} \simeq k_BT^2 \frac{\partial \ln J_{12}}{\partial T}, \tag{1.129}$$

which is readily verified by substituting Eq. (1.126). The approximate expression becomes exact for the homogeneous case, where the effective volumes are temperature independent. However, also for inhomogeneous gases the approximation will be excellent as long as the density distribution may be considered homogeneous over the range r_0 of the interaction; i.e., as long as $r_0^3/V_e \ll 1$. The integral

$$\tilde{U} \equiv \int \mathcal{V}(r) e^{-\mathcal{V}(r)/k_BT} d\mathbf{r} = \int \mathcal{V}(r) g(r) d\mathbf{r} \tag{1.130}$$

is called the *strength of the interaction*. In terms of this interaction strength the trap-averaged interaction energy is given by

$$\bar{\mathcal{V}} = \frac{1}{J_{12}} \frac{V_{2e}}{V_e^2} \tilde{U}.$$

---

[1] Note that $\int e^{-\mathcal{U}_2(\mathbf{R},\mathbf{r})/k_BT} d\mathbf{r}d\mathbf{R} = \int e^{-\mathcal{U}(\mathbf{r}_1)/k_BT} d\mathbf{r}_1 e^{-\mathcal{U}(\mathbf{r}_2)/k_BT} d\mathbf{r}_2 = V_e^2$ because the Jacobian of the transformation $d\mathbf{r}d\mathbf{R} = \left|\frac{\partial(\mathbf{r},\mathbf{R})}{\partial(\mathbf{r}_1,\mathbf{r}_2)}\right| d\mathbf{r}_1 d\mathbf{r}_2$ is unity (see Problem A.3).

In Eq. (1.130) the interaction strength is expressed for *thermally* distributed pairs of classical atoms. More generally the volume integral (1.130) may serve to calculate the interaction strength whenever the $g(r)$ is known, including non-equilibrium conditions.

To obtain the total energy of interaction of the gas we have to multiply the trapped-averaged interaction energy with the number of pairs,

$$E_{int} = \tfrac{1}{2}N(N-1)\bar{\mathcal{V}}. \tag{1.131}$$

Presuming $N \gg 1$ we may approximate $N(N-1)/2 \simeq N^2/2$ and using definition (1.48) to express the effective volume in terms of the maximum density of the gas, $V_e = N/n_0$, we obtain for the interaction energy per atom

$$\varepsilon_{int} = E_{int}/N = \frac{1}{2}\frac{V_{2e}}{J_{12}V_e}n_0\tilde{U}. \tag{1.132}$$

Note that V_e/V_{2e} is a dimensionless constant for any power law trap. For a homogeneous gas $V_e/V_{2e} = 1$ and under conditions where $v_{int} \ll V_e$ we have $J_{12} \simeq 1$.

As discussed in Section 1.2.2 ideal gas behavior is obtained for $\varepsilon_{int} \ll \varepsilon_{kin}$. This condition may be rephrased in the present context by limiting the ideal gas regime to densities for which

$$n|\tilde{U}| \ll k_B T. \tag{1.133}$$

Problem 1.16. Show that the trap-averaged interaction energy per atom as given by Eq. (1.132) can be obtained by averaging the local interaction energy per atom $\varepsilon_{int}(\mathbf{r}) \equiv \frac{1}{2}n(\mathbf{r})\tilde{U}$ over the density distribution,

$$\varepsilon_{int} = \frac{1}{N}\int \varepsilon_{int}(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r}.$$

Solution. Substituting $n(\mathbf{r}) = n_0 e^{-\mathcal{U}(\mathbf{r})/k_B T}$ and using $V_e = N/n_0$ we obtain

$$\frac{1}{N}\int \varepsilon_{int}(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r} = \tfrac{1}{2}\frac{n_0^2}{N}\tilde{U}\int e^{-2\mathcal{U}(\mathbf{r})/k_B T} d\mathbf{r} = \tfrac{1}{2}\frac{V_{2e}}{V_e}n_0\tilde{U}. \qquad \square$$

Problem 1.17. Show that for a harmonically trapped dilute gas

$$V_{2e}/V_e = V_e(T/2)/V_e(T) = (1/2)^{3/2}. \tag{1.134}$$

Solution. The result follows directly with Eq. (1.48). □

1.4.3.1 Example: Van der Waals interaction

As an example we consider a power-law potential consisting of a hard core of radius r_c and a $\sim 1/r^6$ attractive tail (see Fig. 1.4),

$$\mathcal{V}(r) = \infty \text{ for } r \le r_c \text{ and } \mathcal{V}(r) = -C_6/r^6 \text{ for } r > r_c, \tag{1.135}$$

where $C_6 = \mathcal{V}_0 r_c^6$ is the Van der Waals coefficient, with $\mathcal{V}_0 \equiv |\mathcal{V}(r_c)|$ the well depth. Like the well-known *Lennard-Jones* potential this potential is an example of a *Van der Waals* potential, named such because it gives rise to the *Van der Waals equation of state* (see Section 1.4.5). Note that the model potential (1.135) gives rise to an *excluded volume* $b = \frac{4}{3}\pi r_c^3$ around each atom where no other atoms can penetrate.

In the high temperature limit, $k_B T \gg \mathcal{V}_0$, we have

$$\tilde{U} = \int \mathcal{V}(r)e^{-\mathcal{V}(r)/k_B T}d\mathbf{r} \simeq \int_{r_c}^{\infty} \mathcal{V}(r)4\pi r^2 dr = -4\pi r_c^3\mathcal{V}_0\int_1^{\infty} 1/x^4 dx = -b\mathcal{V}_0, \tag{1.136}$$

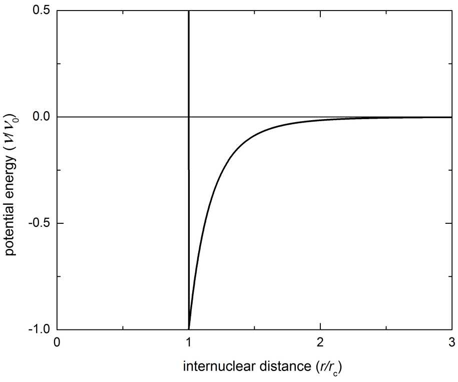

Figure 1.4: Model potential with hard core of diameter r_c and Van der Waals tail.

where $x = r/r_c$ is a dummy variable. Note that the integral only converges for power-law potentials falling-off faster than $1/r^3$ for increasing r; i.e., short-range potentials. The trap-averaged interaction energy (1.132) is given by

$$\varepsilon_{int} = \tfrac{1}{2}\frac{V_{2e}}{V_e} n_0 \tilde{U}. \tag{1.137}$$

For completeness we verify that the interaction volume is indeed small; i.e.,

$$v_{int} \equiv \int_{r_c}^{\infty}\left[e^{-\mathcal{V}(r)/k_BT}-1\right]4\pi r^2 dr \simeq -\frac{1}{k_BT}\int_{r_c}^{\infty}\mathcal{V}(r)4\pi r^2 dr = b\frac{\mathcal{V}_0}{k_BT} \ll V_e. \tag{1.138}$$

This is the case if $k_BT \gg (b/V_e)\,\mathcal{V}_0$. The latter is satisfied because $b/V_e \ll 1$ and Eq. (1.136) was obtained for temperatures $k_BT \gg \mathcal{V}_0$.

1.4.4 Canonical partition function for a nearly ideal gas

To obtain the thermodynamic properties in the low-density limit we consider a small fraction of the gas consisting of $N \ll N_{tot}$ atoms. The canonical partition function for this gas sample is given by

$$Z_N = \frac{1}{N!}(2\pi\hbar)^{-3N}\int e^{-H(\mathbf{p}_1,\mathbf{r}_1;\cdots;\mathbf{p}_N,\mathbf{r}_N)/k_BT} d\mathbf{p}_1\cdots d\mathbf{p}_N d\mathbf{r}_1\cdots d\mathbf{r}_N. \tag{1.139}$$

After integration over momentum space, which is straightforward because the pair hamiltonian (1.118) shows complete separation of the momentum variables $\{\mathbf{p}_i\}$, we obtain

$$Z_N = \frac{1}{N!}\Lambda^{-3N}\int e^{-U(\mathbf{r}_1,\cdots,\mathbf{r}_N)/k_BT} d\mathbf{r}_1\cdots d\mathbf{r}_N = \frac{Z_1^N}{N!}\mathcal{J}, \tag{1.140}$$

where we substituted the single-atom partition function (1.50) and introduced the configuration integral

$$\mathcal{J} \equiv V_e^{-N}\int e^{-U(\mathbf{r}_1,\cdots,\mathbf{r}_N)/k_BT} d\mathbf{r}_1\cdots d\mathbf{r}_N, \tag{1.141}$$

with

$$U(\mathbf{r}_1,\cdots,\mathbf{r}_N) = \sum_i \mathcal{U}(\mathbf{r}_i) + \sum_{i<j}\mathcal{V}(r_{ij}). \tag{1.142}$$

Restricting ourselves to the nearly ideal limit where the gas consists of free atoms and distinct pairs (i.e., atoms and pairs not overlapping with other atoms) we can integrate the configuration integral over all $\mathbf{r}_k$ with $k \neq i$ and $k \neq j$ and obtain[1]

$$\mathcal{J} = (1 - Nb/V_e)^{N-2} \prod_{i<j} J_{ij}, \tag{1.143}$$

where $J_{ij} = V_e^{-2} \int e^{-[\mathcal{U}(\mathbf{r}_i)+\mathcal{U}(\mathbf{r}_j)+\mathcal{V}(r_{ij})]/k_BT} d\mathbf{r}_i d\mathbf{r}_j$ and Nb is the *excluded volume* due to the hard cores of the potentials of the surrounding atoms. The canonical partition function takes the form

$$Z_N = \frac{Z_1^N}{N!} (1 - Nb/V_e)^{N-2} J_{12}^{N(N-1)/2}. \tag{1.144}$$

1.4.5 Example: Van der Waals gas

As an example we consider the high-temperature limit, $k_BT \gg \mathcal{V}_0$, of a harmonically trapped gas of atoms interacting pairwise through the model potential (1.135). In view of Eq. (1.144) the essential ingredients for the calculation of the thermodynamic properties are the excluded volume $b = \frac{4}{3}\pi r_c^3$ and the configuration integral $J_{12} = 1 + v_{int}V_{2e}/V_e^2$ with interaction volume $v_{int} = b\mathcal{V}_0/k_BT$. Substituting these ingredients into Eq. (1.144) we have for the canonical partition function of a nearly ideal gas in the high-temperature limit

$$Z_N = \frac{Z_1^N}{N!} \left(1 - N\frac{b}{V_e}\right)^N \left(1 + \frac{b}{V_e}\frac{V_{2e}}{V_e}\frac{\mathcal{V}_0}{k_BT}\right)^{N^2/2}. \tag{1.145}$$

Here we used $N - 2 \simeq N$ and $N(N-1)/2 \simeq N^2/2$, which is allowed for $N \gg 1$. For power-law traps V_{2e}/V_e is a constant ratio, independent of the temperature.

To obtain the equation of state we start with Eq. (1.33),

$$p_0 = -\left(\partial F/\partial V_e\right)_{T,N} = k_BT \left(\partial \ln Z_N/\partial V_e\right)_{T,N}. \tag{1.146}$$

Then using Eq. (1.50) we obtain for the *pressure* under physical conditions such that $(b/V_e)\,\mathcal{V}_0 \ll k_BT$ and $Nb \ll V_e$

$$p_0 = k_BT\left(\frac{N}{V_e} + b\frac{N^2}{V_e^2} - b\frac{N^2}{V_e^2}\frac{\mathcal{V}_0}{k_BT}\frac{V_{2e}}{V_e}\right). \tag{1.147}$$

This expression may be written in the form

$$\frac{p_0}{n_0k_BT} = 1 + B(T)n_0, \tag{1.148}$$

where

$$B(T) \equiv b[1 - (1/2)^{3/2}\,\mathcal{V}_0/k_BT] = b + (V_{2e}/V_e)\,\tilde{U}/k_BT \tag{1.149}$$

is known as the *second virial coefficient.* For the harmonic trap $V_{2e}/V_e = (1/2)^{3/2}$. Note that $B(T)$ is positive for $k_BT \gg \mathcal{V}_0$, decreasing with decreasing temperature. Not surprisingly, comparing the nearly ideal gas with the ideal gas at equal density we find that the excluded volume gives rise to a higher pressure. Approximating

$$\frac{1}{V_e} + b\frac{N}{V_e^2} \simeq \frac{1}{V_e - Nb}, \tag{1.150}$$

we can bring Eq. (1.147) in the form of the *Van der Waals equation of state*,

$$\left(p_0 + a\frac{N^2}{V_e^2}\right)(V_e - Nb) = Nk_BT, \tag{1.151}$$

where $a = -\left(V_{2e}/V_e\right)\tilde{U} = b\left(V_{2e}/V_e\right)\mathcal{V}_0$ is a positive constant. This famous equation of state was the first expression containing the essential ingredients to describe the *gas to liquid phase transition*

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[1] This amounts to retaining only the leading terms in a cluster expansion.

for decreasing temperatures - see e.g. [60]. For the physics of ultracold gases it implies that weakly interacting classical gases *cannot exist in thermal equilibrium* at low temperature.

The internal energy of the Van der Waals gas is obtained by starting from Eq. (1.30),

$$U = k_B T^2 \left(\partial \ln Z_N / \partial T\right)_{\mathcal{U},N}. \tag{1.152}$$

Then using Eqs. (1.144) and (1.129) we find for $k_B T \gg \mathcal{V}_0$

$$U = k_B T^2 \left(3\frac{N}{T} + \frac{N^2}{2} \frac{\partial \ln J_{12}}{\partial T} \right) = 3N k_B T + \tfrac{1}{2} N^2 \bar{\mathcal{V}}. \tag{1.153}$$

A similar result may be derived for weakly interacting quantum gases under *quasi-equilibrium* conditions near the absolute zero of temperature.

1.5 Thermal wavelength and characteristic length scales

In this chapter we introduced the quasi-classical gas at low density. The central quantity of such gases is the distribution in phase space. Aiming for the highest possible phase-space densities we found that this quantity can be increased by evaporative cooling. This is important when searching for quantum mechanical limitations to the classical description. The quasi-classical approach breaks down when we reach the quantum resolution limit, in dimensionless units defined as the point where the degeneracy parameter $D = n\Lambda^3$ reaches unity. For a given density this happens at sufficiently low temperature. On the other hand, when taking into account the interactions between the atoms we found that we have to restrict ourselves to sufficiently high-temperatures to allow the existence of a weakly interacting quasi-classical gas under equilibrium conditions. This approach resulted in Van der Waals equation of state. It cannot be extended to low temperatures because under such conditions the Van der Waals equation of state gives rise to liquid formation. Hence, the question arises: *what allows the existence of a quantum gas*? The answer lies enclosed in the quantum mechanical motion of interacting atoms at low-temperature.

In quantum mechanics the atoms are treated as atomic *matter waves*, with a wavelength λ_{dB} known as the *De Broglie wavelength.* For a free atom in a plane wave eigenstate the momentum is given by $\mathbf{p} = \hbar\mathbf{k}$, where $k = |\mathbf{k}| = 2\pi/\lambda_{dB}$ is the *wave number.* However, in general the atom will not be in a momentum eigenstate but in some linear combination of such states. Therefore, we better visualize the atoms in a thermal gas as wavepackets composed of the thermally available momenta.

From elementary quantum mechanics we know that the uncertainty in position Δx (i.e., the spatial resolution) is related to the uncertainty in momentum Δp through the Heisenberg uncertainty relation $\Delta p \Delta x \simeq \hbar$. Substituting

$$\Delta p = [\langle (p - \bar{p})^2 \rangle]^{1/2} \simeq [m k_B T/2]^{1/2} \tag{1.154}$$

for the rms momentum spread around the average momentum in a thermal gas (see Problem 1.5), the uncertainty in position is given by

$$\Delta l \simeq \hbar/\Delta p = [2\hbar^2/(m k_B T)]^{1/2}. \tag{1.155}$$

The quantum resolution limit is reached when Δl approaches the interatomic spacing,

$$\Delta l \simeq n_0^{-1/3}. \tag{1.156}$$

Because, roughly speaking, $\Delta p \simeq \bar{p}$ we see that Δl is of the same order of magnitude as the De Broglie wavelength of an atom moving with the average momentum of the gas. Being a statistical quantity Δl depends on temperature and is therefore known as a *thermal wavelength.* Not surprisingly, the precise definition of the resolution limit is a matter of taste, just like in optics. The common convention is to define the quantum resolution limit as the point where the degeneracy parameter $D = n_0\Lambda^3$ becomes unity. Here Λ is the *thermal* De Broglie wavelength introduced in Section 1.3.1 (note that Λ and Δl coincide within a factor of order 2). The quasi-classical description of a gas breaks down when the quantum resolution limit is reached. Hence, many-body quantum behavior emerges for

$$n\Lambda^3 \lesssim 1. \tag{1.157}$$

For a given density this happens at sufficiently low temperature. At elevated temperatures Λ will be smaller than any of the relevant length scales of the gas:

- the size of the gas cloud $V^{1/3}$
- the average interatomic distance $n^{-1/3}$
- the range r_0 of the interatomic potential.

Under such conditions the classical description is adequate.

Non-degenerate quantum gases: For decreasing temperatures the thermal wavelength grows. First it will exceed the range of the interatomic potential ($\Lambda > r_0$) and quantum mechanics will manifest itself in *binary* scattering events. As we show in the Chapter 3, the interaction energy due to binary interaction can be *positive* down to $T = 0$, *irrespective of the depth of the interaction potential.* This implies a positive pressure in the low-density low-temperature limit; i.e., *unbound states.* Normally this will be a gaseous state but also Wigner-solid-like states are conceivable. In all cases these states are *metastable.* With increasing density, when 3-body collisions become important, the system becomes unstable with respect to binding into molecules and droplets, which ultimately leads to the formation of a liquid or solid state.

Degeneracy regime: Importantly, the latter only happens when Λ is already much larger than the interatomic spacing ($n\Lambda^3 > 1$) and quantum statistics has become manifest. In this limit the picture of classical particles has become useless for the description of both the thermodynamic and collisional properties of the gas. We are dealing with a many-body quantum system.

Problem 1.18. A classical gas cloud of rubidium atoms has a temperature $T = 1\ \mu$K.
a. What is the average velocity $\bar{v}$ of the atoms?
b. Compare the expansion speed of the cloud after switching off the trap with the velocity the cloud picks up in the gravitation field
c. What is the average energy E per atom?
d. Calculate the De Broglie wavelength Λ of a rubidium atom at $T = 1\ \mu$K?
e. At what density is the distance between the atoms comparable to Λ at this temperature?
f. How does this density compare with the density of the ambient atmosphere?

2

Quantum motion in a central potential field

The motion of particles in a *central* potential plays an important role in atomic and molecular physics. To understand the properties of the hydrogen atom we rely on careful analysis of the motion of the electron in the Coulomb field of the nucleus. Likewise, many properties related to interactions between atoms, such as collisional properties, can be understood by analyzing the relative atomic motion under the influence of central forces.

In view of the importance of central forces we summarize in this chapter the derivation of the Schrödinger equation for the motion of two particles, say of masses m_1 and m_2, interacting through a *central* potential $\mathcal{V}(r)$, $r = |\mathbf{r}_1 - \mathbf{r}_2|$ being the radial distance between the particles. For such potentials, purly depending on the *relative* distance between the particles, it is (in the absence of externally applied fields) practical to eliminate the center of mass motion of the pair and represent the relative motion by a single particle of *reduced mass* $m_r = m_1 m_2/(m_1+m_2)$ in the same potential field (see Appendix A.7). To further exploit the symmetry we can separate the radial motion from the rotational motion, obtaining the radial and angular momentum operators as well as the hamiltonian operator in spherical coordinates (Section 2.1). Knowing the Hamiltonian we can write down the Schrödinger equation (Section 2.2) and specializing to specific angular momentum values we obtain the *radial wave equation.* The radial wave equation is the central equation for the description of the radial motion associated with specific angular momentum states.

The approach just described amounts mathematically to the method of separation of variables for solving differential equations. This suggests to extend the discussion to cylindrical coordinates, as this opens - with little additional effort - a window onto related problems like quantization of electronic orbitals into Landau levels as well as the description of the flow fields of quantized vortices. In these cases the central potential is absent but the solutions are rotational in character; hence, show a form of central symmetry.

2.1 Hamiltonian

The classical Hamiltonian for the motion of a particle of (reduced) mass m_r in the central potential $\mathcal{V}(r)$ is given by the sum of the kinetic and potential energy,

$$H = \tfrac{1}{2} m_r \mathbf{v}^2 + \mathcal{V}(r), \tag{2.1}$$

where $\mathbf{v} = \dot{\mathbf{r}}$ is the velocity of the particle with $\mathbf{r}$ its position relative to the potential center. In the absence of externally applied fields $\mathbf{p} = m_r \mathbf{v}$ is the canonical momentum of the particle and the Hamiltonian can be written as[1]

$$H_0 = \frac{\mathbf{p}^2}{2m_r} + \mathcal{V}(r). \tag{2.2}$$

---

[1] In the presence of an external electromagnetic field the *non-relativistic* momentum of a *charged* particle of mass m and charge q is given by $\mathbf{p} = m\mathbf{v} + q\mathbf{A}$, with $m\mathbf{v}$ its *kinetic* momentum and $q\mathbf{A}$ its *electromagnetic* momentum.

To exploit the central symmetry we separate the radial motion from the angular motion by writing the Hamiltonian in the form (see Problem 2.1)

$$H_0 = \frac{1}{2m_r}\left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) + \mathcal{V}(r) \quad (r \neq 0). \tag{2.3}$$

Here $p_r = \hat{\mathbf{r}}\cdot\mathbf{p}$ (see Fig. 2.1) is the *radial momentum*, with $\hat{\mathbf{r}} = \mathbf{r}/r$ the unit vector in radial direction, and $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ the *orbital angular momentum* with respect to the potential center. As Eq. (2.3) is well-defined only *outside* the origin any result based on this expression should be tested for its validity at the origin.

Problem 2.1. Derive the vector relation (see also Appendix E).

$$(\hat{\mathbf{r}}\cdot\mathbf{p})^2 + (\hat{\mathbf{r}}\times\mathbf{p})^2 = \mathbf{p}^2. \tag{2.4}$$

Solution. In the Einstein notation with summation over repeating indices the cartesian components of $\hat{\mathbf{r}}\times\mathbf{p}$ are given by $(\hat{\mathbf{r}}\times\mathbf{p})_i = \varepsilon_{ijk}\hat{r}_j p_k$, where $i,j,k \in \{x,y,z\}$ and ε_{ijk} is the Levi-Civita tensor

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{for } \textit{even} \text{ permutations of } x,y,z \\ 0 & \text{for } i=j \text{ or } i=k \text{ or } j=k \\ -1 & \text{for } \textit{odd} \text{ permutations of } x,y,z. \end{cases} \tag{2.5}$$

Using the summation convention, the contraction of the Levi-Civita tensor is given by

$$\varepsilon_{ijk}\varepsilon_{ilm} = \delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}.$$

Since $\mathbf{L}^2 = L_i L_i$ we obtain

$$\begin{aligned}(\hat{\mathbf{r}}\times\mathbf{p})^2 &= (\varepsilon_{ijk}\hat{r}_j p_k)(\varepsilon_{ilm}\hat{r}_l p_m) = (\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl})\,\hat{r}_j p_k \hat{r}_l p_m \\ &= (\hat{r}_j\hat{r}_j)(p_k p_k) - \hat{r}_j p_j \hat{r}_k p_k = \mathbf{p}^2 - (\hat{\mathbf{r}}\cdot\mathbf{p})^2. \qquad \Box\end{aligned}$$

2.1.1 Quantization of the Hamiltonian - basic commutation relations

The transition from classical mechanics to quantum mechanics is made by postulating that the dynamical variables for position and momentum correspond to the following *hermitian operators* in the *position representation*, $\mathbf{p}\to -i\hbar\boldsymbol{\nabla}$ and $\mathbf{r}\to\underline{\mathbf{r}}$.[1] This is known as *quantization by correspondence.* With this quantization rule, Eq. (2.2) becomes the quantum mechanical Hamiltonian and takes the familiar form of the *Schrödinger Hamiltonian* for a particle in a central field,

$$\mathcal{H}_0 = -\frac{\hbar^2}{2m_r}\Delta + \mathcal{V}(r). \tag{2.6}$$

Although the quantization went smoothly in this case, in general we should watch out for ambiguities in the application of the correspondence rules. For instance, whereas in classical mechanics the expressions $p_r = \hat{\mathbf{r}}\cdot\mathbf{p}$ and $p_r = \mathbf{p}\cdot\hat{\mathbf{r}}$ are equivalent this does not hold for $p_r = -i\hbar(\boldsymbol{\nabla}\cdot\hat{\mathbf{r}})$ and $p_r = -i\hbar(\hat{\mathbf{r}}\cdot\boldsymbol{\nabla})$ because $\hat{\mathbf{r}} = \mathbf{r}/r$ and $-i\hbar\boldsymbol{\nabla}$ do not commute.

Up to this point we did not make any choice of coordinate system (metric). To deal with noncommutativity for a given coordinate system the operator algebra has to be completed with commutation relations for the operators. In arbitrary *orthogonal* curvilinear coordinates $\mathbf{r} = \mathbf{r}(r_1,\cdots r_d)$ of a d-dimensional euclidean vector space the gradient vector is given by

$$\boldsymbol{\nabla} = \{h_1^{-1}\partial_1,\cdots,h_d^{-1}\partial_d\} = \hat{\mathbf{e}}_1 h_1^{-1}\partial_1 + \cdots + \hat{\mathbf{e}}_d h_d^{-1}\partial_d, \tag{2.7}$$

---

[1] Here we emphasized in the notation that $\underline{\mathbf{r}}$ is the position *operator* rather than the position $\mathbf{r}$. As this distinction rarely leads to confusion the underscore will be omitted in most of the text.

where the unit vectors are defined by $\hat{\mathbf{u}} \equiv \hat{\mathbf{e}}_u = \partial_u \mathbf{r}/|\partial_u \mathbf{r}|$ and the scale factors by $h_u \equiv |\partial_u \mathbf{r}|$, with $u \in \{r_1, \cdots r_d\}$. Here $\partial_u \equiv \partial/\partial r_u$ is a shorthand notation for the partial derivative operator. Note that $\partial_u \mathbf{r} = h_u \hat{\mathbf{u}}$.

In *cartesian* coordinates we have $\mathbf{r} = (r_1, \cdots r_d) = (x, y, z)$. As the radius vector is given by $\mathbf{r} = \hat{\mathbf{x}}x + \hat{\mathbf{y}}y + \hat{\mathbf{z}}z$ it follows that $\partial_x \mathbf{r} = \hat{\mathbf{x}}$, $\partial_y \mathbf{r} = \hat{\mathbf{y}}$, $\partial_z \mathbf{r} = \hat{\mathbf{z}}$ and $h_x = h_y = h_z = 1$. Note that the property $h_i = 1$, with $i \in \{1, \cdots, d\}$, is valid for an euclidean vector space of arbitrary dimension d. The commutation relations for the components of the operators r_i and $p_j = -i\hbar\partial_j$ are obtained by evaluating the action of the operator $[r_i, p_j]$ on a smooth test function of position $\phi(r_x, r_y, r_z)$,

$$[r_i, p_j]\,\phi = -i\hbar\,(r_i\partial_j - \partial_j r_i)\,\phi = -i\hbar\,(r_i\partial_j\phi - r_i\partial_j\phi - \phi\delta_{ij}) = i\hbar\delta_{ij}\phi. \tag{2.8}$$

Thus we derived the commutation relations

$$[r_i, p_j] = i\hbar\delta_{ij}. \tag{2.9}$$

These commutation relations hold for cartesian coordinates. In general, the direction of the unit vectors depends on position ($h_i \neq 1$) and the commutation relations *do not have this simple form.*

A consequence of the commutation relations (2.9) is that $\mathbf{r}$ and $\mathbf{p}$ do not commute with the Hamiltonian $\mathcal{H}_0$: for $\mathbf{p}$ we have $[p_i, \mathcal{H}_0] = [p_i, \mathcal{V}(r)] \neq 0$, for $\mathbf{r}$ we find an important relation between $\mathbf{p}$ and $\mathbf{r}$

$$[r_i, \mathcal{H}_0] = \left[r_i, \mathbf{p}^2/2m_r\right] = i(\hbar/m_r)p_i, \tag{2.10}$$

which can be written in the form

$$\mathbf{p} = -i\,(m_r/\hbar)\,[\mathbf{r}, \mathcal{H}_0]\,. \tag{2.11}$$

2.1.1.1 Laplacian in spherical coordinates

To explore the central symmetry of our problem we wish to write the laplacian from the Schrödinger Hamiltonian in *spherical coordinates* $\{r, \theta, \phi\}$. The relation between the cartesian coordinates and the spherical coordinates of a point $\mathbf{P} = \mathbf{P}(x, y, z) = \mathbf{P}\,(r, \theta, \phi)$ is given by (see Fig. 2.1)

$$x = r\sin\theta\cos\phi,\;\; y = r\sin\theta\sin\phi,\;\; z = r\cos\theta. \tag{2.12}$$

Using $\partial_a \mathbf{P} = h_a \hat{\mathbf{a}}$, with $a \in (\{r, \theta, \phi\}$, the angular dependence of the unit vectors is given by[1]

$$\hat{\mathbf{r}} = \hat{\mathbf{x}}\sin\theta\cos\phi + \hat{\mathbf{y}}\sin\theta\sin\phi + \hat{\mathbf{z}}\cos\theta \tag{2.13a}$$

$$\hat{\boldsymbol{\theta}} = \hat{\mathbf{x}}\cos\theta\cos\phi + \hat{\mathbf{y}}\cos\theta\sin\phi - \hat{\mathbf{z}}\sin\theta \tag{2.13b}$$

$$\hat{\boldsymbol{\phi}} = -\hat{\mathbf{x}}\sin\phi + \hat{\mathbf{y}}\cos\phi. \tag{2.13c}$$

Using $\mathbf{P} = \hat{\mathbf{r}}r = \mathbf{r}$ we calculate $h_r = |\partial\mathbf{r}/\partial r| = 1$, $h_\phi = |\partial\mathbf{r}/\partial\phi| = r(\sin^2\theta\sin^2\phi + \sin^2\theta\cos^2\phi)^{1/2} = r\sin\theta$ and $h_\theta = |\partial\mathbf{r}/\partial\theta| = r(\cos^2\theta\cos^2\phi + \cos^2\theta\sin^2\phi + \sin^2\theta)^{1/2} = r$.

Hence, in spherical coordinates the gradient operator (2.7) becomes

$$\boldsymbol{\nabla} = \hat{\mathbf{r}}\,\partial_r + \hat{\boldsymbol{\theta}}\frac{1}{r}\partial_\theta + \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\partial_\phi. \tag{2.14}$$

Evaluating the inner product $\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}$ we obtain for the Laplace operator (see Problem 2.2)

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \tag{2.15}$$

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[1] In these lecture notes we use interchangeable notations for the radial unit vector: $\hat{\mathbf{r}} \equiv \Omega \equiv (\theta, \phi)$.

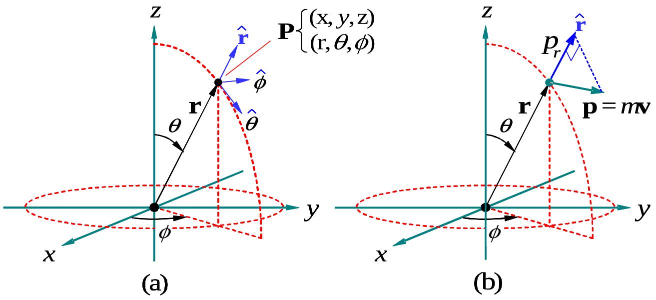

Figure 2.1: Illustration of spherical coordinates of a point $\mathbf{P} = \mathbf{P}(x, y, z) = \mathbf{P}\,(r, \theta, \phi)$: (a) unit vector convention; (b) vector diagram indicating the direction $\hat{\mathbf{r}}$ and amplitude p_r of the radial momentum vector.

Problem 2.2. Derive the expression (2.15) for the laplacian in spherical coordinates.

Solution. Starting from the vector expression (2.14) for the gradient operator the laplacian is obtained by evaluating the inner product

$$\begin{aligned}\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\psi = \hat{\mathbf{r}}\cdot\left(\partial_r\hat{\mathbf{r}}\,\partial_r + [\partial_r\hat{\boldsymbol{\theta}}]\frac{1}{r}\partial_\theta + [\partial_r\hat{\boldsymbol{\phi}}]\frac{1}{r\sin\theta}\partial_\phi\right)\psi \\ + \frac{1}{r}\hat{\boldsymbol{\theta}}\cdot\left([\partial_\theta\hat{\mathbf{r}}]\partial_r + \partial_\theta\hat{\boldsymbol{\theta}}\frac{1}{r}\partial_\theta + [\partial_\theta\hat{\boldsymbol{\phi}}]\frac{1}{r\sin\theta}\partial_\phi\right)\psi \\ + \frac{1}{r\sin\theta}\hat{\boldsymbol{\phi}}\cdot\left([\partial_\phi\hat{\mathbf{r}}]\partial_r + [\partial_\phi\hat{\boldsymbol{\theta}}]\frac{1}{r}\partial_\theta + \partial_\phi\hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\partial_\phi\right)\psi.\end{aligned}$$

Here we dismissed many terms that yield zero due to the orthogonality of the unit operators. Using $\partial_r\hat{\mathbf{r}} = \partial_r\hat{\boldsymbol{\theta}} = \partial_r\hat{\boldsymbol{\phi}} = 0$ and $\partial_\theta\hat{\mathbf{r}} = \hat{\boldsymbol{\theta}}$, $\partial_\theta\hat{\boldsymbol{\theta}} = -\hat{\mathbf{r}}$, $\partial_\theta\hat{\boldsymbol{\phi}} = 0$ and $\partial_\phi\hat{\mathbf{r}} = \hat{\boldsymbol{\phi}}\sin\theta$, $\partial_\phi\hat{\boldsymbol{\theta}} = \hat{\boldsymbol{\phi}}\cos\theta$, $\partial_\phi\hat{\boldsymbol{\phi}} = -\,\hat{\mathbf{r}}\sin\theta - \hat{\boldsymbol{\theta}}\cos\theta$ the expression further simplifies to

$$\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\psi = \partial_r^2\psi + \frac{1}{r}\left(\partial_r + \frac{1}{r}\partial_\theta^2\right)\psi + \frac{1}{r\sin\theta}\left(\sin\theta\partial_r + \cos\theta\frac{1}{r}\partial_\theta + \frac{1}{r\sin\theta}\partial_\phi^2\right)\psi.$$

Collecting the terms we obtain for the Laplace operator

$$\Delta = \partial_r^2 + \frac{2}{r}\partial_r + \frac{1}{r^2}\partial_\theta^2 + \frac{\cos\theta}{r^2\sin\theta}\partial_\theta + \frac{1}{r^2\sin^2\theta}\partial_\phi^2,$$

which can be written in the form (2.15). □

2.1.1.2 Laplacian in cylindrical coordinates

To describe central symmetry in *two-dimensional systems* or systems with *cylindrical symmetry* it is important to be aware of the expression for the laplacian in *cylindrical coordinates* $\mathbf{P} = \mathbf{P}(x, y, z) = \mathbf{P}\,(r_\perp, \phi, z)$. As illustrated in Fig. 2.2 the relation between the cartesian coordinates and the cylindrical coordinates is given by the expressions

$$x = r_\perp\cos\phi,\;\; y = r_\perp\sin\phi,\;\; z = z. \tag{2.16}$$

Using $\partial_a\mathbf{P} = h_a\hat{\mathbf{a}}$, with $a \in \{r_\perp, \phi, z\}$, the angular dependence of the unit vectors is given by

$$\hat{\mathbf{r}}_\perp = +\hat{\mathbf{x}}\cos\phi + \hat{\mathbf{y}}\sin\phi \tag{2.17a}$$

$$\hat{\boldsymbol{\phi}} = -\hat{\mathbf{x}}\sin\phi + \hat{\mathbf{y}}\cos\phi \tag{2.17b}$$

$$\hat{\mathbf{z}} = \hat{\mathbf{z}}. \tag{2.17c}$$

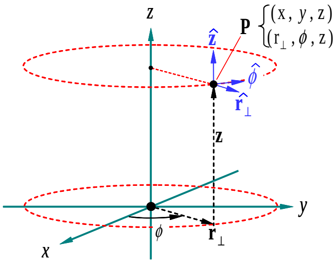

Figure 2.2: Illustration of cylindrical coordinates of a point $\mathbf{P} = \mathbf{P}(x, y, z) = \mathbf{P}\,(r_\perp, \phi, z)$ with unit vector convention.

Using $\mathbf{P} = \hat{\mathbf{r}}_\perp\, r_\perp + \hat{\mathbf{z}}\, z$ we have $\mathbf{P}^2 = r_\perp^2 + z^2$ and calculate $h_{r_\perp} = |\partial\mathbf{P}/\partial r_\perp| = 1$, $h_\phi = |\partial\mathbf{P}/\partial\phi| = r_\perp(\sin^2\phi + \cos^2\phi)^{1/2} = r_\perp$ and $h_z = |\partial\mathbf{P}/\partial z| = 1$.

Hence, in cylindrical coordinates the gradient operator (2.7) is given by

$$\boldsymbol{\nabla} = \hat{\mathbf{r}}_\perp\, \partial_{r_\perp} + \hat{\boldsymbol{\phi}}\frac{1}{r_\perp}\partial_\phi + \hat{\mathbf{z}}\,\partial_z. \tag{2.18}$$

Evaluating the inner product we obtain for the laplacian (see Problem 2.3)

$$\Delta = \frac{\partial^2}{\partial r_\perp^2} + \frac{1}{r_\perp}\frac{\partial}{\partial r_\perp} + \frac{1}{r_\perp^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2}. \tag{2.19}$$

Fixing the value of z this expression also serves to describe two-dimensional systems. In the form (2.19) the laplacian is used to describe the flow field of quantized vortices in superfluids.

Problem 2.3. Derive the expression (2.19) for the laplacian in cylindrical coordinates.

Solution. Starting from the vector expression (2.18) for the gradient operator the laplacian is obtained by evaluating the inner product (here we set $r_\perp \to \mathbf{r}$ for compactness of notation)

$$\begin{aligned}\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\psi = \hat{\mathbf{r}}\cdot\left(\partial_r\hat{\mathbf{r}}\,\partial_r + [\partial_r\hat{\boldsymbol{\phi}}]\frac{1}{r}\partial_\phi + [\partial_r\hat{\mathbf{z}}]\partial_z\right)\psi \\ + \frac{1}{r}\hat{\boldsymbol{\phi}}\cdot\left([\partial_\phi\hat{\mathbf{r}}]\partial_r + \partial_\phi\hat{\boldsymbol{\phi}}\frac{1}{r}\partial_\phi + [\partial_\phi\hat{\mathbf{z}}]\partial_z\right)\psi \\ + \hat{\mathbf{z}}\cdot\left([\partial_z\mathbf{r}]\,\partial_r + [\partial_z\hat{\boldsymbol{\phi}}]\frac{1}{r}\partial_\phi + \partial_z\hat{\mathbf{z}}\,\partial_z\right)\psi.\end{aligned}$$

Here we dismissed the many terms that yield zero due to the orthogonality of the unit operators. Using $\partial_r\hat{\mathbf{r}} = \partial_r\hat{\boldsymbol{\phi}} = \partial_r\hat{\mathbf{z}} = \partial_z\hat{\mathbf{r}} = \partial_z\hat{\boldsymbol{\phi}} = \partial_z\hat{\mathbf{z}} = 0$ and $\partial_\phi\hat{\mathbf{r}} = \hat{\boldsymbol{\phi}}$, $\partial_\phi\hat{\boldsymbol{\phi}} = -\hat{\mathbf{r}} + \hat{\mathbf{z}}\,z$, $\partial_\phi\hat{\mathbf{z}} = 0$ the expression for $\Delta\psi$ further simplifies to

$$\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\psi = \partial_r^2\psi + \frac{1}{r}\left(\partial_r + \partial_\phi\frac{1}{r}\partial_\phi\right)\psi + \partial_z^2\psi.$$

Thus, the Laplace operator can be written in the form (2.19). □

2.1.2 Angular momentum operator L

To obtain the operator expression for the angular momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ in the position representation we use the correspondence rules $\mathbf{p} \to -i\hbar\boldsymbol{\nabla}$ and $\mathbf{r} \to \underline{\mathbf{r}}$. Importantly, although $\mathbf{r}$ and $\mathbf{p}$ do not commute the transition to the quantum mechanical expression,

$$\mathbf{L} = -i\hbar\,(\mathbf{r}\times\boldsymbol{\nabla}), \tag{2.20}$$

can be made without ambiguity because the correspondence rules yield the same result for $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ and for $\mathbf{L} = -\mathbf{p}\times\mathbf{r}$. This is easily verified by using the cartesian vector components of $\mathbf{r}$ and $\mathbf{p}$ and their commutation relations,

$$-\left(\mathbf{p}\times\mathbf{r}\right)_i = -\varepsilon_{ijk}p_j r_k = -\varepsilon_{ijk}r_k p_j = \varepsilon_{ikj}r_k p_j = \varepsilon_{ijk}r_j p_k = \left(\mathbf{r}\times\mathbf{p}\right)_i . \tag{2.21}$$

Note that for $j \neq k$ the operators r_j and p_k commute and for $j = k$ one has $\varepsilon_{ijk} = 0$.

Having identified Eq. (2.20) as the proper operator expression for the orbital angular momentum we can turn to arbitrary *orthogonal* curvilinear coordinates $\mathbf{r} = \mathbf{r}(u, v, w)$. In this case the gradient vector is given by $\boldsymbol{\nabla} = \{h_u^{-1}\partial_u, h_v^{-1}\partial_v, h_w^{-1}\partial_w\}$ and the angular momentum operator can be decomposed in the following form

$$\mathbf{L} = -\,i\hbar\,(\mathbf{r}\times\boldsymbol{\nabla}) = -\,i\hbar \begin{vmatrix} \hat{\mathbf{u}} & \hat{\mathbf{v}} & \hat{\mathbf{w}} \\ r_u & r_v & r_w \\ h_u^{-1}\partial_u & h_v^{-1}\partial_v & h_w^{-1}\partial_w \end{vmatrix} . \tag{2.22}$$

For *spherical coordinates* the components of the radius vector are $r_r = r$ and $r_\theta = r_\phi = 0$. Working out the determinant in Eq. (2.22), while *respecting the order* of the vector components r_u and $h_u^{-1}\partial_u$, we find for the angular momentum operator in spherical coordinates

$$\mathbf{L} = -i\hbar\,(\mathbf{r}\times\boldsymbol{\nabla}) = i\hbar\left(\hat{\boldsymbol{\theta}}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} - \hat{\boldsymbol{\phi}}\frac{\partial}{\partial\theta}\right). \tag{2.23}$$

Importantly, as was to be expected for a rotation operator in a spherical coordinate system, $\mathbf{L}$ depends only on the angles θ and ϕ and not on the radial distance r.

2.1.3 The operator L_z

The operator for the angular momentum along the z direction is a differential operator obtained by taking the inner product of $\mathbf{L}$ with the unit vector along the z direction, $L_z = \hat{\mathbf{z}}\cdot\mathbf{L}$. From Eq. (2.23) we see that

$$L_z = i\hbar\left((\hat{\mathbf{z}}\cdot\hat{\boldsymbol{\theta}})\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} - (\hat{\mathbf{z}}\cdot\hat{\boldsymbol{\phi}})\frac{\partial}{\partial\theta}\right). \tag{2.24}$$

Because the unit vector $\hat{\boldsymbol{\phi}} = -\hat{\mathbf{x}}\sin\phi + \hat{\mathbf{y}}\cos\phi$ has no z component, only the θ component of $\mathbf{L}$ will give a contribution to L_z. Substituting the unit vector decomposition $\hat{\boldsymbol{\theta}} = \hat{\mathbf{x}}\cos\theta\cos\phi + \hat{\mathbf{y}}\cos\theta\sin\phi - \hat{\mathbf{z}}\sin\theta$ we obtain

$$L_z = -i\hbar\frac{\partial}{\partial\phi}. \tag{2.25}$$

The eigenvalues and eigenfunctions of L_z are obtained by solving the equation

$$-\,i\hbar\frac{\partial}{\partial\phi}\Phi_m(\phi) = m\hbar\;\Phi_m(\phi). \tag{2.26}$$

Here, the eigenvalue m is called the *magnetic quantum number* for the projection of the angular momentum $\mathbf{L}$ on the z axis.[1] The eigenfunctions are

$$\Phi_m(\phi) = a_m e^{im\phi}. \tag{2.27}$$

Assuming the solutions of the Schrödinger equation to be single-valued functions of position,[2] the wavefunction has to be invariant under rotation over 2π about the z axis; i.e., we have to

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[1] In this chapter we use the shorthand notation m for the magnetic quantum numbers m_l corresponding to states with orbital quantum number l. When other forms of angular momentum appear we will use the subscript notation to discriminate between the different magnetic quantum numbers; e.g., lm_l, sm_s, jm_j, etc..

[2] For a discussion of the single-valuedness see [47, 25]

impose the boundary condition $e^{im\phi} = e^{im(\phi+2\pi)}$. Thus we require $e^{im2\pi} = 1$, which implies $m \in \{0, \pm1, \pm2, \ldots\}$. In other words we quantized the rotation about the z axis. As the orientation of the coordinate system was not defined up to this point, the chosen z direction is called the *quantization axis*. With the normalization

$$\int_0^{2\pi} |\Phi_m(\phi)|^2 \, d\phi = 1 \tag{2.28}$$

we find the same normalization coefficient for all values of the m quantum number, $a_m = (2\pi)^{-1/2}$.

2.1.4 Commutation relations for L_x, L_y, L_z and $\mathbf{L}^2$

The three cartesian components of the angular momentum operator are differential operators satisfying the following commutation relations

$$[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k \quad \Leftrightarrow \quad [L_x, L_y] = i\hbar L_z,\ [L_y, L_z] = i\hbar L_x \text{ and } [L_z, L_x] = i\hbar L_y. \tag{2.29}$$

These expressions are readily derived with the help of some elementary commutator algebra (see Appendix C.8). We derive the relation $[L_x, L_y] = i\hbar L_z$ explicitly; the other commutators are obtained by cyclic permutation of x, y and z. Starting from the definition $L_i = \varepsilon_{ijk}r_jp_k$ we use subsequently the distributive rule (C.29b), the multiplicative rule (C.29d) and the commutation relation (2.9),

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] = [yp_z, zp_x] + [zp_y, xp_z] \\ &= y\,[p_z, z]\,p_x - x\,[p_z, z]\,p_y = i\hbar(xp_y - yp_x) = i\hbar L_z. \end{aligned} \tag{2.30}$$

A scalar operator always commutes with itself. This well-known commutation rule does *not* hold for vector operators. Two vector operators $\mathbf{A}$ and $\mathbf{B}$ only commute if *all components* of $\mathbf{A}$ commute with all components of $\mathbf{B}$.[1] Hence, $\mathbf{L}$ does *not* commute with itself (see Problem 2.4).

The components of $\mathbf{L}$ commute with $\mathbf{L}^2$,

$$[L_x, \mathbf{L}^2] = 0,\ [L_y, \mathbf{L}^2] = 0,\ [L_z, \mathbf{L}^2] = 0. \tag{2.31}$$

We verify this explicitly for L_z. Using the relation

$$\mathbf{L}^2 = \mathbf{L}\cdot\mathbf{L} = L_x^2 + L_y^2 + L_z^2 \tag{2.32}$$

we obtain with the aid of the multiplicative rule (C.29c)

$$\begin{aligned} &[L_z, L_z^2] = 0 \\ &[L_z, L_y^2] = [L_z, L_y]L_y + L_y[L_z, L_y] = -i\hbar(L_xL_y + L_yL_x) \\ &[L_z, L_x^2] = [L_z, L_x]L_x + L_x[L_z, L_x] = +i\hbar(L_yL_x + L_xL_y). \end{aligned}$$

By adding these terms we find $[L_z, \mathbf{L}^2] = 0$ as well as $[L_z, L_x^2 + L_y^2] = 0$.

Problem 2.4. Vector *operators* differ from classical vectors. Show that

$$\mathbf{L}\times\mathbf{L} = i\hbar\mathbf{L}, \quad [\mathbf{L}, \mathbf{L}] \neq 0, \quad \left[\mathbf{L}^2, \mathbf{L}^2\right] = 0.$$

---

[1] The commutator of two *vectors* is a second order tensor. This becomes evident in the Einstein notation $[\mathbf{A}, \mathbf{B}] \Leftrightarrow [A_i, B_j] = A_iB_j - B_jA_i \Leftrightarrow \mathbf{A}\mathbf{B}^T - (\mathbf{B}\mathbf{A}^T)^T$, where $()^T$ represents matrix transposition.

2.1.5 The operators $L_\pm$

The operators

$$L_\pm = L_x \pm iL_y \tag{2.33}$$

are obtained by taking the inner products of $\mathbf{L}$ with the unit vectors along the x and y direction, $L_\pm = (\hat{\mathbf{x}}\cdot\mathbf{L}) \pm i\,(\hat{\mathbf{y}}\cdot\mathbf{L})$. In spherical coordinates this results in

$$L_\pm = i\hbar\left(\left[(\hat{\mathbf{x}}\cdot\hat{\boldsymbol{\theta}}) \pm i(\hat{\mathbf{y}}\cdot\hat{\boldsymbol{\theta}})\right]\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} - \left[(\hat{\mathbf{x}}\cdot\hat{\boldsymbol{\phi}}) \pm i(\hat{\mathbf{y}}\cdot\hat{\boldsymbol{\phi}})\right]\frac{\partial}{\partial\theta}\right), \tag{2.34}$$

as follows directly with Eq. (2.23). Substituting the unit vector decompositions $\hat{\boldsymbol{\phi}} = -\hat{\mathbf{x}}\sin\phi + \hat{\mathbf{y}}\cos\phi$ and $\hat{\boldsymbol{\theta}} = \hat{\mathbf{x}}\cos\theta\cos\phi + \hat{\mathbf{y}}\cos\theta\sin\phi - \hat{\mathbf{z}}\sin\theta$ we obtain

$$L_\pm = \hbar e^{\pm i\phi}\left(i\cot\theta\frac{\partial}{\partial\phi} \pm \frac{\partial}{\partial\theta}\right). \tag{2.35}$$

These operators are known as *shift operators* and more specifically as *raising* (L_+) and *lowering* (L_-) operators because their action is to raise or to lower the angular momentum along the quantization axis by one quantum of angular momentum (see Section 2.1.6).

Several useful relations for $L_\pm$ follow straightforwardly. Using the commutation relations (2.29) we obtain

$$[L_z, L_\pm] = [L_z, L_x] \pm i\,[L_z, L_y] = i\hbar L_y \pm \hbar L_x = \pm\hbar L_\pm. \tag{2.36}$$

Further we have

$$L_+L_- = L_x^2 + L_y^2 - i\,[L_x, L_y] = L_x^2 + L_y^2 + \hbar L_z = \mathbf{L}^2 - L_z^2 + \hbar L_z \tag{2.37a}$$

$$L_-L_+ = L_x^2 + L_y^2 + i\,[L_x, L_y] = L_x^2 + L_y^2 - \hbar L_z = \mathbf{L}^2 - L_z^2 - \hbar L_z, \tag{2.37b}$$

where we used again one of the commutation relations (2.29). Subtracting these equations we obtain

$$[L_+, L_-] = 2\hbar L_z \tag{2.38}$$

and by adding Eqs. (2.37) we find

$$\mathbf{L}^2 = L_z^2 + \tfrac{1}{2}\left(L_+L_- + L_-L_+\right). \tag{2.39}$$

2.1.6 The operator $\mathbf{L}^2$

To derive an expression for the operator $\mathbf{L}^2$ we use the operator relation (2.39). Substituting Eqs. (2.25) and (2.35) we obtain after some straightforward manipulation

$$\mathbf{L}^2 = -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]. \tag{2.40}$$

The eigenfunctions and eigenvalues of $\mathbf{L}^2$ are obtained by solving the equation

$$-\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]Y(\theta,\phi) = \lambda\hbar^2 Y(\theta,\phi). \tag{2.41}$$

Because the operators $\mathbf{L}^2$ and L_z commute they share a complete set of eigenstates (see Problem B.1); i.e., the shared eigenfunctions $Y(\theta,\phi)$ must be of the form $Y(\theta,\phi) = P(\theta,\phi)\Phi_m(\phi)$, where the function $\Phi_m(\phi)$ is an eigenfunction of the L_z operator. Because of Eq. (2.26) this implies that $L_zP(\theta,\phi) \equiv 0$, which can only be satisfied for arbitrary value of θ if the variables θ and ϕ separate:

$P(\theta,\phi) = P(\theta)Q(\phi)$. In turn this requires $L_zQ(\phi) \equiv 0$, which can only be satisfied if $Q(\phi)$ is a constant. Thus, we conclude that the shared eigenfunctions $Y(\theta,\phi)$ must be of the form

$$Y(\theta,\phi) = P(\theta)\Phi_m(\phi). \tag{2.42}$$

Evaluating the second order derivative $\partial^2/\partial\phi^2$ in Eq. (2.41) we obtain

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{m^2}{\sin^2\theta} + \lambda\right] P(\theta) = 0. \tag{2.43}$$

As this equation is real its solutions are real functions of the variable θ. Introducing the notation $\lambda = l(l+1)$ and $u \equiv \cos\theta$ (with θ restricted to the interval $0 \leq \theta \leq \pi$) this equation takes the form of the associated Legendre differential equation (C.36),

$$\left[\left(1-u^2\right)\frac{d^2}{du^2} - 2u\frac{d}{du} + l(l+1) - \frac{m^2}{1-u^2}\right] P_l^m(u) = 0. \tag{2.44}$$

Since $0 \leq \theta \leq \pi$ we have $\sin\theta = \sqrt{1-u^2} \geq 0$. The solutions are determined up to a constant factor, which has to be fixed by convention. For $m = 0$ the Eq. (2.44) reduces to the Legendre differential equation and its normalized solutions are the *Legendre polynomials*, defined by

$$P_l(u) = \frac{1}{2^l l!}\frac{d^l}{du^l}(u^2-1)^l. \tag{2.45}$$

The solution $P_l(u)$ is a real polynomial of degree $l \in \{0,1,2\cdots\}$ with l zeros in the interval $-1 \leq u \leq 1$. The Legendre polynomials of lowest degree are

$$P_0(u) = 1, \quad P_1(u) = u, \quad P_2(u) = \tfrac{1}{2}(3u^2-1). \tag{2.46}$$

Note that the sign of the highest power term is chosen to be positive. For $m \neq 0$ the solutions are the *associated Legendre functions* $P_l^m(u)$, real functions which can be written as the product of a positive function $(1-u^2)^{m/2}$ and a polynomial of degree $(l-m)$, parity $(-1)^{l-m}$ with $(l-m)$ zeros in the interval $-1 \leq u \leq 1$. For $m = 0$ we define $P_l^0(u) \equiv P_l(u)$. For $m > 0$ the $P_l^m(u)$ are obtained by differentiation of the Legendre polynomials,[1]

$$P_l^m(u) = (-1)^m(1-u^2)^{m/2}\frac{d^m}{du^m}P_l(u). \tag{2.47}$$

The *parity* of the $P_l^m(u)$ is given by

$$P_l^m(-u) = (-1)^{l-m}P_l^m(u) \tag{2.48}$$

and the above definitions fix the normalization,

$$\int_{-1}^{1}\left[P_l^m(u)\right]^2 du = \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!}. \tag{2.49}$$

As Eq. (2.44) depends on m^2 we also can define solutions for $m < 0$. Obviously, $P_l^{-m}(u)$ and $P_l^m(u)$ are in essence the same but for the $P_l^{-m}(u)$ we still have to define sign and normalization. Unfortunately, several competing conventions can be found in the literature. In this course we use a positive sign and adhere to the convention in which the normalization (2.49) is valid for both positive and negative m. This is realized by extending the $P_l^m(u)$ to negative m by the relation

$$P_l^{-m}(u) \equiv (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(u), \tag{2.50}$$

where $0 \leq m \leq l$. The inclusion of the phase factor $(-1)^m$ in *both* Eq. (2.47) and (2.50) is referred to as the *Condon and Shortley phase convention* [11]. It implies that the phase factor $(-1)^m$ is present for positive m but absent for negative m. Note that the $P_l^m(u)$ are nonzero only for $-l \leq m \leq l$; i.e., the index m can assume $2l+1$ possible values for a given value of l.

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[1] Beware of other phase conventions for the $P_l^m(u)$, they affect the recursion relations.

2.1.6.1 Spherical harmonics - Condon and Shortley phase convention

At this point we define the *spherical harmonics* (cf. Section C.9.1)

$$Y_l^m(\theta,\phi) = A_m P_l^m(\cos\theta)e^{im\phi} \tag{2.51}$$

as the joint eigenfunctions of $\mathbf{L}^2$ and L_z in the position representation,

$$\mathbf{L}^2\, Y_l^m(\theta,\phi) = l(l+1)\hbar^2\, Y_l^m(\theta,\phi) \tag{2.52}$$

$$L_z\, Y_l^m(\theta,\phi) = m\hbar\, Y_l^m(\theta,\phi). \tag{2.53}$$

The prefactor A_m is a normalization constant. Combining the normalization integrals (2.28) and (C.46) we obtain

$$Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}, \tag{2.54}$$

with $-l \leq m \leq l$. The Condon and Shortley phase convention assures that the shift operators satisfy the following relations

$$\begin{aligned} L_\pm Y_l^m(\theta,\phi) &= \sqrt{(l\mp m)\,(l\pm m+1)}\,\hbar\, Y_l^{m\pm1}(\theta,\phi) \\ &= \sqrt{l\,(l+1)-m(m\pm1)}\,\hbar\, Y_l^{m\pm1}(\theta,\phi), \end{aligned} \tag{2.55}$$

with a *positive sign* in front of the square root for *all* values of l and m. Eqs. (2.55) are readily obtained with the aid of Eqs. (2.35) and the recursion relations (C.49). The *parity* of the $Y_l^m(\theta,\phi)$ under inversion in 3D, $\hat{\mathbf{r}} = (\theta,\phi) \to -\hat{\mathbf{r}} = (\pi-\theta,\phi+\pi)$, is independent of m and given by

$$Y_l^m(-\hat{\mathbf{r}}) = (-1)^l Y_l^m(\hat{\mathbf{r}}) \tag{2.56}$$

as follows with Eqs. (2.54) and (2.48); i.e., the parity is even for l even and odd for l odd. This makes *parity* into a property defining *selection rules* in atomic transitions.

2.1.7 Orbital angular momentum in Dirac notation

The observables of the orbital angular momentum are represented by the operators $\mathbf{L}^2$ and L_z. In Dirac notation (cf. Appendix B.1.1) their shared basis is defined by

$$\mathbf{L}^2\,|l,m\rangle = l(l+1)\hbar^2\,|l,m\rangle \tag{2.57a}$$

$$L_z\,|l,m\rangle = m\hbar\,|l,m\rangle\,, \tag{2.57b}$$

where the $|l,m\rangle$ are abstract state vectors in Hilbert space, with l and m the *rotational quantum numbers.* The spherical harmonics

$$Y_l^m(\theta,\phi) \equiv Y_l^m(\hat{\mathbf{r}}) = \langle\hat{\mathbf{r}}|l,m\rangle \tag{2.58}$$

are the corresponding wavefunctions in the position representation using spherical coordinates. The action of the shift operators $L_\pm$ is given by

$$L_\pm\,|l,m\rangle = \sqrt{l\,(l+1)-m(m\pm1)}\,\hbar\,|l,m\pm1\rangle\,, \tag{2.59}$$

with a *positive sign* in front of the square root for *all* values of l and m. The latter requirement constitutes the Condon and Shortley phase convention for the eigenstates $|l,m\rangle$ (cf. Section 2.1.6.1).

2.1.8 Radial momentum operator p_r

Thus far we succeeded in quantizing the Schrödinger Hamiltonian $\mathcal{H}_0$ and the angular momentum $\mathbf{L}$. Let us now turn to the radial momentum $p_r = \hat{\mathbf{r}} \cdot \mathbf{p}$. Here we have a difficulty because the correspondence rules are not unambiguous in this case. In classical mechanics the expressions $p_r = \hat{\mathbf{r}} \cdot \mathbf{p}$ and $p_r = \mathbf{p} \cdot \hat{\mathbf{r}}$ are identities but since $\hat{\mathbf{r}} = \mathbf{r}/r$ and $-i\hbar\boldsymbol{\nabla}$ do not commute this is not the case for $p_r = -i\hbar\,(\boldsymbol{\nabla} \cdot \hat{\mathbf{r}})$ and $p_r = -i\hbar\,(\hat{\mathbf{r}} \cdot \boldsymbol{\nabla})$. There is a way around this problem. Since we know how to quantize $\mathbf{p}^2$ and $(\hat{\mathbf{r}} \times \mathbf{p})^2$, we infer with the aid of Eq. (2.4) that the radial momentum must be given by

$$p_r^2 = (\hat{\mathbf{r}} \cdot \mathbf{p})^2 = \mathbf{p}^2 - (\hat{\mathbf{r}} \times \mathbf{p})^2 = -\hbar^2\Delta - \mathbf{L}^2/r^2. \tag{2.60}$$

Substituting Eqs. (2.15) and (2.40) this yields

$$p_r^2\psi = -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\psi = -\hbar^2\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)^2\psi = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)\,. \tag{2.61}$$

Hence, up to a sign, the radial momentum in spherical coordinates is given by

$$p_r\psi = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\psi = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}(r\psi). \tag{2.62}$$

We shall use the sign convention of Eq. (2.62). This implies the commutation relation

$$[r, p_r] = i\hbar. \tag{2.63}$$

Importantly, since L is independent of r and p_r is independent of θ and ϕ, we find that p_r^2 commutes with both L_z and $\mathbf{L}^2$,

$$\left[p_r^2, L_z\right] = 0 \quad \text{and} \quad \left[p_r^2, \mathbf{L}^2\right] = 0. \tag{2.64}$$

In Problem 2.5 it is shown that p_r is only *hermitian* if one restricts oneself to the sub-class of normalizable wavefunctions which are *regular* in the origin; i.e.,

$$\lim_{r\to 0} r\psi(\mathbf{r}) = 0.$$

This additional condition is essential to select *physically relevant solutions* for the (radial) wavefunction. Here we mean by physically relevant that the wavefunction satisfies not only the laplacian in spherical coordinates (which is not defined in the origin) but also the laplacian in cartesian coordinates (which is defined throughout space).

Problem 2.5. Show that p_r is hermitian for square-integrable functions $\psi(r)$ only if they are regular at the origin, i.e. $\lim_{r\to 0} r\psi(r) = 0$.

Solution. For p_r to be hermitian we require the following expression to be zero for *any* wavefunction ψ within its Hilbert space:

$$\begin{aligned}
\langle\psi, p_r\psi\rangle - \langle\psi, p_r\psi\rangle^* &= -i\hbar\int\left[\psi^*\frac{1}{r}\frac{\partial}{\partial r}(r\psi) + \frac{1}{r}\psi\frac{\partial}{\partial r}(r\psi^*)\right]r^2 dr d\Omega \\
&= -i\hbar\int\left[r\psi^*\frac{\partial}{\partial r}(r\psi) + r\psi\frac{\partial}{\partial r}(r\psi^*)\right]dr d\Omega \\
&= -i\hbar\int\frac{\partial}{\partial r}|r\psi|^2\,dr d\Omega.
\end{aligned}$$

For this to be zero we require

$$\int\frac{\partial}{\partial r}|r\psi|^2\,dr = \left[|r\psi|^2\right]_0^\infty = 0.$$

Because $\psi(r)$ is taken to be a square-integrable function; i.e., $\int |r\psi|^2\, dr = \mathcal{N}$ with $\mathcal{N}$ finite, we have $\lim_{r\to\infty} r\psi(r) = 0$ and $\lim_{r\to 0} r\psi(r) = \chi_0$, where χ_0 is (in general) finite. Thus, for p_r to be hermitian we require $\psi(r)$ to be *regular* in the origin ($\chi_0 = 0$) on top of being square-integrable. However, square-integrable eigenfunctions of p_r can also be *irregular* at the origin and have complex eigenvalues, e.g.

$$p_r \frac{\exp[-\alpha r]}{r} = -\frac{i\hbar}{r}\frac{\partial}{\partial r} r \frac{\exp[-\alpha r]}{r} = i\hbar\alpha \frac{\exp[-\alpha r]}{r}. \qquad \Box$$

Problem 2.6. Show that the radial momentum operator can be written in the form

$$p_r = \tfrac{1}{2}\left(\hat{\mathbf{r}}\cdot\mathbf{p} + \mathbf{p}\cdot\hat{\mathbf{r}}\right) = -\frac{i\hbar}{2}\left[\frac{\mathbf{r}}{r}\cdot\boldsymbol{\nabla} + \boldsymbol{\nabla}\cdot\left(\frac{\mathbf{r}}{r}\right)\right]. \tag{2.65}$$

Verify that in two dimensions p_r cannot be written in the form given on the r.h.s..

2.2 Schrödinger equation

2.2.1 Schrödinger equation in spherical coordinates

We are now in a position to write down the Schrödinger equation of a (reduced) mass m_r moving at energy E in a *central* potential field $\mathcal{V}(r)$

$$\left[\frac{1}{2m_r}\left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) + \mathcal{V}(r)\right]\psi(r,\theta,\phi) = E\psi(r,\theta,\phi). \tag{2.66}$$

Because the operators $\mathbf{L}^2$ and L_z commute with the Hamiltonian[1] they share a complete set of eigenstates with that Hamiltonian (See Problem B.1); i.e., the shared eigenfunctions $\psi(r,\theta,\phi)$ must be of the form $\psi = R(r,\theta,\phi)Y_l^m(\theta,\phi)$, which implies $\mathbf{L}^2 R(r,\theta,\phi) \equiv 0$ in view of Eq. (2.52). This can only be satisfied for arbitrary values of r if the radial variable can be separated from the angular variables, $R(r,\theta,\phi) = R(r)X(\theta,\phi)$. In turn this requires $\mathbf{L}^2 X(\theta,\phi) \equiv 0$, which implies that $X(\theta,\phi)$ must be a constant. Thus, we conclude that the shared eigenfunctions $\psi(r,\theta,\phi)$ must be of the form

$$\psi(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi), \tag{2.67}$$

where the quantum number n appears to allow for more than one solution of given l. Hence, using Eq. (2.52) and substituting Eqs. (2.61) and (2.67) into Eq. (2.66) we obtain

$$\left[\frac{\hbar^2}{2m_r}\left(-\frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r} + \frac{l(l+1)}{r^2}\right) + \mathcal{V}(r)\right] R_{nl}(r)Y_l^m(\theta,\phi) = ER_{nl}(r)Y_l^m(\theta,\phi). \tag{2.68}$$

Here the term

$$\mathcal{V}_{\text{rot}}(r) \equiv \frac{l(l+1)\hbar^2}{2m_r r^2} \tag{2.69}$$

is called the *rotational energy barrier* and represents the *centrifugal energy* at a given distance from the origin and for a given value of the angular momentum. Because the operator on the left of Eq. (3.2) is independent of θ and ϕ we can eliminate the functions $Y_l^m(\theta,\phi)$ from this equation. The remaining equation takes the form of the *radial wave equation.*

$$\left[\frac{\hbar^2}{2m_r}\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2}\right) + \mathcal{V}(r)\right] R_{nl}(r) = ER_{nl}(r), \tag{2.70}$$

where the solutions $R_{nl}(r)$ must depend on r but be independent of θ and ϕ. Note that the solutions do not depend on m because the Hamiltonian does not depend on L_z. This is a property of central potentials.

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[1] Note that L_z commutes with $\mathbf{L}^2$ (see Section 2.1.6); L_z and $\mathbf{L}^2$ commute with r and p_r (see Section 2.1.8).

Reduction to one-dimensional Schrödinger equation

Eq. (2.70) is the starting point for the description of the relative radial motion of any particle in a central potential field. Introducing the quantities

$$\varepsilon = 2m_r E/\hbar^2 \quad \text{and} \quad U(r) = 2m_r \mathcal{V}(r)/\hbar^2, \tag{2.71}$$

Suppressing the quantum number n, Eq. (2.70) can be written in the compact form

$$R_l'' + \frac{2}{r}R_l' + \left[\varepsilon - U(r) - \frac{l(l+1)}{r^2}\right] R_l = 0, \tag{2.72}$$

where the prime refers to a derivative with respect to r. Eq. (2.61) suggests to introduce so-called *reduced* radial wavefunctions

$$\chi_l(r) = rR_l(r), \tag{2.73}$$

which allows us to reduce the radial wave equation (2.70) to the form of a one-dimensional Schrödinger equation

$$\chi_l'' + \left[\frac{2m_r}{\hbar^2}(E - \mathcal{V}) - \frac{l(l+1)}{r^2}\right] \chi_l = 0. \tag{2.74}$$

The 1D-Schrödinger equation is a second-order differential equation of the following general form

$$\chi'' + F(r)\chi = 0. \tag{2.75}$$

Equations of this type satisfy some general properties. These are related to the Wronskian theorem, which is derived and discussed in appendix C.13.

Not all solutions of the 1D Schrödinger equation are physically acceptable. The physical solutions must be normalizable; i.e., for bound states

$$\int r^2 |R(r)|^2 \, dr = \int |\chi(r)|^2 \, dr = \mathcal{N}, \tag{2.76}$$

where $\mathcal{N}$ is a finite number. However, there is an additional requirement. Because the Hamiltonian (2.3) is only valid outside the origin ($r \neq 0$) the solutions of the radial wave equation are not necessarily valid *at* the origin. To be valid for all values of r the solutions must, in addition to be being normalizable, also be *regular* in the origin; i.e., $\lim_{r\to 0} rR(r) = \lim_{r\to 0} \chi(r) = 0$. Although this is stated without proof we demonstrate in Problem 2.7 that normalizable wavefunctions $\psi(\mathbf{r})$ scaling like $R(r) \sim 1/r$ near the origin do not satisfy the Schrödinger equation in the origin. All this being said, only wavefunctions based on the *regular* solutions of Eqs. (2.70) and (2.74) can be valid solutions for all values of r, *including the origin.*

Problem 2.7. Show that a normalizable radial wavefunction scaling like $R(r) \sim 1/r$ for $r \to 0$ does not satisfy the Schrödinger equation in the origin.

Solution. Next we turn to solutions $\psi(\mathbf{r}) = R_l(r)Y_l^m(\theta, \phi)$ of the Schrödinger equation for the motion of a particle in a central field. We presume that the wavefunction is well behaved everywhere but diverges like $R_l(r) \sim 1/r$ for $r \to 0$. We ask ourselves whether this is a problem because - after all - the wavefunction is normalizable. However, the divergent wavefunction $R_l(r)$ is defined everywhere except in the origin. This is more than a technicality because it implies that the Schrödinger equation is *not* satisfied in the origin. Using Problem 2.9 we find

$$\left(-\frac{\hbar^2}{2m_r}\Delta + \mathcal{V}(r) - E\right)\psi(\mathbf{r}) = -\frac{4\pi\hbar^2}{2m_r}\delta(\mathbf{r}),$$

which is zero everywhere *except in the origin.* Apparently, by solving the Schrödinger equation *after* separation in radial and angular variables we have generated a solution that does not satisfy the original equation (which is valid everywhere in space - *including the origin*). □

Problem 2.8. Show that for a normalizable radial wavefunction scaling like $R(r) \sim 1/r$ for $r \to 0$ the kinetic energy diverges in the origin.

Solution. We first write the radial wavefunction in the form $R_0(r) = (\chi_0(r)/r)$, where $\chi_0(r)$ is nonzero in the origin, $\lim_{r\to 0} \chi_0(r) = \chi_0(0) \neq 0$. Calculating the kinetic energy we find

$$\begin{aligned}
-\int R_0(r)Y_0^0(\theta,\phi)\,\frac{\hbar^2}{2m_r}\Delta R_0(r)Y_0^0(\theta,\phi)\,d\mathbf{r} &> -\frac{\hbar^2}{2m_r}\chi_0^2(0)\lim_{\epsilon\to 0}\int_V \frac{1}{4\pi r}\Delta\frac{1}{r}d\mathbf{r} \\
&= -\frac{\hbar^2}{2m_r}\chi_0^2(0)\lim_{\epsilon\to 0}\int_V \frac{1}{r}\delta(\mathbf{r})\,d\mathbf{r} \to \infty. \qquad \square
\end{aligned}$$

Problem 2.9. Use the Gauss theorem to demonstrate the relation $\Delta(1/r) = -4\pi\delta(\mathbf{r})$.

Solution. We first integrate this expression on both sides over a small sphere V of radius ϵ centered at the origin,

$$\int_V \Delta\frac{1}{r}d\mathbf{r} = -4\pi.$$

Here we used $\int_V \delta(\mathbf{r})\,d\mathbf{r} = 1$ for an arbitrarily small sphere at the origin. The l.h.s. also yields -4π as follows with the divergence theorem (Gauss theorem)

$$\lim_{\epsilon\to 0}\int_V \Delta\frac{1}{r}d\mathbf{r} = \lim_{\epsilon\to 0}\oint_S d\mathbf{S}\cdot\boldsymbol{\nabla}\frac{1}{r} = \lim_{\epsilon\to 0}\oint_S d\mathbf{S}\cdot\hat{\mathbf{r}}\left(-\frac{1}{r^2}\right) = \lim_{\epsilon\to 0}4\pi\epsilon^2\left(-\frac{1}{\epsilon^2}\right) = -4\pi. \qquad \square$$

2.2.2 Schrödinger equation in cylindrical coordinates

In systems with cylindrical symmetry about the z axis (see Fig. 2.2) the motion separates into motion parallel to the z axis and motion in planes orthogonal to the z axis,

$$\mathbf{p}^2 = (\hat{\mathbf{z}}\cdot\mathbf{p})^2 + (\hat{\mathbf{r}}_\perp\cdot\mathbf{p}_\perp)^2 + (\hat{\mathbf{r}}_\perp\times\mathbf{p}_\perp)^2, \tag{2.77}$$

where $\hat{\mathbf{r}}_\perp$ is defined in Eq. (2.17a) and $\hat{\mathbf{z}}$ is independent of position; $\mathbf{p}_\perp$ is the momentum in the xy plane. The quantization rule for the linear momentum in the z direction, $p_z\phi = \hat{\mathbf{z}}\cdot\mathbf{p}\phi \to -i\hbar\hat{\mathbf{z}}\cdot\boldsymbol{\nabla}\phi = -i\hbar\partial_z\phi$, can be applied without ambiguity and we have for the p_z^2 operator

$$p_z^2 = (\hat{\mathbf{z}}\cdot\mathbf{p})^2 = -\hbar^2\partial^2/\partial z^2. \tag{2.78}$$

With regard to the motion in planes orthogonal to the z axis we run into the same dilemma as we encountered with spherical coordinates. The quantization rules for $\hat{\mathbf{r}}_\perp\cdot\mathbf{p}_\perp = \mathbf{p}_\perp\cdot\hat{\mathbf{r}}_\perp$ are not unambiguous since $\hat{\mathbf{r}}_\perp\cdot\boldsymbol{\nabla}_\perp\phi \neq \boldsymbol{\nabla}_\perp\cdot\hat{\mathbf{r}}_\perp\phi$ (the direction of the unit vector $\hat{\mathbf{r}}_\perp$ depends on position). This dilemma can be circumvented in the same way as we did for p_r in Section 2.1.8. By rewriting Eq. (2.77) in the form

$$p_{r_\perp}^2 = (\hat{\mathbf{r}}_\perp\cdot\mathbf{p}_\perp)^2 = \mathbf{p}^2 - (\hat{\mathbf{r}}_\perp\times\mathbf{p}_\perp)^2 - (\hat{\mathbf{z}}\cdot\mathbf{p})^2 \tag{2.79}$$

we obtain an expression where $p_{r_\perp}$ is expressed in quantities for which the correspondence rules can be applied without ambiguity: $\mathbf{p}^2 \to -\hbar^2\Delta$ and $\hat{\mathbf{r}}_\perp\times\mathbf{p}_\perp \to -i\hbar\hat{\mathbf{r}}_\perp\times\boldsymbol{\nabla}_\perp$. Note that for cylindrical coordinates the angular momentum along the symmetry axis, $\mathbf{L}_\perp = \mathbf{r}_\perp\times\mathbf{p}_\perp$, satisfies the property

$$\mathbf{L}_\perp = -i\hbar\frac{\partial}{\partial\phi} = L_z. \tag{2.80}$$

Replacing the dynamical variables by their operators Eq. (2.79) takes the form

$$p_{r_\perp}^2 = -\hbar^2\left(\Delta - \frac{1}{r_\perp^2}\frac{\partial^2}{\partial\phi^2} - \frac{\partial^2}{\partial z^2}\right). \tag{2.81}$$

Substituting Eq. (2.19) for the laplacian we obtain

$$p_{r_\perp}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial r_\perp^2} + \frac{1}{r_\perp} \frac{\partial}{\partial r_\perp} \right). \tag{2.82}$$

At this point we can quantize the Hamiltonian and starting from Eq. (2.77) the Schrödinger equation takes the form

$$\left[-\frac{\hbar^2}{2m_r} \left(\frac{\partial^2}{\partial r_\perp^2} + \frac{1}{r_\perp} \frac{\partial}{\partial r_\perp} + \frac{\partial^2}{\partial z^2} \right) + \frac{L_z^2}{2m_r r_\perp^2} + \mathcal{V}(r_\perp, \phi, z) \right] \psi(r_\perp, \phi, z) = E\psi(r_\perp, \phi, z). \tag{2.83}$$

If the potential only depends on the $r_\perp$ variable, $\mathcal{V}(r_\perp, \phi, z) = \mathcal{V}(r_\perp)$, we have separation of variables for the axial, radial and angular motion and we find for the radial Schrödinger equation in this case

$$\frac{\hbar^2}{2m_r} \left(-\frac{d^2}{dr_\perp^2} - \frac{1}{r_\perp} \frac{d}{dr_\perp} + \frac{l^2}{r_\perp^2} + \mathcal{V}(r_\perp) \right) R_{nl}(r_\perp) = E R_{nl}(r_\perp). \tag{2.84}$$

Reduction to one-dimensional Schrödinger equation

Suppressing the quantum number n and using the definitions (2.71) the radial wave equation (2.84) takes the compact form

$$R_l'' + \frac{1}{r_\perp} R_l' + \left[\varepsilon - U(r_\perp) - \frac{m^2}{r_\perp^2} \right] R_l = 0, \tag{2.85}$$

where the prime refers to a derivative with respect to $r_\perp$. Introducing the functions

$$y_l(r_\perp) = r_\perp^{1/2} R_l(r_\perp), \tag{2.86}$$

also in this case the radial wave equation is reduced to the form of a one-dimensional Schrödinger equation,

$$y_l'' + \left[\frac{2m_r}{\hbar^2} (E - \mathcal{V}) + \frac{1/4 - m^2}{r_\perp^2} \right] y_l = 0. \tag{2.87}$$

2.3 Symmetry properties, conserved quantities and good quantum numbers

To conclude this chapter we return to the Schrödinger Hamiltonian,

$$\mathcal{H}_0 = -\frac{\hbar^2}{2m_r} \Delta + \mathcal{V}(r), \tag{2.88}$$

and discuss the main findings of the chapter against the background of the symmetry properties of this Hamiltonian. In general, the symmetries of a physical quantity are defined by the set of coordinate transformations that leave this quantity invariant. With each symmetry we associate an operator that generates the corresponding coordinate transformation. The transformations may be continuous (e.g., translation and rotation) or discrete (e.g., reflection and inversion). For instance, an equilateral triangle is invariant under rotation over 120° about an axis through the center of mass and perpendicular to the plane of the triangle; this reveals a three-fold symmetry under rotation (a finite rotation symmetry in this case). The mathematical discipline for the investigation of symmetry properties is called *Group theory* [69].

What are the symmetries of the Schrödinger Hamiltonian? For the potential energy term this is self evident from the notation because the central potential $\mathcal{V}(r)$ depends only on the radial distance $r = |\mathbf{r}|$ to the atomic center of mass. This manifestly being the case, $\mathcal{V}(r)$ is said to be *manifestly invariant* under any transformation that does not affect $|\mathbf{r}|$. This is the case for all *rotations* about the origin, all *reflections* about a plane through the origin and for *inversion* about the origin. For the kinetic energy term the symmetry under such operations is certainly not manifest and we need to have a closer look.

As an example we consider the *space inversion* by the *parity operator* P. This operator transforms the position $\mathbf{r}$ into position $-\mathbf{r}$, which is equivalent to sign reversal of the cartesian coordinates ($x \to -x$, $y \to -y$, $z \to -z$). As this operation conserves $|\mathbf{r}|$, the potential energy is invariant under space inversion. To determine the inversion symmetry of the kinetic energy operator we write the laplacian in cartesian coordinates,

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{2.89}$$

As this expression only contains second derivatives with regard to position it also is invariant under sign reversal. In other words the *Schrödinger Hamiltonian conserves parity for any interaction that conserves parity.* Note that by inverting twice we obtain the unit operator, $P^2 = \mathbb{1}$. In group theory P and P^2 are said to be the elements of a group of order 2: the inversion group (P^2 is the identity element). In the language of quantum mechanics we say that P commutes with the Hamiltonian. This implies that P is a hermitian operator; hence, its eigenvalues are real. As $P^2 = \mathbb{1}$ these eigenvalues are 1 (*even parity*) or -1 (*odd parity*). The radius vector is odd under parity (such vectors are called *polar vectors*). Angular momentum is even under parity (such vectors are called *axial vectors* or *pseudovectors*). As P commutes with $\mathcal{H}_0$, also the energy eigenstates must be parity eigenstates. This property was already noticed in Section 2.1.6.

What about rotational symmetry? From the commutation of L_z with $\mathcal{H}_0$ we find by using the product rule for differentiation

$$\left(\frac{\partial}{\partial\phi}\mathcal{H}_0 - \mathcal{H}_0\frac{\partial}{\partial\phi}\right)\psi(r,\theta,\phi) = \left(\frac{\partial\mathcal{H}_0}{\partial\phi}\right)_{\psi}\psi(r,\theta,\phi) = 0. \tag{2.90}$$

Because this relation is valid for any function $\psi(r,\theta,\phi)$ it implies the *invariance* of $\mathcal{H}_0$ under an *infinitesimal* rotation about the z axis,

$$\frac{\partial\mathcal{H}_0}{\partial\phi} = 0. \tag{2.91}$$

As the quantization axis was chosen in an arbitrary direction, this invariance of $\mathcal{H}_0$ holds for *any* infinitesimal rotation about the origin. Inversely, it is this invariance that makes L_z commute with $\mathcal{H}_0$, which implies that L_z is a conserved quantity (see Appendix B.2.4). The operator L_z can be identified with the operator for an infinitesimal rotation about the z axis as introduced above. The Hamiltonian is also invariant under any *finite* rotation about the origin because any such rotation can be realized by an infinite sequence of infinitesimal rotations about the origin. The infinite set of all rotations about the origin constitutes the elements of a continuous group: the *full rotation group*.

In this course we raise awareness for the symmetry properties but do not enter into the systematics of group theory. With regard to rotation we emphasize that for the Hamiltonian $\mathcal{H}_0$ the expectation values of $\mathbf{L}^2$ and L_z are *conserved* whatever the radial motion, showing that $\mathbf{L}^2$ and L_z are *observables* (observable constants of the motion). This means that the corresponding eigenvalues and eigenstates can be measured simultaneously to arbitrary precision and are uniquely determined by the quantum numbers l and m_l. Whenever a quantum number is conserved, it is called a *good quantum number* of the Hamiltonian under consideration. As a counter example we consider p_r^2. As p_r^2 does not commute with r (see Section 2.1.8), it does not commute with the Hamiltonian. This means that p_r^2 is not a conserved quantity and no good quantum number can be identified with the radial kinetic energy. This is no surprise from the physical point of view because the radial motion is oscillatory.

3

Motion of interacting neutral atoms

3.1 Introduction

In this chapter we investigate the relative motion of two neutral atoms under conditions typical for quantum gases. This means that the atoms are presumed to move slowly, typically at large separation, and to interact pair wise through a potential of the Van der Waals type. In Section 1.5 the term slowly was quantified as $\Lambda \gg r_0$, where Λ is the thermal wavelength and r_0 the range of the interaction potential. Associating with Λ a typical wavenumber for the relative motion of free atoms, $k \sim 1/\Lambda$, the inequality can be expressed in the form

$$kr_0 \ll 1. \tag{3.1}$$

As the Van der Waals interaction gives rise to elastic collisions, the total energy of the relative motion is conserved in time. As the potential energy vanishes at large interatomic separation the total energy is usually expressed in the form $E = \hbar^2 k^2/2m_r$. This implies that also the wavenumbers for the relative motion before and after the collision must be the same and shows that, far from the potential center, the collision can only affect the phase of the wavefunction - not its wavelength. Apparently, the appearance of a shift in phase relative to the free atomic motion provides the key to the quantum mechanical description of elastic collisions. This being said, we postpone the discussion of the actual collisional behavior to Chapter 4. First we prepare ourselves for this discussion by analyzing the stationary states for the relative motion in the presence of an interaction potential.

An important simplifying factor in the description of ultracold collisions is the emergence of universal behavior in the relative motion of the atoms. The latter applies to low-energy collisional states as well as to weakly bound states. Universal means in this context that, asymptotically (for $r \gg r_0$), the wavefunctions become independent of the details of the interaction potential but can be characterized in terms of a few parameters, each representing some characteristic length scale of the collisional system. In other words, very different short-range physics can give rise to the same scattering behavior. From a theory point of view this universality has the enormous advantage that the essential features of ultracold collisions can be described with the aid of simple model potentials for which analytical solutions can be obtained.

In our analysis of the collisional motion three characteristic length scales will appear, the *interaction range* r_0, the *scattering length* a and the *effective range* r_e, each expressing a different aspect of the interaction. The range r_0 was already introduced in Chapter 1 as the distance beyond which the interaction may be neglected even for $k \to 0$. The second characteristic length, the s-wave scattering length a, acts as an effective *hard-sphere diameter*. It is a measure for the *interaction strength* and determines the *collision cross section* in the limit $k \to 0$ as will be elaborated on in Chapter 4. The third characteristic length, the effective range r_e expresses how the potential affects the energy dependence of the cross section and determines when the $k \to 0$ limit is reached.

The s-wave scattering length is the central parameter for the theoretical description of bosonic quantum gases. It determines both the *thermodynamic* and the *collisional properties* of these gases. In single-component fermionic gases the s-wave scattering length plays no role because the wavefunction for the relative motion of the atoms has to be antisymmetric. In two-component fermionic gases this restriction is absent for collisions between atoms of different components. As a consequence, in these systems the inter-component s-wave scattering length determines the collision related properties - for instance the thermalization rate.

This chapter consists of three main sections. In Section 3.2 we show how the phase shift appears as a result of interatomic interaction in the wavefunction for the relative motion of two atoms. For free particles the phase shift is zero. An integral expression for the phase shift is derived. In Section 3.3 and beyond we specialize to the case of low-energy collisions ($kr_0 \ll 1$). First, the basic phenomenology is introduced and analyzed for simple model potentials like the *hard-sphere* (Section 3.3) and the *spherical well* (Section 3.4), where the existence of a short range is manifest. Then we show that this phenomenology also holds for arbitrary *short-range* potentials (Section 3.6). For the case $l = 0$ we derive general expressions for the energy dependence of the s-wave phase shift, both in the absence (Sections 3.6.3) and in the presence (Section 3.6.4) of a weakly bound s level. Unfortunately the existence of a finite range is in general far from obvious. Therefore, in order to clarify this issue for the Van der Waals interaction we introduce in Section 3.7 power-law potentials $\mathcal{V}(r) = C_s r^{-s}$ and show that for this class of potentials a finite r_0 can only be defined for low angular momentum values $l < \frac{1}{2}(s-3)$. For $l \geq \frac{1}{2}(s-3)$ we have to rely on a different method and use perturbation theory to derive an analytic expression for the phase shift in the $k \to 0$ limit (Section 3.7.2). This method works as long as so called shape resonances ($l > 0$) play no role. In the last section of this chapter (Section 3.9) we analyze how the pair interaction energy is related to their scattering properties and how this differs for identical bosons as compared to unlike particles.

3.2 The collisional phase shift

3.2.1 Schrödinger equation

The starting point for the description of the relative motion of two atoms at energy E is the Schrödinger equation (2.66),

$$\left[\frac{1}{2m_r}\left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) + \mathcal{V}(r)\right]\psi(r,\theta,\phi) = E\psi(r,\theta,\phi). \tag{3.2}$$

Here m_r is the reduced mass of the atom pair and $\mathcal{V}(r)$ the interaction potential. As discussed in Section 2.1.6 the eigenfunctions $\psi(r,\theta,\phi)$ can be separated in a radial and a angular part,

$$\psi = R_l(r)Y_l^m(\theta,\phi), \tag{3.3}$$

where the functions $Y_{lm}(\theta,\phi)$ are spherical harmonics and the functions $R_l(r)$ satisfy the *radial wave equation*

$$\left[\frac{\hbar^2}{2m_r}\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2}\right) + \mathcal{V}(r)\right]R_l(r) = ER_l(r). \tag{3.4}$$

By the separation procedure the angular momentum term is replaced by a repulsive *effective potential*

$$\mathcal{V}_{\mathrm{rot}}(r) = l(l+1)\frac{\hbar^2}{2m_r r^2}, \tag{3.5}$$

representing the *rotational energy* of the atom pair at a given distance and for *a given rotational quantum number l*. In combination with an attractive interaction it gives rise to a *centrifugal barrier* for the radial motion of the atoms. This is illustrated in Fig. 3.1 for the example of hydrogen.

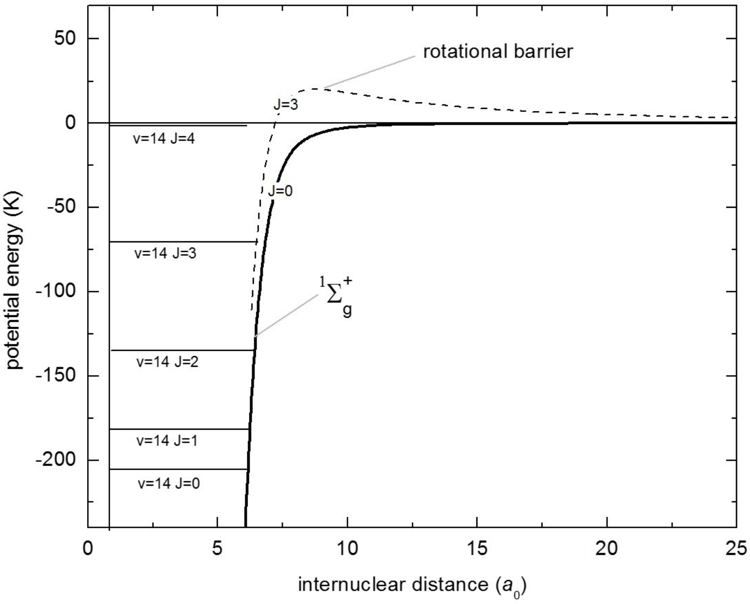

Figure 3.1: Example showing the high-lying bound states near the continuum of the singlet potential $^1\Sigma_g^+$ (the bonding potential) of the hydrogen molecule; v and J are the vibrational and rotational quantum numbers, respectively. The dashed line shows the effect of the $J = 3$ centrifugal barrier.

To analyze the radial wave equation we introduce *reduced energies*

$$\varepsilon = 2m_r E/\hbar^2 \quad \text{and} \quad U(r) = 2m_r \mathcal{V}(r)/\hbar^2, \tag{3.6}$$

which put Eq. (3.4) in the form

$$R_l'' + \frac{2}{r}R_l' + \left[\varepsilon - U(r) - \frac{l(l+1)}{r^2}\right] R_l = 0. \tag{3.7}$$

With the substitution $\chi_l(r) = rR_l(r)$ it reduces to a 1D Schrödinger equation

$$\chi_l'' + [\varepsilon - U(r) - \frac{l(l+1)}{r^2}]\chi_l = 0. \tag{3.8}$$

The latter form is particularly convenient for the case $l = 0$,

$$\chi_0'' + [\varepsilon - U(r)]\chi_0 = 0. \tag{3.9}$$

In this chapter we shall use the *wave number* notation $\varepsilon = k^2$ for $\varepsilon > 0$. Here $k = \pm[2m_r E/\hbar^2]^{1/2}$; the + sign will be identified with "outgoing" waves and the − sign with "incoming" waves. Similarly, we shall write $\varepsilon = -\kappa^2$ for $\varepsilon < 0$. Hence, for a bound state of energy $E_b < 0$ we have $\kappa = [-2m_r E_b/\hbar^2]^{1/2} = [2m_r|E_b|/\hbar^2]^{1/2}$.

3.2.1.1 Complex notation

From a mathematical point of view we can equally well use complex k values denoted by $\bar{k} = |\bar{k}|e^{i\phi}$. In the latter case positive energies ($E > 0$) correspond to real $\bar{k} = \pm\sqrt{2m_r|E|/\hbar^2}$ and negative energies ($E < 0$) to imaginary $\bar{k} = \pm i\sqrt{2m_r|E|/\hbar^2}$. Introducing the complex energy

$$\bar{E} = \hbar^2\bar{k}^2/2m_r = (\hbar^2|\bar{k}|^2/2m_r)e^{i2\phi} = |\bar{E}|e^{i\Phi}, \tag{3.10}$$

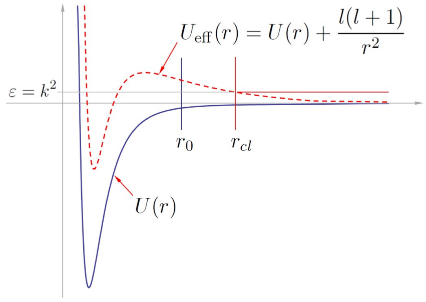

Figure 3.2: The presence of a rotational barrier gives rise to an exponential suppression of the radial wavefunction for $r < r_{\mathrm{cl}}$ and is negligible at distances where the interaction becomes noticeable $r \ll r_0$.

where $|\bar{E}| = \hbar^2|\bar{k}|^2/2m_r$ and $\Phi = 2\phi$; i.e., the complex angle of $\bar{E}$ increases twice as fast as that of $\bar{k}$. Inversely, the complex wavevector $\bar{k}$ is a double-valued function of the complex energy $\bar{E}$,

$$\bar{k} = \pm\sqrt{2m_r|\bar{E}|/\hbar^2}\, e^{i\Phi/2} \quad \text{with } 0 \leq \Phi < 2\pi. \tag{3.11}$$

This double valuedness can be removed by introducing a Riemann surface consisting of two sheets, a first Riemann sheet (the *first* sheet) with $0 < \Phi = 2\phi \leq 2\pi$ corresponding to the *positive sign* $\left(\mathrm{Im}\,\bar{k} > 0\right)$ and a second Riemann sheet (the *second* sheet) with $2\pi \leq \Phi = 2\phi < 4\pi$ corresponding to the *negative sign* $\left(\mathrm{Im}\,\bar{k} < 0\right)$,

$$\bar{k} = \sqrt{2m_r|\bar{E}|/\hbar^2}\, e^{i\Phi/2} \quad \text{with } 2\pi \leq \Phi < 4\pi.$$

By convention the bound states are represented by points on the positive sheet of the Riemann surface. This is called the *physical* sheet. The points on the negative sheet of the Riemann surface can be associated with so-called *virtual levels* ($l = 0$) and scattering resonances ($l > 0$).

3.2.2 Low-energy limit - s-wave regime

For two atoms with relative angular momentum $l > 0$ there exists a distance r_{cl}, called the *classical turning point*, below which the rotational energy exceeds the total energy E,

$$k^2 = \frac{l\,(l+1)}{r_{\mathrm{cl}}^2}. \tag{3.12}$$

This is illustrated in Fig. 3.2. In the *classically inaccessible* region of space ($r < r_{\mathrm{cl}}$) the radial wavefunction is exponentially suppressed.[1] Combining Eq. (3.12) with the condition (3.1) we obtain the inequality $kr_0 = \sqrt{l\,(l+1)}r_0/r_{\mathrm{cl}} \ll 1$, which implies that the classical turning point is found at a distance much larger than the range of the interaction,

$$kr_0 \ll 1 \Leftrightarrow r_{\mathrm{cl}} \gg r_0 \text{ for } l \neq 0. \tag{3.13}$$

As the range r_0 defines the distance beyond which the potential can be neglected, this inequality shows that the radial motion is *not* affected by the presence of the potential $\mathcal{V}(r)$ in the radial wave equation. The *notable exception* is the case $l = 0$, where the barrier is absent and the potential gives rise to a substantial distortion of the radial waves. In other words, for $kr_0 \ll 1$ phase shifts (i.e., scattering) can only arise from collisions with zero angular momentum. The range of collision energies where the inequalities (3.13) are valid is called the *s-wave regime*.

---

[1] At this point we exclude tunneling through the barrier and the occurrence of shape resonances.

3.2.3 Free particle motion - spherical Bessel functions

We first have a look at the case of free particles. In this case $\mathcal{V}(r) = 0$ and the radial wave equation (3.7) becomes

$$R_l'' + \frac{2}{r}R_l' + \left[k^2 - \frac{l(l+1)}{r^2}\right] R_l = 0, \tag{3.14}$$

which can be rewritten in the form of the *spherical Bessel* differential equation by introducing the dimensionless variable $\varrho \equiv kr$,

$$R_l'' + \frac{2}{\varrho}R_l' + \left[1 - \frac{l(l+1)}{\varrho^2}\right] R_l = 0. \tag{3.15}$$

Here the derivatives are with respect to the new variable.

The general solution of Eq. (3.15) for angular momentum l is a linear combination of two particular solutions, one *regular*, the *spherical Bessel* function $j_l(\varrho)$ (see Fig. 3.3), and one *irregular*, the *spherical Neumann* function $n_l(\varrho)$ (not shown Fig. 3.3):

$$R_l(\varrho) = A_l j_l(\varrho) + B_l n_l(\varrho). \tag{3.16}$$

Properties of the functions $j_l(\varrho)$ and $n_l(\varrho)$ are given in Appendix C.12.1. The coefficients A_l and B_l are called the *scattering parameters.* To best represent the radial motion it is conventional to define alternative scattering parameters

$$\{A_l, B_l\} \to \{c_l, \eta_l\}, \quad \text{where} \left\{ \begin{array}{l} A_l = c_l \cos \eta_l \\ B_l = c_l \sin \eta_l. \end{array} \right. \tag{3.17}$$

The new parameters represent the amplitude c_l and the *asymptotic phase*

$$\eta_l = \arctan B_l/A_l \tag{3.18}$$

of the wavefunction. In terms of these new parameters Eq. (3.16) becomes

$$R_l(\varrho) = c_l \left[\cos \eta_l \, j_l(\varrho) + \sin \eta_l \, n_l(\varrho)\right]. \tag{3.19}$$

Note that this equation is singular in the origin except for the case of vanishing phase shifts. Therefore, in the case of free particles we require $\eta_l = 0$ for *all* angular momentum values l. This implies that the general solution reduces to the regular one, $j_l(kr)$.

3.2.4 Free particle motion for the case $l = 0$

The solution of the radial Schrödinger equation is particularly simple for the case $l = 0$ (s waves). Writing the radial wave equation in the form of the 1D-Schrödinger equation (3.9) we have for free particles

$$\chi_0'' + k^2 \chi_0 = 0, \tag{3.20}$$

with general solution $\chi_0(k, r) = c_0 \sin(kr + \eta_0)$. The s waves are special because $\chi_0(k, r)$ has the simple sinusoidal shape not only asymptotically but for all values $r > 0$. The corresponding wavefunction is

$$R_0(k, r) = \frac{c_0}{kr} \sin(kr + \eta_0). \tag{3.21}$$

Again we require $\eta_0 = 0$ for the case of free particles to assure that Eq. (3.21) is non-singular in the origin. For $\eta_0 = 0$ we observe that $R_0(k, r)$ reduces to the spherical Bessel function $j_0(kr)$ shown in Fig. 3.3.

3.2.5 Significance of the phase shifts

To investigate the effect of a *short-range* interaction potential $\mathcal{U}(r)$ we return to the radial wave equation (3.7). As the potential is of short range it may be neglected for $r \gg r_0$ and the general solutions coincide with those of the spherical Bessel equation,

$$R_l(k,r) \underset{r\gg r_0}{\simeq} c_l \left[\cos\eta_l \, j_l(kr) + \sin\eta_l \, n_l(kr)\right]. \tag{3.22}$$

For $r \gg 1/k$ the spherical Bessel and Neumann functions assume their asymptotic form and we find - see Eqs. (C.106a) and (C.106b)

$$R_l(k,r) \underset{kr\to\infty}{\simeq} \frac{c_l}{kr}\{\cos\eta_l \sin(kr - \tfrac{1}{2}l\pi) + \sin\eta_l \cos(kr - \tfrac{1}{2}l\pi)\}. \tag{3.23}$$

This asymptotic expression can be rewritten in a convenient form with the aid of the angle-addition formula for the sine,

$$R_l(k,r) \underset{r\to\infty}{\simeq} \frac{c_l}{kr}\sin(kr + \eta_l - \tfrac{1}{2}l\pi). \tag{3.24}$$

Hence, the constant $\eta_l(k)$ represents the *asymptotic phase shift.* For a given value of k this phase shift fixes the general solution of the radial wavefunction $R_l(k,r)$ up to an l dependent normalization constant c_l. Note that in view of the k dependence of the phase shift, R_l is a function of k and r rather than a function of the product kr. Whereas in the case of free particles the phase shifts must all vanish, in the presence of the interaction they provide the proper asymptotic form of the *distorted waves*. The non-zero asymptotic phase shift is the signature of the interaction at short distance; the motion becomes free-particle like (undistorted) only at large distance from the scattering center. In elastic scattering the relative energy $\hbar^2k^2/2m$ is conserved; hence, asymptotically also k and the de Broglie wavelength. This leaves only the asymptotic phase of the wave to be affected.

3.2.5.1 Scattering matrix

Real wavefunctions like Eq. (3.19) are convenient for visualization but the complex notation is at least as valuable. Rewriting Eq. (3.24) in the form

$$R_l(k,r) \underset{r\to\infty}{\simeq} \frac{c_l}{2k} i \left[e^{-i\eta_l}\frac{e^{-i(kr-\frac{1}{2}l\pi)}}{r} - e^{i\eta_l}\frac{e^{i(kr-\frac{1}{2}l\pi)}}{r} \right], \tag{3.25}$$

we note that for $r \to \infty$ the stationary solution $R_l(k,r)$ can be regarded as an "incoming" spherical wave $e^{-i(kr-\frac{1}{2}l\pi)}/r$, interfering with an "outgoing" spherical wave $e^{i(kr-\frac{1}{2}l\pi)}/r$. It is convention to choose the phase of the normalization constant such that the phase of the incoming wave is zero,

$$R_l(k,r) \underset{r\to\infty}{\simeq} \frac{c_l'}{2k}\left[\frac{e^{-ikr}}{r} - e^{-il\pi}e^{2i\eta_l}\frac{e^{ikr}}{r}\right]. \tag{3.26}$$

Apart from the sign, the ratio of the phase factors of the outgoing over the incoming wave is

$$S_l \equiv e^{2i\eta_l}. \tag{3.27}$$

This quantity is called the *scattering matrix* (S matrix) or, better, the l-wave contribution to the S matrix. Being unitary it does not suffer from the divergences of the ratio $B_l/A_l = \tan\eta_l$. In the present context the name scattering matrix is a bit heavy because we only have a single matrix element (1×1 matrix). The term matrix finds its origin in the description of scattering of particles with an internal degree of freedom (like spin), for which the phase factor is replaced by a unitary matrix.

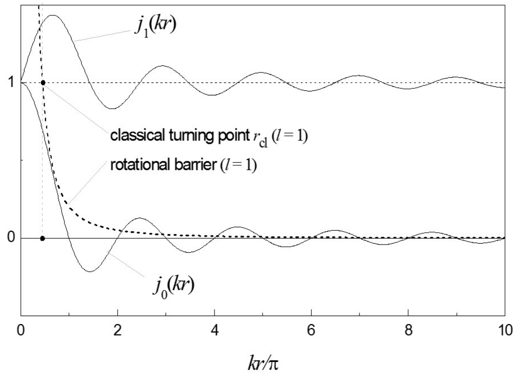

Figure 3.3: The lowest-order spherical Bessel functions $j_0(kr)$ and $j_1(kr)$, which are the $l = 0$ and $l = 1$ eigenfunctions of the radial wave equation in the absence of interactions (free atoms). Also shown is the $l = 1$ rotational barrier and the corresponding classical turning point for the radial motion. The $j_1(kr)$ is shifted up to the horizontal dashed line only for convenience of display. Note that $j_1(kr) \ll j_0(kr)$ for $kr_c \ll 1$.

3.2.5.2 Riccati-Bessel functions

The spherical-Bessel differential equation (3.15) can be reduced to a 1D Schrödinger equation

$$\chi_l'' + \left[1 - \frac{l(l+1)}{\varrho^2}\right]\chi_l = 0, \tag{3.28}$$

by changing to reduced wavefunctions of the type $\chi_l(\varrho) = \varrho R_l(\varrho)$. Therefore, the general solution of Eq. (3.28) follow directly from the solutions for the radial wavefunction $R_l(\varrho)$. To keep the notation compact one introduces *Riccati-Bessel* functions $\hat{\jmath}_l(\varrho) = \varrho j_l(\varrho)$ (for the *regular* solutions) and *Riccati-Neumann* function $\hat{n}_l(\varrho) = \varrho n_l(\varrho)$ (for the *irregular* solutions). For $\eta_l \to 0$ the general solution

$$\chi_l(\varrho) = c_l \left[\cos\eta_l \, \hat{\jmath}_l(\varrho) + \sin\eta_l \, \hat{n}_l(\varrho)\right]. \tag{3.29}$$

reduces to the regular one, $\hat{\jmath}_l(kr)$, which is the physical solution for free particles. For $\varrho \to \infty$ the general solution has the following asymptotic form

$$\chi_l(k,r) \underset{r\to\infty}{\simeq} c_l \sin(kr + \eta_l - \tfrac{1}{2}l\pi), \tag{3.30}$$

which can be written in the form

$$\chi_l(k,r) \underset{r\to\infty}{\simeq} \frac{c_l}{2} i \left[e^{-i\eta_l} e^{-i(kr - \frac{1}{2}l\pi)} - e^{i\eta_l} e^{i(kr + \frac{1}{2}l\pi)}\right]. \tag{3.31}$$

3.2.5.3 Riccati-Hankel functions

The general solution (3.29) of the 1D Schrödinger equation for angular momentum l can also be written in the form (see Problem 3.1)

$$e^{i\eta_l}\chi_l(k,r) = \frac{c_l}{2} i \left[\hat{h}_l^-(kr) - e^{2i\eta_l}\hat{h}_l^+(kr)\right], \tag{3.32}$$

where the functions $\hat{h}_l^{\pm}(\varrho) = \hat{n}_l(\varrho) \pm i\,\hat{\jmath}_l(\varrho)$ are *Riccati-Hankel* functions of the first (+) and second (−) kind, mutually related by

$$\hat{h}_l^{\pm}(kr) = (-1)^l \hat{h}_l^{\mp}(-kr) \tag{3.33}$$

(cf. Appendix C.12.1). Note that for $\eta_l \to 0$ the general solution reduces to the regular one, $\hat{\jmath}_l(kr)$.

Problem 3.1. Show that the general solution of the Riccati-Bessel differential equation for angular momentum l, Eq. (3.29), can be written in the form

$$\chi_l(\varrho) = \tfrac{1}{2}i\left[e^{-i\eta_l}\hat{h}_l^-(\varrho) - e^{i\eta_l}\hat{h}_l^+(\varrho)\right],$$

where we set have $c_l = 1$ and the $\hat{h}_l^{\pm}(\varrho)$ are Riccati-Hankel functions.

Solution. The general solution of the spherical Bessel equation is given by Eq. (3.29),

$$\chi_l(\varrho) = \cos\eta_l\, \hat{\jmath}_l(\varrho) + \sin\eta_l\, \hat{n}_l(\varrho).$$

Writing $\sin\eta_l$ and $\cos\eta_l$ in the form of complex exponents we find

$$\begin{aligned}\chi_l(\varrho) &= \tfrac{1}{2}\left(e^{i\eta_l} + e^{-i\eta_l}\right)\hat{\jmath}_l(\varrho) - \tfrac{1}{2}i\left(e^{i\eta_l} - e^{-i\eta_l}\right)\hat{n}_l(\varrho)\\ &= \tfrac{1}{2}e^{i\eta_l}\left[\hat{\jmath}_l(\varrho) - i\,\hat{n}_l(\varrho)\right] + \tfrac{1}{2}e^{-i\eta_l}\left[\hat{\jmath}_l(\varrho) + i\,\hat{n}_l(\varrho)\right].\end{aligned}$$

Using definition (C.95) of the Hankel functions we obtain the desired expression. □

3.2.6 Integral representations for the phase shift

Exact integral expressions for the phase shift can be obtained with the aid of the *Wronskian Theorem.* In this approach we compare the *distorted wave* solutions $\chi_l = krR_l(r)$ with the *regular* solutions $\hat{\jmath}_l(kr)$ and the *irregular* solutions $\hat{n}_l(kr)$ of Eq. (3.28); i.e., we compare solutions of the 1D Schrödinger equation obtained for $U \neq 0$ with those obtained by setting $U = 0$. As will be shown, the resulting expressions hold for potentials $U(r)$ that vanish for $r \to \infty$ more rapidly than $1/r$ and diverge slower than $1/r^2$ for $r \to 0$. Because the distorted waves $\chi_l(k,r)$ are the physical solutions they have to be regular. Furthermore, it will be shown that for the mentioned class of potentials the condition of being regular is equivalent to the statement that close to the origin they may be replaced by Riccati-Bessel functions,

$$\chi_l(k,r) \sim \hat{\jmath}_l(kr) \quad \text{for } r \to 0. \tag{3.34}$$

This canonical form for the $r \to 0$ limiting behavior is allowed because (as will be shown) it does not effect the value obtained for the phase shift.

Comparing first the regular solutions $\hat{\jmath}_l(kr)$ of Eq. (3.28) with the solutions $\chi_l(k,r)$ of Eq. (3.8) for the same value $\varepsilon = k^2$ we use the Wronskian Theorem in the form (C.148)

$$W(\chi_l, \hat{\jmath}_l)|_a^b = -\int_a^b U(r)\chi_l(r)\hat{\jmath}_l(r)dr. \tag{3.35}$$

Here $W(\chi_l, \hat{\jmath}_l) = \chi_l(r)\hat{\jmath}_l'(r) - \chi_l'(r)\hat{\jmath}_l(r)$ is the wronskian of χ_l and $\hat{\jmath}_l$. Because both χ_l and $\hat{\jmath}_l$ are regular at the origin this wronskian is zero in the origin, $W(\chi_l, \hat{\jmath}_l)|_0 = 0$. Asymptotically we find $\hat{\jmath}_l(r)$ and $\hat{\jmath}_l'(r)$ with the aid of Eq. (C.106a), $\lim_{r\to\infty}\hat{\jmath}_l(r) = \sin(kr - \frac{1}{2}l\pi)$ and $\lim_{r\to\infty}\hat{\jmath}_l'(r) = k\cos(kr - \frac{1}{2}l\pi)$. For the distorted waves we have $\lim_{r\to\infty}\chi_l(r) = \sin(kr + \eta_l - \frac{1}{2}l\pi)$ and $\lim_{r\to\infty}\chi_l'(r) = k\cos(kr + \eta_l - \frac{1}{2}l\pi)$. Hence, asymptotically the wronskian is given by

$$\lim_{r\to\infty} W(\chi_l, y_l) = k\sin\eta_l. \tag{3.36}$$

With the Wronskian Theorem (3.35) we obtain the following integral expression for the phase shift,

$$\sin\eta_l = -\frac{1}{k}\int_0^\infty U(r)\chi_l(k,r)\hat{\jmath}_l(kr)dr \tag{3.37}$$

Analogously, by comparing the distorted wave solutions $\chi_l = krR_l(r)$ with the *irregular* solutions $\hat{n}_l(kr)$ we obtain (see Problem 3.2),

$$\cos\eta_l = 1 + \frac{1}{k}\int_0^\infty U(r)\chi_l(k,r)\hat{n}_l(kr)dr. \tag{3.38}$$

Let us verify that the integrals (3.37) and (3.38) converge as long as $U(r)$ diverges slower than $1/r^s$ with $s < 2$ for $r \to 0$. This condition is most difficult to satisfy for Eq. (3.38) because the Riccati-Neumann functions with $l \neq 0$ diverge for $r \to 0$. Since $\chi_l(k,r)$ is regular in the origin it satisfies the relation $\chi_l(k,r) \leq \hat{\jmath}_l(kr)$. The integrand of Eq. (3.38) for $r \to 0$ satisfies the condition

$$r^{-s}\chi_l(k,r)\hat{n}_l(kr) \leq r^{-s}\hat{\jmath}_l(kr)\hat{n}_l(kr) \underset{r\to 0}{\sim} r^{-s+1}. \tag{3.39}$$

The primitive of this expression is r^{-s+2}, which vanishes for $r \to 0$ only for $s < 2$ as was mentioned above.

Analogously we can verify that the integrals (3.37) and (3.38) converge for potentials falling off faster than $U(r) \sim 1/r^s$ with $s > 1$ for $r \to \infty$. We demonstrate this for Eq. (3.37). Using the asymptotic expressions for $\chi_l(k,r)$ and $\hat{\jmath}_l(kr)$ the integrand of takes the asymptotic form

$$\begin{aligned} U(r)\chi_l(k,r)\hat{\jmath}_l(kr)r &\underset{r\to\infty}{\sim} (1/r)^s \left\{\sin(kr - \tfrac{1}{2}l\pi)\cos\eta_l + \cos(kr - \tfrac{1}{2}l\pi)\sin\eta_l\right\}\sin(kr - \tfrac{1}{2}l\pi) \\ &\underset{r\to\infty}{\sim} (1/r)^s \left\{\cos\eta_l\left[1 - \cos(2kr - l\pi)\right] + \tfrac{1}{2}\sin(2kr - l\pi)\sin\eta_l\right\}. \end{aligned} \tag{3.40}$$

The oscillatory terms are bounded in the integration. Therefore, only the first term may be divergent. Its primitive is $1/r^{s-1}$, which tends to zero for $r \to \infty$ only for $s > 1$.

Problem 3.2. Show that the phase shift can be expressed in the form

$$\cos\eta_l = 1 + \frac{1}{k}\int_0^\infty U(r)\chi_l(k,r)\hat{n}_l(kr)dr.$$

Solution. Comparing the distorted wave solutions $\chi_l = rR_l(r)$ with the *irregular* solutions $\hat{n}_l(kr)$ of the 1D Schrödinger equation. In this case the wronskian is given by

$$W(\chi_l, \hat{n}_l) = \chi_l(r)\hat{n}_l'(r) - \chi_l'(r)\hat{n}_l(r).$$

Because χ_l is regular we may replace $\chi_l(r)$ by $\hat{\jmath}_l(r)$ for $r \to 0$. Thus, we have

$$W(\chi_l, \hat{n}_l) \underset{r\to 0}{\simeq} \hat{\jmath}_l(r)\hat{n}_l'(r) - \hat{\jmath}_l'(r)\hat{n}_l(r) = -k \tag{a}$$

and the wronskian in the origin is given by $W(\chi_l, \hat{n}_l)|_0 = -k$. Asymptotically we have for $\hat{n}_l(r)$ with Eq. (C.106b) $\lim_{r\to\infty}\hat{n}_l(r) = \cos(kr - \frac{1}{2}l\pi)$ and $\lim_{r\to\infty}\hat{n}_l'(r) = -k\sin(kr - \frac{1}{2}l\pi)$. For the distorted waves we have $\lim_{r\to\infty}\chi_l(r) = \sin(kr + \eta_l - \frac{1}{2}l\pi)$ and $\lim_{r\to\infty}\chi_l'(r) = k\cos(kr + \eta_l - \frac{1}{2}l\pi)$. Hence, asymptotically the wronskian is given by

$$\lim_{r\to\infty} W(\chi_l, \hat{n}_l) = -k\cos\eta_l.$$

With the wronskian theorem (a) we obtain the desired integral expression for the phase shift. □

3.2.6.1 Alternative expressions for the phase shifts

Since $e^{-i\eta_l} = \cos\eta_l - i\sin\eta_l$, we obtain by substitution of Eqs. (3.37) and (3.38)

$$e^{-i\eta_l} = 1 + \frac{1}{k}\int_0^\infty U(r)\chi_l(k,r)\hat{h}_l^+(kr)dr, \tag{3.41}$$

Similarly, since $e^{2i\eta_l} = 1 + 2ie^{i\eta_l}\sin\eta_l$ we obtain the S matrix by substituting Eq. (3.37)

$$S_l = e^{2i\eta_l} = 1 - \frac{2i}{k}\int_0^\infty U(r)\left[e^{i\eta_l}\chi_l(k,r)\right]\hat{\jmath}_l(kr)dr. \tag{3.42}$$

3.3 Hard-sphere potentials

We now turn to analytical solutions for model potentials in the limit of low energy. We first consider the case of two hard spheres of equal size. These can approach each other to a minimum distance equal to their *diameter* a. For $r \leq a$ the radial wave function vanishes, $R_l(r) = 0$. Outside the hard sphere we have free atoms, $\mathcal{V}(r) = 0$, with relative wave number $k = [2m_r E/\hbar^2]^{1/2}$. Thus, for $r \geq a$ the general solution for the radial wave functions of angular momentum l is given by the free atom expression (3.19),

$$R_l(k,r) = c_l[\cos\eta_l j_l(kr) + \sin\eta_l n_l(kr)]. \tag{3.43}$$

Asymptotically this takes the form (3.24) of a phase-shifted spherical Bessel function,

$$R_l(k,r) \underset{r\to\infty}{\simeq} \frac{c_l}{kr}\sin(kr + \eta_l - \tfrac{1}{2}l\pi). \tag{3.44}$$

To determine the phase shift we require as a boundary condition that $R_l(k,r)$ vanishes at the surface of the hard sphere (see Fig. 3.4),

$$\cos\eta_l j_l(ka) + \sin\eta_l n_l(ka) = 0. \tag{3.45}$$

Hence, the phase shift follows from the expression

$$\tan\eta_l = -\frac{j_l(ka)}{n_l(ka)}. \tag{3.46}$$

We analyze two limiting cases using the asymptotic expressions (C.106) and (C.107):

- For $ka \ll 1$ the phase shift can be written as [1]

  $$\tan\eta_l \underset{k\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}(ka)^{2l+1} \Longrightarrow \eta_l \underset{k\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}(ka)^{2l+1} \tag{3.47}$$

  and the radial wavefunction becomes

  $$R_l(k,r) \underset{r\to\infty}{\simeq} \frac{c_l}{kr}\sin\left(kr - (2l+1)(ka)^{2l+1}/[(2l+1)!!]^2 - \tfrac{1}{2}l\pi\right). \tag{3.48}$$

  In particular, for s waves we find

  $$R_0(k,r) \underset{r\to\infty}{\simeq} \frac{c_0}{kr}\sin[k(r-a)]. \tag{3.49}$$

- For $ka \gg 1$ we find

  $$\tan\eta_l \underset{k\to\infty}{\simeq} -\tan(ka - \tfrac{1}{2}l\pi) \Longrightarrow \eta_l \underset{k\to\infty}{\simeq} -ka + \tfrac{1}{2}l\pi \tag{3.50}$$

  and for the radial wavefunction

  $$R_l(k,r) \underset{r\to\infty}{\simeq} \frac{c_l}{kr}\sin[k(r-a)]. \tag{3.51}$$

  Note that this expression is independent of l; i.e., for large k all wavefunctions are shifted by the diameter of the hard sphere. This is only the case for hard-sphere potentials.

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[1] The double factorial is defined as $n!! = n(n-2)(n-4)\cdots$.

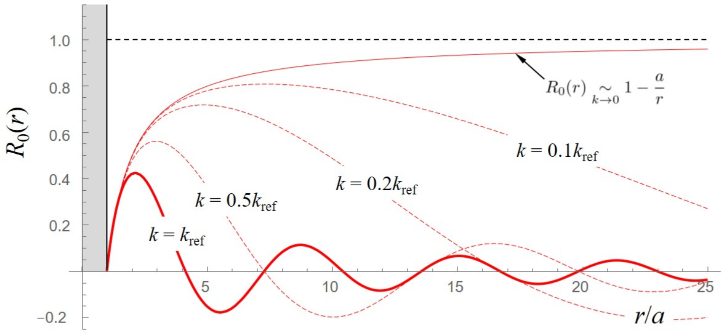

Figure 3.4: Radial wavefunctions ($l = 0$) for decreasing values of k (down to the $k \to 0$ limit) in the case of a hard sphere potential. The boundary condition is fixed by the requirement that the wavefunction vanishes at the edge of the hard sphere, $R_0(ka) = 0$.

3.3.1 s-wave phase shifts for hard spheres

The case $l = 0$ is special because the Eqs. (3.49) and (3.51) are not valid only asymptotically but for *all* values of k and for the *full* range of distances outside the sphere ($r \geq a$). This follows directly from the general solution (3.43) with the aid of Eq. (C.105a) for the case $l = 0$,

$$R_0(k,r) = \frac{c_0}{kr}\left(\cos\eta_0 \sin kr + \sin\eta_0 \cos kr\right) = \frac{c_0}{kr}\sin(kr+\eta_0). \tag{3.52}$$

The phase shift follows from the boundary condition $R_0(k,a) = 0$, which can be written in the form

$$\cos\eta_0 \sin ka + \sin\eta_0 \cos ka = 0. \tag{3.53}$$

Hence, the phase shift is

$$\eta_0 = -ka. \tag{3.54}$$

With this expression Eq. (3.52) reduces to

$$R_0(k,r) = \frac{c_0}{kr}\sin\left[k(r-a)\right]. \tag{3.55}$$

This expression is exact for *any* value of k, as announced above. The linear k dependence of η_0 simply expresses its definition in which the shift of the wave (by a) is compared to the de Broglie wavelength $\lambda_{\rm dB}$, $\eta_0 = -2\pi a/\lambda_{\rm dB}$. As a consequence the phase shift vanishes for $k \to 0$,

$$\lim_{k\to 0}\eta_0(k) = 0. \tag{3.56}$$

This result is obvious when comparing the *finite* shift a to the diverging wavelength Λ.

Interestingly, in the limit $k \to 0$ the expression (3.55) becomes k independent,

$$R_0(r) \underset{k\to 0}{\sim} 1 - \frac{a}{r} \quad \text{for } a \leq r \ll 1/k. \tag{3.57}$$

This important result is illustrated in Fig. 3.4. In the limit $k \to 0$ the wavefunction is essentially constant throughout space (up to a distance $1/k \to \infty$ at which it starts to oscillate), except for a small region of radius a about the potential center.

In preparation for comparison with the phase shift induced by other potentials and for the calculation of scattering amplitudes and collision cross sections (cf. Chapter 4) we rewrite Eq. (3.54) in the form of a series expansion of $k\cot\eta_0$ in powers of k^2,

$$k\cot\eta_0(k) = -\frac{1}{a} + \frac{1}{3}ak^2 + \frac{1}{45}a^3k^4 + \cdots. \tag{3.58}$$

This expansion is known as an *effective-range expansion* of the phase shift. Note that whereas Eq. (3.54) is exact for *any* value of k this effective-range expansion is only valid for $ka \ll 1$.

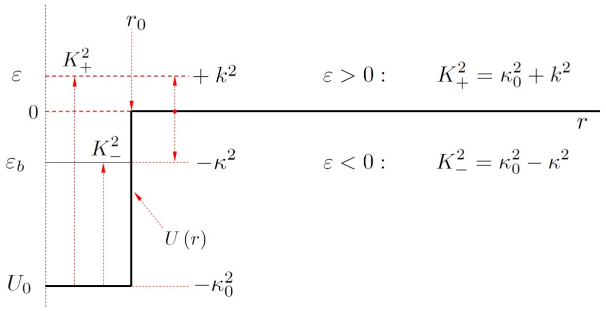

Figure 3.5: Plot of square well potential with related notation.

3.4 Spherical wells with a flat bottom

3.4.1 General

The second model potential to consider is the *spherical well* of range r_0 sketched in Fig. 3.5,

$$U(r) = \begin{cases} 2m_r\mathcal{V}_0/\hbar^2 = U_0 = -\kappa_0^2 & \text{for } r \leq r_0 \\ 0 & \text{for } r > r_0. \end{cases} \tag{3.59}$$

Here $|U_0| = \kappa_0^2$ is called the *well depth* (κ_0 is chosen to be real and *positive*, $\kappa_0 > 0$). This potential is an example of a larger class of potentials called *piece wise constant* potentials (another example is discussed in Section 3.5). The energy of the continuum states is given by $\varepsilon = k^2$. In analogy, the energy of the bound states is written as

$$\varepsilon_b = -\kappa^2. \tag{3.60}$$

With the spherical well potential (3.59) the radial wave equation (3.7) takes the form

$$R_l'' + \frac{2}{r}R_l' + \left[\varepsilon - U_0 - \frac{l(l+1)}{r^2}\right] R_l = 0 \quad \text{for } r \leq r_0 \tag{3.61a}$$

$$R_l'' + \frac{2}{r}R_l' + \left[\varepsilon - \frac{l(l+1)}{r^2}\right] R_l = 0 \quad \text{for } r > r_0. \tag{3.61b}$$

Since the potential is constant inside the well ($r \leq r_0$) the wavefunction has to be free-particle like with the wave number given by

$$K_+ = [2m_r(E - \mathcal{V}_0)/\hbar^2]^{1/2} = [\kappa_0^2 + k^2]^{1/2}. \tag{3.62}$$

As the wavefunction has to be regular in the origin, inside the well it is given by

$$R_l(r) = C_l\, j_l(K_+ r) \quad \text{for } r \leq r_0, \tag{3.63}$$

where C_l is a normalization constant. This expression is valid for $E > \mathcal{V}_0$ (both $E > 0$ and $E \leq 0$).

Outside the well ($r > r_0$) we have for $E > 0$ free atoms, $U(r) = 0$, with relative wavevector $k = [2m_r E/\hbar^2]^{1/2}$. Thus, for $r > r_0$ the general solution for the radial wave functions of angular momentum l is given by the free atom expression (3.19),

$$R_l(k, r) = c_l\,[\cos\eta_l\, j_l(kr) + \sin\eta_l\, n_l(kr)] \quad \text{for } r > r_0. \tag{3.64}$$

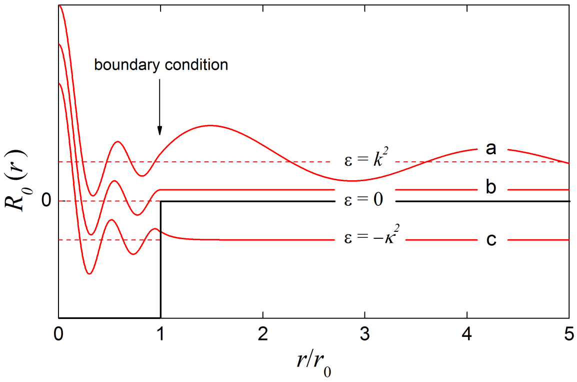

Figure 3.6: Radial wavefunctions for square wells: a.) continuum state ($\varepsilon = k^2 > 0$); b.) Zero energy state ($\varepsilon = k^2 = 0$) in the presence of an asymptotically bound level ($\varepsilon = -\kappa^2 = 0$); c.) bound state ($\varepsilon = -\kappa^2 < 0$). Note the continuity of $R_0(r)$ and $R_0'(r)$ at $r = r_0$. The wavefunctions are not normalized. They are shifted with respect to each other to highlight the differences.

The full solution (see Fig. 3.6) is obtained by the *continuity conditions* for $R_l(r)$ and $R_l'(r)$ at the boundary $r = r_0$. These imply continuity of the *logarithmic derivative* with respect to r

$$\beta_l = \left.\frac{\chi_l'(r)}{\chi_l(r)}\right|_{r=r_0} = \frac{K_+ j_l'(K_+ r_0)}{j_l(K_+ r_0)} = k\frac{\cos\eta_l\, j_l'(kr_0) + \sin\eta_l\, n_l'(kr_0)}{\cos\eta_l\, j_l(kr_0) + \sin\eta_l\, n_l(kr_0)}, \tag{3.65}$$

where the prime refers to the derivatives of $j_l(\varrho)$ and $n_l(\varrho)$ with respect to the variable ϱ. This important ratio suffices to determine η_l *independently* of the normalization constants C_l and c_l. Once the phase shift is known the relation between C_l and c_l follows from the continuity condition for $R_l(r)$. Furthermore, it shows that the *asymptotic phase shift* η_l can take *any* (real) value depending on the depth of the well. In view of the importance of the S matrix in scattering theory (cf. Chapter 4), it is advantageous to determine $e^{2i\eta_l}$ rather than η_l itself. Expressing $\sin\eta_l$ and $\cos\eta_l$ in terms of $e^{i\eta_l}$ and $e^{-i\eta_l}$ Eq. (3.65) becomes

$$\beta_l = kr_0\frac{e^{2i\eta_l}\left[j_l'(kr_0) - in_l'(kr_0)\right] + \left[j_l'(kr_0) + in_l'(kr_0)\right]}{e^{2i\eta_l}\left[j_l(kr_0) - in_l(kr_0)\right] + \left[j_l(kr_0) + in_l(kr_0)\right]}. \tag{3.66}$$

Solving for $e^{2i\eta_l}$ this leads to the following expression for the l-wave contribution to the S matrix,

$$e^{2i\eta_l} = -\frac{j_l(kr_0) + i\,n_l(kr_0)}{j_l(kr_0) - i\,n_l(kr_0)}\left[1 + kr_0\frac{\frac{j_l'(kr_0) - i\,n_l'(kr_0)}{j_l(kr_0) - i\,n_l(kr_0)} - \frac{j_l'(kr_0) + i\,n_l'(kr_0)}{j_l(kr_0) + i\,n_l(kr_0)}}{\beta_l - kr_0\frac{j_l'(kr_0) - i\,n_l'(kr_0)}{j_l(kr_0) - i\,n_l(kr_0)}}\right]. \tag{3.67}$$

This expression may look a bit heavy but is valuable as it represents the exact result for arbitrary l. As it lacks transparency from the physical point of view, we analyze in the coming sections the case $l = 0$.

Problem 3.3. Show that the following two boundary conditions are equivalent

$$\lim_{r\uparrow r_0}\frac{R_l'(r)}{R_l(r)} = \lim_{r\downarrow r_0}\frac{R_l'(r)}{R_l(r)} \quad\Leftrightarrow\quad \lim_{r\uparrow r_0}\frac{\chi_l'(r)}{\chi_l(r)} = \lim_{r\downarrow r_0}\frac{\chi_l'(r)}{\chi_l(r)}.$$

Solution. Substituting $\chi_l(r) = rR_l(r)$ the equivalence follows from the relation

$$\frac{\chi_l'(k,r)}{\chi_l(k,r)} = \frac{rR_l'(r) + R_l(r)}{rR_l(r)} = \frac{R_l'(r)}{R_l(r)} + \frac{1}{r}. \qquad \square$$

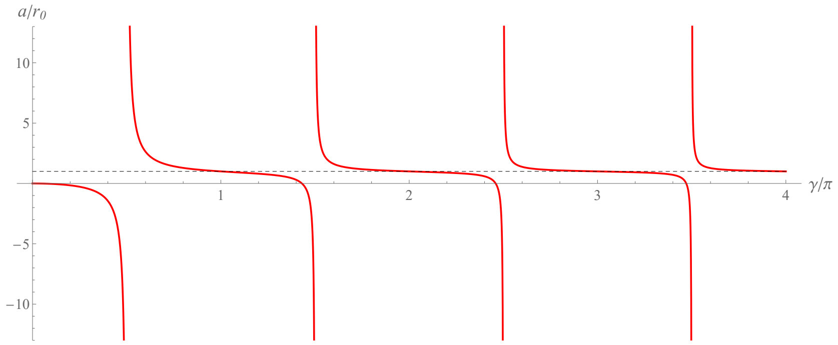

Figure 3.7: The s-wave scattering length a normalized on r_0 as a function of the depth of a spherical square potential well. Note that, typically, $a \simeq r_0$, except near the resonances at $\kappa_0 r_0 = (n + \frac{1}{2})\pi$ with n being an integer.

3.4.2 The case $l = 0$ for $E > 0$ - s-wave scattering length

The analysis of spherical well potentials becomes particularly simple for the case $l = 0$. Let us first consider the case $E > 0$, for which the radial wave equation can be written as a 1D-Schrödinger equation (3.9) of the form

$$\chi_0'' + [k^2 - U(r)]\chi_0 = 0. \tag{3.68}$$

The solution is

$$\chi_0(k,r) = \begin{cases} C_0 \sin(K_+ r) & \text{for } r \le r_0 \\ c_0 \sin(kr + \eta_0) & \text{for } r > r_0. \end{cases} \tag{3.69}$$

To determine $\eta_0(k)$ it is sufficient to apply the boundary condition for continuity of the logarithmic derivative at the edge of the well,

$$\chi_0'/\chi_0|_{r=r_0} = K_+ \cot K_+ r_0 = k \cot(kr_0 + \eta_0). \tag{3.70}$$

Note that this expression coincides with the general result given by Eq. (3.65) for the case $l = 0$; i.e., the boundary condition of continuity for χ_0'/χ_0 coincides with that for R_0'/R_0, as we know from Problem 3.3. Furthermore, for a vanishing potential ($\kappa_0 \to 0$) we have $K_+ \to k$ and the boundary condition properly yields a zero phase shift ($\eta_0 = 0$).

At this point we introduce the *effective hard-sphere diameter* $a(k)$ to describe, in analogy with Eq. (3.54), the behavior of the phase shift

$$\eta_0(k) \equiv -ka(k). \tag{3.71}$$

Preferring $a(k)$ over $\eta_0(k)$ amounts to a change of scattering parameter,

$$\{c_0, \eta_0(k)\} \to \{c_0, a(k)\}. \tag{3.72}$$

By this change we free ourselves from the prefactor $-k$ in the expression for the phase shift. This is a good idea because the linear k dependence does not arise from the potential but simply from the definition of the phase in which, as discussed in Section 3.3.1, the shift of the wave is compared to the de Broglie wavelength. In the limit $k \to 0$, we have $K_+ r_0 \to \kappa_0 r_0$ and with the definition

$$a \equiv \lim_{k\to 0} a(k) = -\lim_{k\to 0} \eta_0(k)/k \tag{3.73}$$

the boundary condition (3.70) becomes

$$\chi_0'/\chi_0|_{r=r_0} = \kappa_0 \cot \kappa_0 r_0 = \frac{1}{r_0 - a}. \tag{3.74}$$

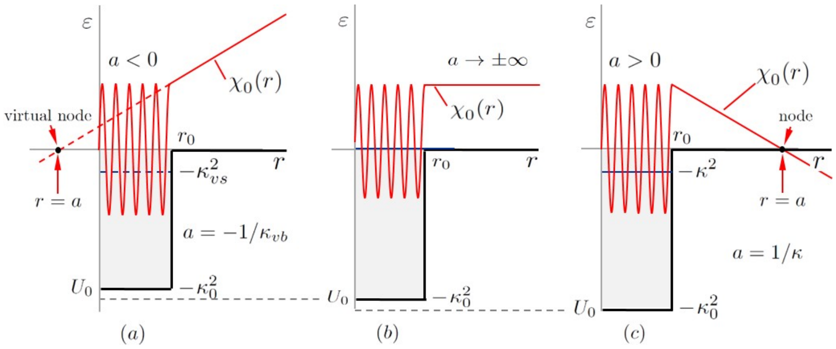

Figure 3.8: Reduced radial wavefunction $\chi_0(r)$ for continuum states ($\varepsilon > 0$) in the $k \to 0$ limit for increasing well depth near the threshold value $\kappa_0 r_0 = (n + \frac{1}{2})\pi$: ($a$) in the presence of a *virtual* level ($a < 0$); (b) for resonance at threshold ($\kappa_{vs} = 0$, $a \to \pm\infty$); (c) in the presence of a weakly bound state ($a > 0$). For $r > r_0$ the wavefunction is given by $\chi_0(r) = c_0(r - a)$; hence, the value of a is given by the intercept with the horizontal axis. This gives rise to a characteristic node at $r = a$. This node is real for $a > 0$ (just as for hard spheres of diameter a) but *virtual* for $a < 0$.

Solving for a we find

$$a = r_0 \left(1 - \tan\gamma/\gamma\right), \tag{3.75}$$

where the dimensionless *positive* quantity

$$\gamma \equiv \kappa_0 r_0 \tag{3.76}$$

is called the *well parameter*. As shown in Fig. 3.7 the value of a can be positive, negative or zero depending on the value of γ. Therefore, rather than using the pictorial term *effective hard-sphere diameter* the name *scattering length* is used for a. Next to the range, the scattering length represents the second characteristic length that can be associated with the interaction potential. As the name suggest it is a measure for the scattering behavior of atoms and we elaborate on this in Chapter 4. At the end of the present chapter we will find a also to be a measure for the effective *strength* of the interaction.

Fig. 3.7 and Eq. (3.75) show that a and r_0 are typically of the same size, although for $\gamma = \tan\gamma$ it is zero and for $\gamma = (\nu + \frac{1}{2})\pi$, with ν being an integer, it diverges. In the coming sections we show that the latter condition points to the occurrence of a resonance phenomenon, occurring when (with increasing γ) a new bound level enters the potential well. For the square well potential the scattering length is mostly positive; it is negative in the regions with $\gamma < \tan\gamma$, which become narrower for increasing γ. We shall find that this unlikely occurrence of negative a is a-typical for the general case; e.g., for Van der Waals potentials we find a 25% probability to find a negative scattering length (see the end of Section 3.7.3).

For $r \geq r_0$ the radial wavefunction corresponding to Eq. (3.69) is of the form

$$R_0(k,r) = \frac{c_0}{kr} \sin\left[kr - ka(k)\right]. \tag{3.77}$$

Recalling the definitions (3.71) and (3.73) we find that for $k \to 0$ this radial wavefunction becomes k independent,

$$R_0(r) \underset{k\to 0}{\sim} 1 - \frac{a}{r} \quad \text{for } r_0 < r \ll 1/k. \tag{3.78}$$

The latter two expressions for the radial wavefunction have the same formal appearance as the hard sphere results (3.55) and (3.57). However, whereas the diameter of the hard-sphere has a fixed value, the scattering length for the well depends on γ. As shown in Fig. 3.8, for *positive* scattering length the s wave has a *characteristic node* at $r = a$; for negative scattering length this becomes a *virtual node.*

Importantly, because Eq. (3.78) reaches the asymptotic value 1 only for distances $r \gg a$, the use of this equation in the modeling of dilute gases is only justified if a is much smaller than the interparticle spacing,

$$na^3 \ll 1. \tag{3.79}$$

Otherwise, the interaction with neighboring atoms will distort the relative motion of the colliding pair. This violates the binary scattering approximation on which Eq. (3.78) is based. The dimensionless quantity na^3 is called the *gas parameter.* When its value is small the gas is called *nearly ideal* or *weakly interacting.*[1]

3.4.3 The case $l = 0$ for $E \leq 0$ - bound s levels

Let us turn to the case $E \leq 0$. We shall show that the divergences of the scattering length obtained by analyzing the continuum states ($E > 0$) result from the appearance of the next bound s level when increasing the well parameter. The 1D Schrödinger equation takes the form

$$\chi_0'' + [-\kappa^2 - U(r)]\chi_0 = 0, \tag{3.80}$$

where $\varepsilon = -\kappa^2$ is the *discrete* energy eigenvalue of a bound state with $l = 0$. The solutions are of the type (see Fig. 3.10)

$$\chi_0(\kappa, r) = \begin{cases} C_0 \sin(K_- r) & \text{for } r \leq r_0 \\ c_0 e^{-\kappa r} & \text{for } r > r_0, \end{cases} \tag{3.81}$$

where $\kappa > 0$ because the bound state wavefunction has to be normalized. The bound state energy is obtained by requiring the continuity of the logarithmic derivative when connecting the inner part of the wavefunction to the outer part,

$$\chi_0'/\chi_0|_{r=r_0} = K_- \cot K_- r_0 = -\kappa, \tag{3.82}$$

where $\kappa > 0$ and

$$K_- = [2m_r(E - \mathcal{V}_0)/\hbar^2]^{1/2} = (\kappa_0^2 - \kappa^2)^{1/2}. \tag{3.83}$$

Let us calculate the binding energies of the bound states as a function of γ. With decreasing γ, the least bound level disappears in the limit $\kappa \to 0$, $K_- \to \kappa_0$. In this limit Eq. (3.82) reduces to

$$\chi_0'/\chi_0|_{r=r_0} = \kappa_0 \cot \kappa_0 r_0 = 0 \text{ for } \kappa \to 0. \tag{3.84}$$

Inversely, increasing γ from zero the vibrational levels appear sequentially for

$$\gamma = (v + \tfrac{1}{2})\pi, \tag{3.85}$$

where $v = 0, 1, \cdots v_{\max}$ is the *vibrational quantum number.* This is illustrated in Fig. 3.9. Note that a minimum well parameter ($\gamma = \frac{1}{2}\pi$) is required to bind the first state.[2] For the least-bound level, $v_{\max}$, we have

$$(v_{\max} + \tfrac{1}{2})\pi = \mathrm{Int}(\gamma/\pi - \tfrac{1}{2}) \tag{3.86}$$

and the total number of bound s levels follows with

$$N_b = v_{\max} + 1 = \mathrm{Int}(\gamma/\pi + \tfrac{1}{2}). \tag{3.87}$$

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[1] Note that weakly interacting does not mean that that the potential is "shallow". Any gas can be made weakly interacting by making the density sufficiently small.

[2] This conclusion cannot be extended to lower dimensions; in two dimensions bound states appear for arbitrarily shallow potentials.

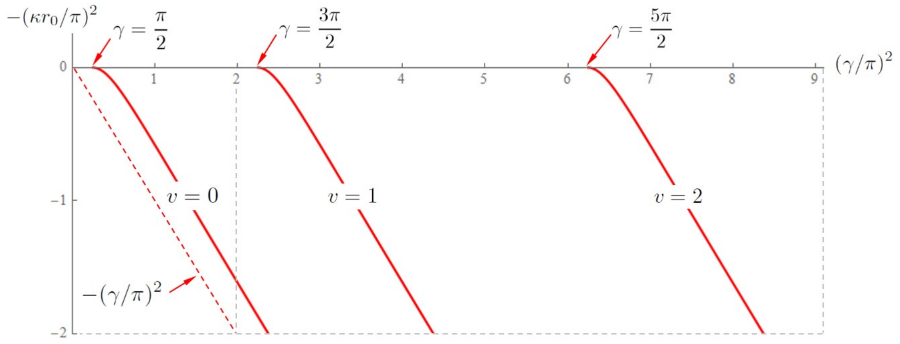


Figure 3.9: Appearance and increase of binding of the first three bound levels for increasing well depth. The quadratic dependence near threshold is universal (i.e., independent of the well shape). The full crossover curve is obtained by numerical solution of Eq. (3.82) and corresponds to a $\pi/2$ phase shift of $K_- r_0$ near threshold. The dashed line shows the increase in well depth.

The relation between κ and γ for a given vibrational level depends on the ratio κ/K_- and is given by

$$\cot K_- r_0 = -\kappa/K_-. \tag{3.88}$$

Note that this relation corresponds to $K_- r_0 \simeq (v_{\max} + \frac{1}{2})\pi$ for the least-bound state ($\kappa/K_- \ll 1$) close to threshold (see Fig. 3.10b.), crossing over to $K_- r_0 \simeq (v+1)\,\pi$ once the level becomes more deeply bound. Once sufficiently bound (far from threshold) the level shifts linearly with well depth,

$$-\kappa_\nu^2 = (\nu+1)^2\pi^2 - \gamma^2.$$

The crossover from weakly bound to deeply bound levels is illustrated in Fig. 3.10a.

3.4.4 Weakly bound s level - halo states

For weakly bound s levels ($0 < \kappa r_0 \ll 1$) we have $K_- \to \kappa_0$ and Eq. (3.82) may be approximated by

$$\chi_0'/\chi_0|_{r=r_0} = \kappa_0 \cot \kappa_0 r_0 = -\kappa. \tag{3.89}$$

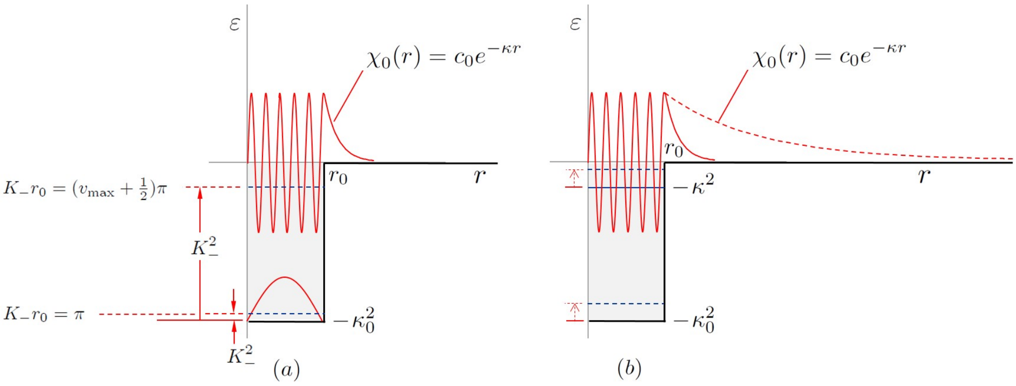
Furthermore, we recall that in the presence of a weakly bound s level the scattering length is *large and positive,* $a \gg r_0$. From Eq. (3.74) we recall that for $k \to 0$ the logarithmic derivative also satisfies the relation

$$\chi_0'/\chi_0|_{r=r_0} = \kappa_0 \cot \kappa_0 r_0 = \frac{1}{r_0 - a} \simeq -\frac{1}{a}. \tag{3.90}$$

Interestingly, for $a \gg r_0$ the logarithmic derivative of the continuum states becomes independent of r_0 and κ_0; i.e., it becomes independent of the shape of the potential well. As we shall see it only depends on the well parameter (γ) and not on the well shape. This points to a *universal* limiting shape of the wavefunction for large scattering length. As is sketched in Fig. 3.10b, for decreasing κ the least-bound state turns into a *halo state*; i.e., for $\kappa r_0 \ll 1$ most of the probability of the bound state is found in the classically inaccessible region *outside* the potential well, thus surrounding the potential center like a halo. In Section 3.6.4 this behavior is shown to hold for arbitrary short-range potentials. We return to this important observation when discussing zero-range potentials and the Bethe-Peierls boundary condition in Section 3.4.11.

With Eqs. (3.89) and (3.90) we have obtained two expressions for $\kappa_0 \cot \kappa_0 r_0$ and arrive at the conclusion that in the presence of a weakly bound state the scattering length is given by

$$a \underset{\kappa\to 0}{\simeq} 1/\kappa. \tag{3.91}$$



(a) (b)

Figure 3.10: Bound states oscillate inside the well and decay exponentially outside the well: (a) the boundary condition depends on the ratio κ / K_-; (b) a slight reduction of the well depth can turn the least bound state into a halo state.

This expression reveals the tight relation between the binding energy of the least-bound state, given by Eq. (3.60), and the scattering length

$$E_b = -\frac{\hbar^2 \kappa^2}{2m_r} \underset{\kappa \to 0}{\simeq} -\frac{\hbar^2}{2m_r a^2}. \tag{3.92}$$

The crossover from the universal quadratic increase of the binding energy with trap depth to a linear increase is illustrated in Fig. 3.9.

3.4.5 s-wave resonances deep in the continuum - Breit-Wigner formula

To obtain the k dependence of the phase shift for a large but otherwise arbitrary well parameter ($\gamma \gg 1$) we rewrite the boundary condition (3.70) in the form

$$\eta_0(k) = -kr_0 + \arctan\left(\frac{kr_0}{K_+ r_0 \cot K_+ r_0}\right). \tag{3.93}$$

The first term,

$$\eta_{bg}(k) = -kr_0, \tag{3.94}$$

is called the *background* contribution to the phase shift and the second term,

$$\eta_{\text{res}}(k) = \arctan\left[kr_0 / \left(K_+ r_0 \cot K_+ r_0\right)\right], \tag{3.95}$$

the *s-wave resonance* contribution. Note that the background contribution shows the same phase development as we found in Section 3.3.1 for hard spheres. The phase development of the resonance contribution is shown in Fig. 3.11a for the case of a large well parameter slightly detuned from the threshold value (at $\gamma = 98.960169$) such that the scattering length is negative ($\Delta\gamma = -0.5$). For potentials with $\gamma \gg 1$ the argument of the arctangent is predominantly small, $kr_0 / |K_+ r_0 \cot K_+ r_0| \ll 1$, because

$$K_+ r_0 = \kappa_0 r_0 (1 + k^2/\kappa_0^2)^{1/2} > \gamma \gg 1. \tag{3.96}$$

However, the argument of the arctangent diverges when $\cot K_+ r_0$ passes through zero; i.e., for

$$K_+ r_0 = (\tilde{v} + \tfrac{1}{2})\pi, \tag{3.97}$$

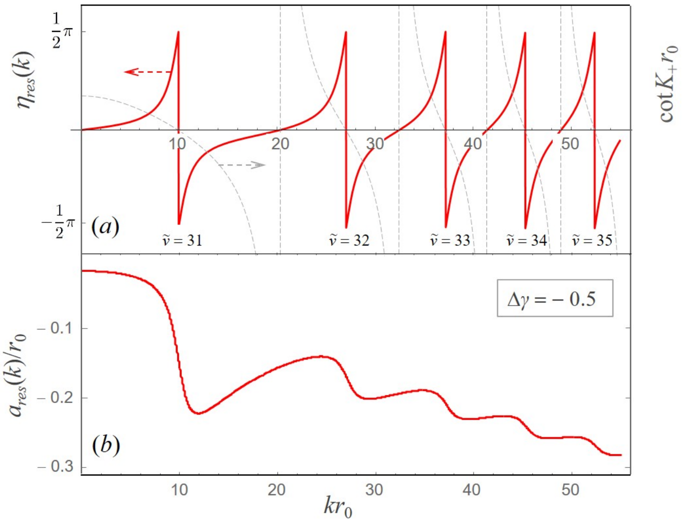


Figure 3.11: (a) Resonance contribution to the s-wave phase shift $\eta_0(k)$ for a large well parameter slightly detuned from the threshold value (at $\gamma = 98.960169$) such that the scattering length is negative ($\Delta\gamma = -0.5$). The linear shift of the background contribution is *not* included in the plot. Note that the π phase jumps arise from the modulo-π representation of the arctangent and do not represent an observable phenomenon; the physical phase increases monotonically and equals $\eta_{\rm res} = \frac{1}{2}\pi$ (modulo π) at the center of the resonances; (b) contribution of the resonances to the effective hard sphere diameter $a(k) = -\eta_0(k)/k$. As (in this example) the lowest resonance is not close to threshold the resonant enhancement is small, $|a_{\rm res}(k)|/r_0 \ll 1$.

where $\tilde{v}$ is an integer called the *resonance index*. This divergence is observed as a *small* resonant enhancement of $a(k)$ as shown in Fig. 3.11b. The physical phase is a *continuous* function of k which changes by π when sweeping across the resonance. Because the arctangent remains finite for $\cot K_+ r_0 = 0$ also the resonant phase shift remains finite, having the value $\eta_{\rm res}(k) = \frac{1}{2}\pi$ (modulo π) at the center of each resonance.

In the remainder of this section we shall analyze the width and separation of the s-wave resonances for the case $\gamma \gg 1$. Since $K_+ \geq \kappa_0 \geq K_-$ we have

$$\tilde{v} \geq \gamma/\pi - \tfrac{1}{2} \geq v_{\rm max}\,, \tag{3.98}$$

which shows that for $\gamma \gg 1$ the value of $\tilde{v}$ is large ($\tilde{v}_{\rm min} \geq v_{\rm max} \gg 1$). Hence, the resonance numbering starts where the numbering of bound states ends. To discuss the resonances we denote the wavevectors k and K_+ at resonance by $k_{\rm res}$ and $K_{\rm res} \equiv (\kappa_0^2 + k_{\rm res}^2)^{1/2}$, respectively. The *resonance energies* $\varepsilon_{\rm res} = k_{\rm res}^2$ satisfy the condition

$$\varepsilon_{\rm res} = K_{\rm res}^2 - \kappa_0^2 = (\tilde{v} + \tfrac{1}{2})^2\,(\pi/r_0)^2 - \kappa_0^2 \geq 0. \tag{3.99}$$

The exceptional case for which the equal sign applies ($\tilde{v} = v_{\rm max}$) corresponds to a *resonant bound state* ($\kappa = 0$) and the resonance is called a *resonance at threshold* or *zero-energy resonance* ($k_{\rm res} = 0$).

Let us first analyze s-wave resonances for large well parameters ($\gamma \gg 1$) and far from threshold, $kr_0 \gg 1$. The energy spacing between two subsequent resonances is

$$\Delta\varepsilon_{\rm res} = \varepsilon_{\rm res}^{(\tilde{v}+1)} - \varepsilon_{\rm res}^{(\tilde{v})} = 2(\tilde{v}+1)\left(\pi^2/r_0^2\right) \simeq 2\pi\gamma/r_0^2. \tag{3.100}$$

To analyze a given resonance we expand $K_+ \cot K_+ r_0$ about the point of zero crossing. For this purpose we introduce the notation

$$K_+ = [\kappa_0^2 + (k_{\rm res} + \delta k)^2]^{1/2} = K_{\rm res} + \delta k\, k_{\rm res}/K_{\rm res} + \cdots\,, \tag{3.101}$$

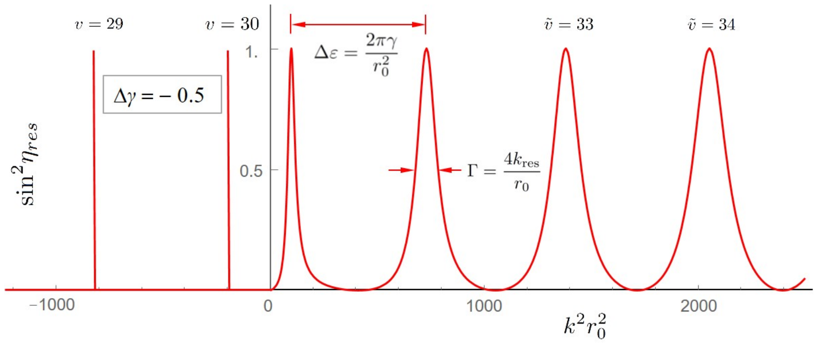


Figure 3.12: Transition from bound states to Breit-Wigner s-wave resonances plotted for $\Delta\gamma = -0.5$ with respect to the threshold at $\gamma = 98.960169$ (same conditions as Fig. 3.11). The bound states are indicated as zero-width spikes at energies $\varepsilon = -\kappa^2$, with κ following from Eq. (3.82). For $\varepsilon > 0$ the plot is based on Eqs. (3.93). The width of the resonances increases with the square root of the energy. Note that the band of energies typical for the quantum gases ($kr_0 \ll 1$) corresponds to a narrow zone, unresolved on the energy scale of the plot.

where $\delta k = k - k_{\rm res}$ is called the *detuning* from resonance. Thus, restricting ourselves to the low-energy (but not *zero* energy) s-wave resonances ($1 < k_{\rm res}r_0 \ll K_{\rm res}r_0 \approx \gamma$), we may approximate $K_+ \cot K_+ r_0 \simeq K_{\rm res} \cot K_+ r_0$. Expanding $\cot K_+ r_0$ about the zero crossing at $K_+ r_0 = (\tilde{v} + \frac{1}{2})\pi$ and retaining only the linear term we obtain (See Problem 3.4)

$$K_{res} \cot K_+ r_0 = -\delta k \, k_{res} r_0. \tag{3.102}$$

Hence, the diverging argument of the arctangent becomes

$$\tan \eta_{\rm res} = \frac{k}{K_+ \cot K_+ r_0} \simeq -\frac{1}{\delta k \, r_0} = \frac{-(k + k_{\rm res})}{(k^2 - k_{\rm res}^2) r_0} \simeq \frac{-2k_{res}/r_0}{\varepsilon - \varepsilon_{res}}. \tag{3.103}$$

The expansion (3.101) is valid over the full range of the resonant change in phase provided

$$\delta k \ll K_{\rm res}/k_{\rm res} \simeq \gamma / k_{\rm res} r_0, \tag{3.104}$$

which is satisfied for the lowest resonances as long as the well parameter is sufficiently large ($\gamma \gg k_{\rm res} r_0$). As long as $\delta k \ll k_{\rm res}$ we may further approximate $k \simeq k_{\rm res}$. With these approximations and after restoring the dimensions, Eq. (3.103) can be written as a function of the energy $E = \hbar^2 k^2 / 2m_r$,

$$\tan \eta_{\rm res} = \frac{k}{K_+ \cot K_+ r_0} \simeq \frac{-\Gamma/2}{E - E_{\rm res}}, \tag{3.105}$$

where

$$\Gamma = (\hbar^2/m_r)(2k_{\rm res}/r_0) \tag{3.106}$$

is called the *spectral width* of the resonance. Comparing the expressions for the width, Γ, and the spacing, $\Delta E_{\rm res}$, we find that for given r_0 the width Γ is independent of γ, whereas the resonance spacing is proportional to γ. Thus, only for sufficiently large well parameters ($\gamma \gg 1$) the spectral width becomes smaller than the resonance spacing,

$$\Gamma \ll \Delta E_{\rm res} \Leftrightarrow k_{\rm res} r_0 \ll \pi\gamma. \tag{3.107}$$

In this limit the typical features of an oscillator near resonance become evident. Knowing the tangent of $\eta_{\rm res}$, we readily obtain the sine and Eq. (3.105) is replaced by the *Breit-Wigner formula*

$$\sin^2 \eta_{\rm res} = \frac{(\Gamma/2)^2}{(E - E_{\rm res})^2 + (\Gamma/2)^2}. \tag{3.108}$$

For optical resonances this energy dependence is known as the *Lorentz lineshape.* Note that Γ corresponds to the full-width-at-half-maximum (FWHM) of this line shape. The lowest energy resonances are plotted in Fig. 3.12 along with the highest-energy bound states. In Chapter 4 we return to the Breit-Wigner formula in relation with elastic scattering phenomena.

The *resonance near threshold* deserves special attention as this type of resonance is the only one that can play an important role within the band of energies relevant for the quantum gases ($kr_0 \ll 1$). Fig. 3.12 shows that near the threshold (at $\gamma_t \simeq 98.960169$) the resonance narrows down and becomes asymmetric, which means that the Breit-Wigner lineshape is lost. Using Eq. (3.87) we calculate $\tilde{v} = 31$. The narrow line is reminiscent of a bound level but the scattering length is negative (see Fig. 3.11). Under these conditions the wavefunction has a *virtual* node at $r = -|a|$ (see Fig. 3.8). The system behaves as if the resonant enhancement is caused by a *virtual* level (defined by $\kappa = -\kappa_{vs}$). Note that the corresponding wavefunction cannot be normalized because it diverges exponentially for $r \to \infty$- see Eq. (3.81). In analogy with the real bound states its energy is written as $\varepsilon_{vs} = -\kappa^2 = -\kappa_{vs}^2$, where κ_{vs} is to be defined later. The discussion of resonances near threshold is continued in Section 3.4.9. In preparation we analyze, for arbitrary values of γ, the behavior of the phase shift for relative energies approaching zero, $kr_0 \ll 1$.

Problem 3.4. Derive the expansion (3.102).

Solution. We calculate the linear expansion of $K_{res} \cot K_+ r_0$ near the zero crossing at $K_+ r_0 = (\tilde{v} + \frac{1}{2})\pi$ where $\cot K_+ r_0 = 0$. This follows from the derivative evaluated at $K_+ r_0 = (\tilde{v} + \frac{1}{2})\pi$:

$$\left.\frac{d\, K_{res} \cot K_+ r_0}{d\delta k}\right|_{K_+ r_0 = (\tilde{v}+\frac{1}{2})\pi} = -\left.\frac{k_{res} r_0}{\sin^2 K_+ r_0}\right|_{K_+ r_0 = (\tilde{v}+\frac{1}{2})\pi} = -k_{res} r_0.$$

Multiplying the derivative with δk we obtain the desired result. □

3.4.6 s-wave resonances for $kr_0 \ll 1$ - effective-range expansion

The leading energy dependence of the phase shift is obtained by applying the angle-addition formula of the tangent to the r.h.s. of Eq. (3.93) and expanding $\tan kr_0$ in (odd) powers of k,

$$kr_0 \cot \eta_0 = \frac{K_+ r_0 \cot K_+ r_0 + k^2 r_0^2 + \cdots}{1 - \left(1 + \frac{1}{3} k^2 r_0^2 + \cdots\right) K_+ r_0 \cot K_+ r_0}. \tag{3.109}$$

In view of the expansion, the validity of this expression is restricted to $kr_0 \ll 1$. Next we expand $K_+ r_0$ in even powers of k,

$$K_+ r_0 = \kappa_0 r_0 [1 + k^2/\kappa_0^2]^{1/2} = \gamma + \tfrac{1}{2} k^2 r_0^2/\gamma + \cdots , \tag{3.110}$$

which is valid for $\gamma \gtrsim 1$, and using the angle-addition formula for the cotangent we find

$$K_+ r_0 \cot K_+ r_0 = \gamma \cot \gamma - \tfrac{1}{2} k^2 r_0^2 \left[1 + (1 - \tan\gamma/\gamma) \cot^2 \gamma\right] + \cdots . \tag{3.111}$$

Actually, since $K_+ r_0 \cot K_+ r_0$ is an even function of $K_+ r_0$ we infer that $K_+ r_0 \cot K_+ r_0$ and $kr_0 \cot \eta_0$ only depend on the even powers of k. Substituting Eq. (3.111) into Eq. (3.109) we arrive after some calculus at the following expansion in even powers of k

$$kr_0 \cot \eta_0 = -\frac{1}{1 - \tan\gamma/\gamma} + \tfrac{1}{2} k^2 r_0^2 \left(1 - \frac{3\,(1 - \tan\gamma/\gamma) + \gamma^2}{3\gamma^2\,(1 - \tan\gamma/\gamma)^2}\right) + \cdots . \tag{3.112}$$

Since $\lim_{k\to 0} kr_0 \cot \eta_0 = -r_0/a$, we regain in the limit $k \to 0$ the expression (3.75) for the scattering length. Divided by r_0, the expansion is called the *effective-range expansion*,

$$k \cot \eta_0 = -\frac{1}{a} + \tfrac{1}{2} k^2 r_e + \cdots , \tag{3.113}$$

and

$$r_e = r_0 \left(1 - \frac{3ar_0 + \gamma^2 r_0^2}{3\gamma^2 a^2}\right) \tag{3.114}$$

is called the *effective range*. In view of the derivation this expansion is valid valid for $kr_0 \ll 1$ and $\gamma \gtrsim 1$. For $\gamma \to \infty$ the effective range becomes

$$r_e = r_0(1 - \tfrac{1}{3} r_0^2/a^2). \tag{3.115}$$

Next to the range and the scattering length, the effective range r_e represents the third characteristic length that may be associated with the scattering potential. It provides a measure for the energy dependence of the scattering length. Comparing the first two terms of Eq. (3.113) we find that the scattering length approximation is valid for

$$kr_e \ll \frac{2}{k|a|}. \tag{3.116}$$

This inequality shows that the range of energies for which this energy dependence may be neglected becomes narrow ($kr_e \ll kr_0$) for large values of $|a|$.

3.4.7 Scattering length approximation

Rather than expanding $kr_0 \cot \eta_0$ in even powers of k we can also expand its reciprocal,

$$\frac{1}{k \cot \eta_0} = -\frac{a}{1 - \frac{1}{2}k^2 r_e a + \cdots} = -a(1 + \tfrac{1}{2}k^2 r_e a + \cdots). \tag{3.117}$$

This is the preferred expansion for $a \to 0$ but can also be used to determine the range of k values for which the *scattering length approximation* is valid; i.e., the range of k values for which $a(k)$ has reached its limiting value, $a = \lim_{k\to 0} a(k)$. Substituting Eq. (3.114) we obtain

$$\frac{1}{k \cot \eta_0} = -a + \tfrac{1}{6}k^2 r_0^3 [1 - 3\,(a/r_0)^2 + (3/\gamma^2)\,(a/r_0)] + \cdots . \tag{3.118}$$

Hence, $a(k)$ is given by the arctangent,

$$ka(k) = \arctan[ka - \tfrac{1}{6}k^3 r_0^3 [1 - 3\,(a/r_0)^2 + (3/\gamma^2)\,(a/r_0)] + \cdots]. \tag{3.119}$$

Expanding the arctangent to the cubic power of k we obtain

$$a(k) = a - \tfrac{1}{6}k^2 r_0^3 [1 + 2\,(a/r_0)^3 - 3\,(a/r_0)^2 + (3/\gamma^2)\,(a/r_0)] + \cdots . \tag{3.120}$$

This expansion is valid as long as the conditions $kr_0 \ll 1$ and $k\,|a| \ll 1$ are both satisfied. To estimate the domain of validity of the scattering length approximation we analyze the expansion (3.120) for ordinary quantum gases ($\gamma \gg 1$). If the scattering length is *not* resonantly enhanced ($-1 < a/r < 1$) we find that the k^2 term becomes important only for $kr_0 \gtrsim 1$. Since $kr_0 \ll 1$ in all quantum gases, this means that the effective hard-sphere diameter has reached its limiting value $a(k) \simeq a$. For large $|a|$ the situation is different because the k^2 term in Eq. (3.120) may only be neglected for the lowest values of k.

$$kr_0 \ll r_0/\,|a|\,. \tag{3.121}$$

Note that the curvature is negative for $0.5 \lesssim a/r_0 \lesssim 1$ (see also Fig. 3.13).

3.4.8 Scattering length - regimes of interest

As r_e can be expressed in terms of r_0 and a it is instructive to have a closer look at the relation between r_e and a for some special cases:

- *Regular scattering length:* For $a = \pm r_0$ we find with the aid of Eq. (3.114)

  $$r_e = r_0(\tfrac{2}{3} \mp 1/\gamma^2) \simeq \tfrac{2}{3} r_0, \tag{3.122}$$

  where the last step is valid for sufficiently large γ. This result coincides with that of the hard sphere - see Eq. (3.58). The effective-range expansion is given by

  $$k \cot \eta_0 = \mp \frac{1}{r_0} + \tfrac{1}{3} k^2 r_0 + \cdots . \tag{3.123}$$

  From Eq. (3.116) we find with $|a| = r_0$ that the scattering length approximation is valid for ultracold gases ($kr_0 \ll 1$) throughout the energy range of interest; i.e., the k dependence may be neglected for most practical purposes.

- *Anomalously large scattering length:* For $|a| \gg r_0$ we obtain with Eq. (3.114)

  $$r_e = r_0 \left(1 - \frac{r_0}{\gamma^2 a} - \frac{r_0^2}{3a^2}\right) \simeq r_0, \tag{3.124}$$

  which corresponds to an effective-range expansion of the form

  $$k \cot \eta_0 = -\frac{1}{a} + \tfrac{1}{2} k^2 r_0 + \cdots . \tag{3.125}$$

  From Eq. (3.116) we find that for $|a| \gg r_0$ the scattering length approximation is valid for

  $$kr_0 \ll \frac{2}{k|a|}, \tag{3.126}$$

  which implies that for ultracold gases within the energy range of interest ($kr_0 \ll 1$) the k dependence becomes relevant for $k|a| \gg 1$; i.e., the scattering length approximation is only valid up to $k|a| \simeq 1$.

- *Anomalously small scattering length:* The case $|a| \ll r_0$ demands another approach. For $1 - \tan\gamma/\gamma = 0$ the effective-range expansion breaks down, which emerges as a divergence of the effective range,

  $$r_e \simeq -\tfrac{1}{3} r_0 \left(r_0/a\right)^2 \qquad \text{for } a \to 0 \text{ and } \gamma \neq 0. \tag{3.127}$$

  This being the case it is advantageous to turn to the reciprocal expansion (3.118), which remains well defined for $|a| \ll r_0$. For the special case $a = 0$ the leading k dependence is found to be

  $$\frac{1}{k \cot \eta_0} = \tfrac{1}{6} k^2 r_0^3 + \cdots \qquad (a = 0) . \tag{3.128}$$

  This expression shows that the phase shift only vanishes exactly in the limit $k = 0$. For small values of $\eta_0(k) = -ka(k)$ we find that $a(k)$ grows linearly with k^2,

  $$a(k) = -\tfrac{1}{6} k^2 r_0^3. \tag{3.129}$$

  For ultracold gases ($kr_0 \ll 1$) this implies that $a(k)$ *remains effectively zero*, $a(k) \ll r_0$, throughout the energy range of interest; i.e., the k dependence may be neglected for most practical purposes.

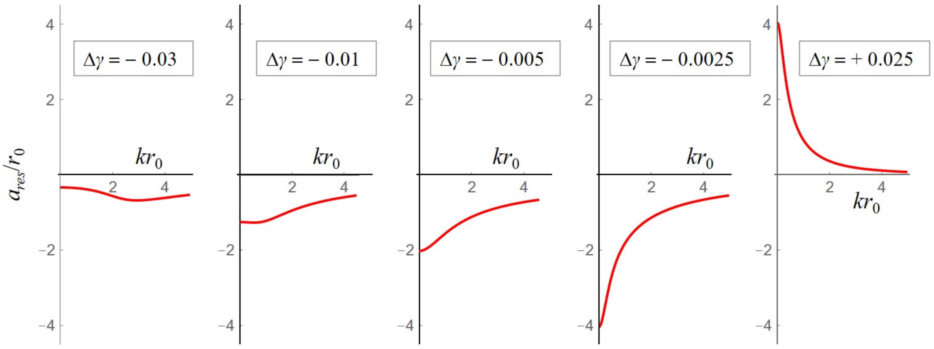


Figure 3.13: From left to right: change in resonance shape for the s level $\tilde{v} = 31$ reaching the threshold at $\gamma = (31 + \frac{1}{2})\,\pi = 98.960169$ calculated with the the exact expression (3.130). Note that only close to threshold the resonance contribution exceeds the background value (horizontal line). The dashed vertical lines indicate the center of the resonance (as defined by a $\pi/2$ resonant phase shift). For $a_{res} > 0$ the resonance is below threshold.

The above analysis shows that an estimate of the range r_0 can be obtained by extracting r_e from a measurement of the energy dependence of $k \cot \eta_0$; i.e., of the phase shift. For a large scattering length, $|a| \gg r_0$, this is possible for energies typical in ultracold gases, otherwise it requires energies beyond that range. The example of the *large* $|a|$ shows that even for *small* r_e a strong k dependence can be observed in ultracold gases. We also found that the scattering length can remain *small*, $|a| \ll r_0$, although r_e is *large* for all energies of interest ($kr_0 \ll 1$). Apparently, a large effective range is not equivalent to a strong energy dependence. This shows that the added value of the notion effective range for the quantum gases is not so obvious. We certainly do not need it to determine r_0 because the Van der Waals interaction is usually accurately known from quantum chemistry. For the time being we shall remember the effective range as a measure for the width of the energy band over which the s-wave scattering length is resonantly enhanced.

Historically, the effective range has been important in nuclear physics as it enabled the first experimental determination of the deuteron size by measuring the energy dependence of proton-neutron s-wave scattering under the assumption $r_e \simeq r_0$. Note also that the early neutron-proton scattering was done in the s-wave regime. The nuclear size is some six orders of magnitude smaller than a typical Van der Waals range. Therefore, the s-wave regime extends in this case to energies which are some 12 orders of magnitude higher than those typical in ultracold gases.

3.4.9 Resonant enhancement of s-wave scattering length

As long as the lowest-energy resonance and the highest-energy bound state are far from threshold the scattering length is regular and the *scattering length approximation* is valid; i.e., $a(k)$ has reached its limiting value a for $kr_0 \ll 1$. However, as mentioned at the end of Section 3.4.5, the situation changes if a s-wave resonance ($a < 0$) or a weakly bound state ($a > 0$) approaches the threshold. In this case the scattering length is resonantly enhanced and the scattering properties become k dependent even at low energies. Upon crossing the threshold the scattering length changes sign and the resonance becomes a weakly bound level or *vice versa.* To elucidate this behavior we analyze the expression for effective hard-sphere diameter - see Eq. (3.71),

$$a(k) = -\eta_0(k)/k = r_0 - \frac{1}{k} \arctan\left(\frac{k}{K_+ \cot K_+ r_0}\right). \tag{3.130}$$

Here the first term is called the *background* contribution to the scattering length ($r_0 = a_{bg}$) and the second term,

$$a_{\mathrm{res}}(k) = -(1/k) \arctan\left[k/\left(K_+ \cot K_+ r_0\right)\right], \tag{3.131}$$

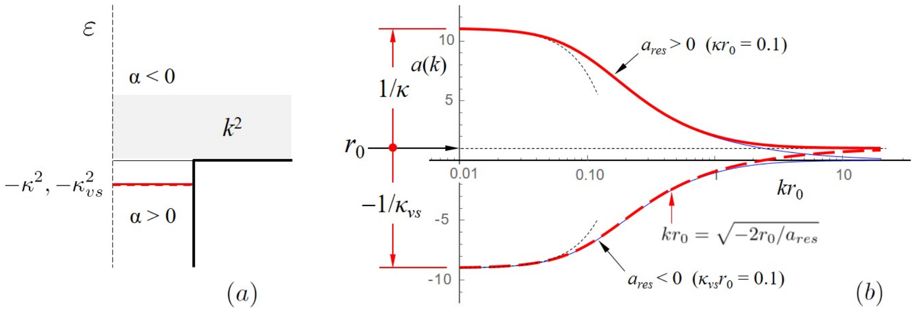


Figure 3.14: (a) Level diagram chosen such that $\kappa^2 = \kappa_{vs}^2$ and $\gamma \gg 1$. (b) The red curves represent the corresponding scattering lengths based on the exact expression (3.130) plotted as a function of kr_0 in the presence of a weakly bound s level (solid line; $\varDelta\gamma = 0.00101 \Leftrightarrow \kappa r_0 = 0.1$) or virtual s level near threshold (dashed line; $\varDelta\gamma = -0.00101 \Leftrightarrow \kappa_{vs} r_0 = 0.1$). The threshold value is $\gamma = (31 + \frac{1}{2})\,\pi = 98.960169$. The center of the s-wave resonance corresponding to the virtual level is indicated by the vertical arrow at $kr_0 = 0.458$ and corresponds to the zero crossing of $\cot K_+ r_0$ at $n = 31$. A convenient analytical expression for the solid red curves is given by Eq. (3.140). The black dashed lines correspond to the leading k dependence of $a(k)$ as given by Eq. (3.120). The thin blue lines correspond to the effective range expansion as given by Eq. (3.141).

the *s-wave resonance* contribution. In terms of the well parameter, the product $K_+ r_0$ is given by

$$K_+ r_0 = \gamma\sqrt{1 + (kr_0/\gamma)^2}. \tag{3.132}$$

Note that these expressions are exact for spherical wells of arbitrary γ.

We now specialize to large well parameters, $\gamma \gg 1$. For the s-wave resonances discussed in Section 3.4.5 the resonant contribution $a_{\mathrm{res}}(k)$ for $\gamma = 303$ is plotted in Fig. 3.11b; note that for this value of γ the resonance contribution is small, $a_{\mathrm{res}}(k) \ll r_0$. However, as shown in Fig. 3.13, for the resonance approaching the threshold at $\gamma = (31 + \frac{1}{2})\,\pi = 98.960169$ the $a_{\mathrm{res}}(k)$ becomes increasingly important; it develops a qualitatively different shape and the region of validity of the scattering length approximation narrows down sharply. In Fig. 3.14 the crossing of the threshold is illustrated in detail by plotting Eq. (3.130) for two values of γ, corresponding to a virtual level (dashed line $\kappa_{vs} r_0 = 0.1$) and a weakly bound level (solid line $\kappa r_0 = 0.1$). In both cases the enhancement of $|a|$ with respect to the background level is roughly 10 fold. For the virtual level we define $a = -1/\kappa_{vs}$. As illustrated in Fig. 3.8, at threshold the sign switches and we have $a \simeq 1/\kappa$, which corresponds to the resonant enhancement by a weakly bound level (halo state) discussed in Section 3.4.3. The symmetry about the threshold is striking. It arises because r_0 may be neglected if $|a|$ is sufficiently large. Returning to the virtual level, the center of the s-wave resonance (i.e., the point with $\eta_{res} = \frac{1}{2}\pi$ modulo π) at

$$kr_0 = \sqrt{2r_0/|a_{res}|} = 0.458 \tag{3.133}$$

is indicated by the vertical arrow in Fig. 3.14. This resonance corresponds to the zero crossing of $\cot K_+ r_0$ at $\tilde{v} = 31$ (the corresponding sign change is an artifact of the modulo π representation of the arctangent and is suppressed in the plot - recall that the phase development has to be continuous). At first sight it may be surprising that the center of the resonance does not correspond to the maximum value of $a(k)$. However, as the resonance has a finite width and the arctangent is bounded between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$, the decrease of the absolute value of the arctangent (when detuning towards $k = 0$ away from the "center") is more than compensated by the prefactor $1/k$. Ultimately, for $k \to 0$, the increase has to saturate at the value of the scattering length. This behavior is characteristic for s-wave resonances near threshold. With increasing $|a_{res}|$ the width of the enhancement region narrows down proportionally to $\sqrt{2r_0/|a_{res}|}$. On the other side of the threshold the scattering length is also resonantly enhanced but, as the weakly bound state has

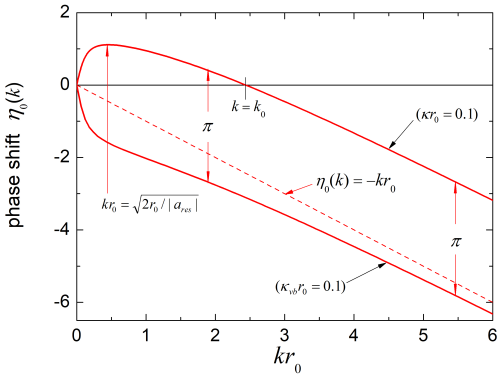


Figure 3.15: The s-wave phase shift as a function of k shown for the presence of a weakly bound s level ($\kappa r_0 = 0.1$ - lower curve) or a virtual s level near threshold ($\kappa_{vs} r_0 = 0.1$ - upper curve). The dashed line corresponds to the background contribution. The center of the s-wave resonance ($\eta_{res} = \frac{1}{2}\pi$) is indicated by the vertical dash-dotted line at $kr_0 = 0.458$. Note that asymptotically (i.e., far from threshold) the phase of the two curves differs by π.

negative energy, the resonance condition cannot be reached for $k \to 0$. In the latter case the resonance is said to be below threshold.

Knowing $a(k)$, it is straightforward to determine the consequences for the phase shift. With regard to the background contribution, the phase behavior is trivial, it is negative and shifts linearly with k. The full phase development is obtained by multiplying the red curves in Fig. 3.14 by $-k$. For the virtual level near threshold an interesting feature arises. As can be seen in Fig. 3.14 at some wavenumber, $k = k_0$, the effective hard sphere diameter crosses the value zero. As in this case the phase shift is positive, the zero crossing occurs when the background contribution and the resonance contribution exactly cancel, which implies a total phase shift of zero. The phase development is shown in Fig. 3.15. Zero phase shift means that at $k = k_0$ the presence of the interaction potential leaves no trace on the asymptotic ($r \to \infty$) shape of the wavefunction. What happens on the other side of the threshold? Fig. 3.14 suggests a difference because for a weakly bound level the zero crossing is absent. Closer inspection shows however that a similar phenomenon occurs because at the threshold the scattering length changes sign, which means that far from the center of the resonance the phase has to be shifted by π. As can be seen in Fig. 3.15, at $k = k_0$ the phase is $-\pi$.

3.4.9.1 Example: resonant enhancement by a weakly bound s level

Let us have a closer look at potential wells with many bound levels ($\gamma \gg 1$) of which the last one, of binding energy $\varepsilon = -\kappa^2$, is a weakly bound s level ($\kappa r_0 \lesssim 1$). In view of Eq. (3.91), the scattering length is large and positive, $a \simeq 1/\kappa$ for $\kappa \to 0$. A compact expression for the phase shift can be obtained starting from Eq. (3.93). For $kr_0 \ll 1$ we approximate $K_+ \cot K_+ r_0 \simeq \kappa_0 \cot \kappa_0 r_0 \simeq -\kappa$. Thus, we immediately obtain

$$\eta_0(k) \simeq -kr_0 - \arctan\frac{k}{\kappa}. \tag{3.134}$$

This approximation becomes exact for $\kappa \to 0$. However, we can do better and obtain an expression valid for $kr_0 \ll \gamma$. Using the procedure of Problem 3.5 we find

$$\eta_0(k) = -kr_0 - \arctan[k/(\kappa + \tfrac{1}{2}\kappa^2 r_0 + \tfrac{1}{2}k^2 r_0)] + \cdots, \tag{3.135}$$

where the higher order terms may be neglected as long as the binding energy of the level is much less than the well depth, $(k^2 + \kappa^2)r_0^2 \ll \gamma^2$. Since $\gamma \gg 1$ the latter condition remains satisfied well

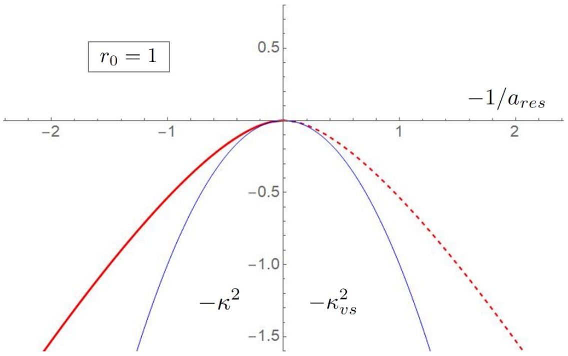


Figure 3.16: Solid red curve: binding energy of weakly bound level $(-\kappa^2)$ versus $-1/a_{res}$; dashed red curve: the "binding energy" of a virtual level $(-\kappa_{vs}^2)$ versus $1/a_{res}$. Note that close to the threshold $(-0.2 \le r_0/|a_{res}| \le 0.2)$ the curves merge with the universal curve $(1/a_{res} = \kappa;\ 1/a_{res} = -\kappa_{vs})$ shown as the blue parabola. The curves are normalized to r_0.

beyond the s-wave regime and for bound states with $\kappa r_0 > 1$. To illustrate this point we analyze the corresponding expression for the effective hard sphere diameter,

$$a(k) = -\eta_0(k)/k = r_0 + \frac{1}{k}\arctan[k/(\kappa + \tfrac{1}{2}\kappa^2 r_0 + \tfrac{1}{2}k^2 r_0)]. \tag{3.136}$$

In the limit $k \to 0$ we obtain for the scattering length,

$$a = \lim_{k\to 0} a(k) = r_0 + \frac{1}{\kappa + \frac{1}{2}\kappa^2 r_0}. \tag{3.137}$$

Hence, the resonance contribution to the scattering length is given by

$$a_{res} = a - r_0 = \frac{1}{\kappa + \frac{1}{2}\kappa^2 r_0}. \tag{3.138}$$

Solving for the binding energy we obtain the dependence on the resonant contribution to the scattering length

$$\varepsilon_v = -\kappa^2 = -(1/r_0^2)\left(\sqrt{1 + 2r_0/a_{res}} - 1\right)^2. \tag{3.139}$$

This dependence is plotted in Fig. 3.16. The scattering length increases for decreasing binding energy (red solid curve). It diverges when the weakly bound level reaches threshold $(\kappa \to 0)$. The curvature near threshold $(\kappa r_0 \lesssim 1)$ reflects the crossover to the universal κ dependence $(1/a_{res} = \kappa)$ indicated as the thin blue curve.

In terms of the *positive* quantity a_{res} Eq. (3.136) can be written in a more compact form,

$$a(k) = r_0 + \frac{1}{k}\arctan[k a_{res}/(1 + \tfrac{1}{2}k^2 r_0 a_{res})]. \tag{3.140}$$

At the resolution of Fig. 3.14, Eq. (3.140) cannot be distinguished from the exact result represented by the solid red curve. It is interesting to compare Eq. (3.140) with the corresponding expression based on the leading terms of effective-range expansion Eq. (3.113),

$$a(k) = \frac{1}{k}\arctan[ka/(1 - \tfrac{1}{2}k^2 r_e a)], \tag{3.141}$$

where $a = r_0 + a_{res}$. This approximation is shown for the example $\kappa r_0 = 0.1$ as the thin blue solid line in Fig. 3.14. As the value $\kappa r_0 = 0.1$ corresponds to an enhancement of a by an order of magnitude we may approximate the effective range by Eq. (3.124), which yields $r_e \simeq r_0$. This also follows by expansion of Eq. (3.140) in powers of k (see Problem 3.6). Whereas Eq. (3.140) correctly approaches the background value r_0 for growing kr_0, Eq. (3.141) decays to zero. Note that Eq. (3.141) becomes inaccurate for $kr_0 \approx 1$. This can be traced back to the Taylor expansion of $\tan kr_0$ used in the derivation of the effective-range expansion. For smaller enhancements the scattering length approximation becomes valid across the s-wave regime and the expansion (3.120) can be used to fit the leading k dependence. Also this approximation is indicated in Fig. 3.14. Note that it applies to a much smaller range of k values but is sufficient to establish the presence (or absence) of the resonance and to obtain a and r_e by a fitting procedure. Experimentally this is done by studying elastic scattering (cf. Chapter 4).

A famous example of a system with a bound s level is the *deuteron*, the bound state of a proton and a neutron with total spin $I = 1$. When scattering slow neutrons from protons (with "parallel" spin) the $a(k)$ increases with decreasing energy in accordance with Eq. (3.120). The fitting procedure yields $a = 5.41 \times 10^{-15}\,\mathrm{m}$ and $r_e = 1.75 \times 10^{-15}\,\mathrm{m}$ ($\kappa r_e = 0.31$) [52]. Among the quantum gases a famous example of a system with a weakly bound s level is doubly spin-polarized $^{133}\mathrm{Cs}$, where $a \approx 2400\,a_0$ and $r_0 \approx 101\,a_0$ ($\kappa r_0 \approx 0.042$) [3, 42].

Problem 3.5. Consider a spherical well with a large well parameter ($\gamma \gg 1$) and a weakly bound level ($\kappa r_0 \lesssim 1$) or a virtual level ($\kappa_{vs} r_0 \lesssim 1$) near threshold. Show that for k^2 , κ^2 and κ_{vs}^2 much smaller than κ_0^2 the following approximations hold to leading order in k and κ or κ_{vs}:

$$\tan\eta_{\mathrm{res}} = \frac{k}{K_+ \cot K_+ r_0} \simeq \begin{cases} \dfrac{-k}{\kappa + \frac{1}{2}(k^2+\kappa^2) r_0} & (\textit{weakly bound } s \text{ level}) \\[2ex] \dfrac{-k}{-\kappa_{vs} + \frac{1}{2}(k^2-\kappa_{vs}^2) r_0} & (\textit{virtual } s \text{ level near threshold}). \end{cases}$$

Solution. (a) To find an expression for $K_+ \cot K_+ r_0$ in the presence of a *weakly bound* level ($\kappa r_0 \lesssim 1$) we express K_+ in terms of K_- using the relation

$$K_+ = [\kappa_0^2 - \kappa^2 + k^2 + \kappa^2]^{1/2} = K_-[1 + \left(k^2+\kappa^2\right)/K_-^2]^{1/2}.$$

Since $\gamma \gg 1$ we have $\left(k^2+\kappa^2\right)/K_-^2 \ll 1$ close to threshold. Hence, it suffices to expand K_+ to first order in powers of $\left(k^2+\kappa^2\right)/K_-^2$ and approximate $K_+ \simeq K_- + \left(k^2+\kappa^2\right)/2K_-$. To evaluate $1/\cot K_+ r_0$ we use the angle addition formula for the tangent and obtain

$$\frac{k}{K_+ \cot K_+ r_0} \simeq \frac{k}{K_-} \frac{1}{1 + (k^2+\kappa^2)/2K_-^2} \frac{\tan K_- r_0 + \tan[(k^2+\kappa^2) r_0/2K_-]}{1 - \tan K_- r_0 \tan[(k^2+\kappa^2) r_0/2K_-]}.$$

Since $\left(k^2+\kappa^2\right)/2K_-^2 \ll 1$ this quantity can be neglected in the denominator. Furthermore, since $(k^2+\kappa^2) r_0/2K_- \ll 1$ we can replace the tangent by its argument. Thus we obtain

$$\frac{k}{K_+ \cot K_+ r_0} \simeq k \frac{1/(K_- \cot K_- r_0) + (k^2+\kappa^2) r_0/2K_-^2}{1 - \frac{1}{2}(k^2+\kappa^2) r_0/(K_- \cot K_- r_0)}.$$

Next we use the boundary condition for bound states, $K_- \cot K_- r_0 = -\kappa$, and neglect the second term in the numerator because $(k^2+\kappa^2)\kappa r_0/2K_-^2 \ll 1$. Thus we arrive at

$$\frac{k}{K_+ \cot K_+ r_0} \simeq \frac{-k}{\kappa + \frac{1}{2}(k^2+\kappa^2) r_0} \underset{k \ll \kappa}{\simeq} \frac{-k}{\kappa + \frac{1}{2}\kappa^2 r_0}.$$

(b) The symmetry of $K_+ \cot K_+ r_0$ with respect to the position of the level closest to the threshold (see Fig. 3.14) suggest to *define* the wavenumber of a *virtual* level near threshold ($\kappa_{vs} r_0 \lesssim 1$) by the expression $K_- \cot K_- r_0 = \kappa_{vs}$, with $K_- \equiv [\kappa_0^2 - \kappa_{vs}^2]^{1/2}$. This (purely formal) definition replaces the boundary condition (3.82) when dealing with virtual levels. Using the same approach as above we express K_+ in terms of $K_{vs} \equiv [\kappa_0^2 + \kappa_{vs}^2]^{1/2}$,

$$K_+ = [\kappa_0^2 + \kappa_{vs}^2 + k^2 - \kappa_{vs}^2]^{1/2} = K_{vs}[1 + \left(k^2 - \kappa_{vs}^2\right)/K_{vs}^2]^{1/2}.$$

Expanding in powers of $\left(k^2 - \kappa_{vs}^2\right)/K_{vs}^2$ we obtain $K_+ = K_{vs} + (k^2 - \kappa_{vs}^2)/2K_{vs} + \cdots$. Under similar conditions as under (a) this leads to

$$\frac{k}{K_+ \cot K_+ r_0} = \frac{-k}{-\kappa_{vs} + \frac{1}{2}(k^2 - \kappa_{vs}^2)r_0 + \cdots} \underset{k \ll \kappa}{\simeq} \frac{k}{\kappa_{vs} + \frac{1}{2}\kappa_{vs}^2 r_0 + \cdots}. \qquad \square$$

Problem 3.6. Show by expansion in powers of k that Eq.(3.140) corresponds to an effective range given by the expression

$$r_e \simeq r_0(1 - \tfrac{1}{3}r_0^2/a^2).$$

Note that this result coincides with Eq.(3.115) as is expected because Eq.(3.140) was derived for potentials with many bound states ($\gamma \gg 1$).

Solution. Starting from Eq. (3.140) we find for the phase shift

$$\eta_0(k) = -kr_0 - \arctan[ka_{res}/(1 + \tfrac{1}{2}k^2 r_0 a_{res})].$$

Using the angle addition formula for the tangent and expanding $\tan kr_0$ in powers of k we obtain

$$\tan \eta_0(k) \simeq \frac{-(kr_0 + \frac{1}{3}k^3 r_0^3 + \cdots) - ka_{res}/(1 + \frac{1}{2}k^2 r_0 a_{res})}{1 - k^2 r_0 a_{res}/(1 + \frac{1}{2}k^2 r_0 a_{res})}.$$

Turning to the cotangent and retaining terms up to order k^2 this expression becomes

$$-k \cot \eta_0(k) \simeq \frac{1 + \frac{1}{2}k^2 r_0 a_{res} - k^2 r_0 a_{res}}{a + \frac{1}{2}k^2 r_0^2 a_{res} + \frac{1}{3}k^2 r_0^3}.$$

Expanding to order k^2 we find for strong resonant enhancement ($|a| \gg r_0$)

$$-k \cot \eta_0(k) \simeq \frac{1}{a} - \tfrac{1}{2}k^2 r_0 \left[\frac{a_{res}}{a} + \frac{a_{res}}{a}\frac{r_0}{a} + \tfrac{2}{3}\left(\frac{r_0}{a}\right)^2\right].$$

Substituting $a_{res} = a - r_0$ this becomes

$$k \cot \eta_0(k) \simeq -\frac{1}{a} + \tfrac{1}{2}k^2 r_0(1 - \tfrac{1}{3}r_0^2/a^2),$$

which corresponds to the given expression for the effective range. $\square$

3.4.9.2 Example: resonant enhancement by a virtual s level near threshold

The boundary condition (3.130) also describes cases in which the scattering length is large and *negative*. In these cases the k dependence of $a(k)$ is very similar to that of a weakly bound state. In Fig. 3.14 this is shown for an enhancement by one order of magnitude. The symmetry about the threshold makes it possible to describe the phase shift by the (purely formal) introduction of a *virtual level*, defined by $\kappa = -\kappa_{vs}$, for which the boundary condition (3.82) is replaced by the expression

$$K_- \cot K_- r_0 = \kappa_{vs}, \qquad (3.142)$$

with $\kappa_{vs} > 0$ and

$$K_{-} \equiv (\kappa_0^2 - \kappa_{vs}^2)^{1/2}. \tag{3.143}$$

For $kr_0 \ll 1$ and $\kappa_{vs}r_0 \ll 1$ we may approximate $K_{+}r_0 \cot K_{+}r_0 = \kappa_0 \cot \kappa_0 r_0 = \kappa_{vs}$ and obtain

$$\eta_0(k) \simeq -kr_0 + \arctan\frac{k}{\kappa_{vs}}. \tag{3.144}$$

This approximation becomes exact for $\kappa_{vs} \to 0$. In terms of κ_{vs} the boundary condition (3.93) can be written in the form (see Problem 3.5)

$$\eta_0(k) = -kr_0 - \arctan[k/(-\kappa_{vs} + \tfrac{1}{2}k^2 r_0 - \tfrac{1}{2}\kappa_{vs}^2 r_0)]. \tag{3.145}$$

Higher order terms can be neglected for $(k^2 - \kappa_{vs}^2)r_0^2 \ll 2\gamma^2$. This implies that for $\gamma \gg 1$ the approximation comfortably allows us to describe the contribution of virtual states in the region of strong resonant enhancement (see Fig. 3.15). The corresponding expression for the effective hard sphere diameter is

$$a(k) = r_0 + \frac{1}{k}\arctan[k/(-\kappa_{vs} + \tfrac{1}{2}k^2 r_0 - \tfrac{1}{2}\kappa_{vs}^2 r_0)], \tag{3.146}$$

which implies for the s-wave scattering length

$$a = \lim_{k\to 0} -\eta_0(k)/k = r_0 - \frac{1}{\kappa_{vs} + \tfrac{1}{2}\kappa_{vs}^2 r_0 + \cdots}. \tag{3.147}$$

Hence, the resonance contribution to the scattering length is

$$a_{res} = a - r_0 \simeq \frac{1}{-\kappa_{vs} - \tfrac{1}{2}\kappa_{vs}^2 r_0 + \cdots}, \tag{3.148}$$

which is a *negative* quantity close to theshold.

Interestingly, expressing Eq. (3.146) in terms of a_{res} we obtain

$$a(k) = r_0 + \frac{1}{k}\arctan[ka_{res}/(1 + \tfrac{1}{2}k^2 r_0 a_{res}), \tag{3.149}$$

which is exactly the *same expression* as was obtained for the weakly bound level - see Eq. (3.140). The two cases differ in the sign of a_{res}, which is positive for the weakly bound level ($a_{res} = |a_{res}|$) and negative for the virtual level ($a_{res} = -|a_{res}|$). From Eq. (3.149) it immediately follows that the "center" of the s-wave resonance near threshold (i.e., the point with $\eta_{res} = \tfrac{1}{2}\pi$ modulo π) is given by

$$kr_0 = \sqrt{2r_0/|a_{res}|}. \tag{3.150}$$

Eq. (3.149) is plotted in Fig. 3.14. At the resolution of the figure it cannot be distinguished from the exact result represented by the dashed red curve. It is interesting to compare Eq. (3.140) with the corresponding expression based on the leading terms of effective-range expansion Eq. (3.113),

$$a(k) = \frac{1}{k}\arctan[ka/(1 - \tfrac{1}{2}k^2 r_e a)]. \tag{3.151}$$

This approximation is shown as the blue dashed line in Fig. 3.14 using $a = r_0 + a_{res}$ for the example $\kappa_{vs}r_0 = 0.1$. A nice quantitative indicator for the excellent quality of the approximation (3.145) for large γ is obtained by calculating the zero crossing of the phase shift. Setting $\eta_0 = 0$ in Eq. (3.145) we obtain the condition

$$\tan k_0 r_0 = k_0 r_0/(\kappa_{vs} r_0 + \tfrac{1}{2}\kappa_{vs}^2 r_0^2 - \tfrac{1}{2}k_0^2 r_0^2) \underset{\kappa_{vs}\to 0}{\simeq} -2/k_0 r_0. \tag{3.152}$$

For the example of Fig. 3.14 ($\kappa_{vs}r_0 = 0.1$) we calculate $k_0 r_0 = 2.43656$, which turns out an excellent estimate when compared with the exact value $k_0 r_0 = 2.43659$. With increasing resonant enhancement the location of the zero crossing becomes κ_{vs} independent and reaches the limiting value $k_0 r_0 = 2.45871$ for $\kappa_{vs} \to 0$.

A virtual s level is present in low-energy neutron-proton collisions through the anti-symmetric spin channel (singlet channel), $a = -2.38 \times 10^{-14}\,\mathrm{m}$ and $r_e = 2.67 \times 10^{-15}\,\mathrm{m}$ ($\kappa_{vs} r_e = 0.11$) [52]. An example of the presence of a virtual bound state in the quantum gases is doubly polarized ^{85}Rb, where $a \approx -369\,a_0$ and $r_0 \approx 83\,a_0$ ($\kappa_{vs} r_0 \approx 0.22$) [62].

Universal regime about threshold - summary

For convenience of reference we summarize the results for the universal regime near threshold, where the scattering length only depends on the location of the weakest bound- or virtual level,

$$a(k) = r_0 + \frac{1}{k}\arctan[k/(\pm\kappa_\pm \pm \tfrac{1}{2}\kappa_\pm^2 r_0 + \tfrac{1}{2}k^2 r_0 + \cdots)]. \tag{3.153}$$

Here we adopt the notation with $+$ signs for bound levels ($\kappa_+ \equiv \kappa$) and $-$ signs for virtual levels ($\kappa_- \equiv \kappa_{vs}$). The resonance contribution to the scattering length is obtained by taking the $k \to 0$ limit,

$$a_{res} \simeq \frac{1}{\pm\kappa_\pm \pm \frac{1}{2}\kappa_\pm^2 r_0}. \tag{3.154}$$

In terms of this quantity Eq. (3.153) can be written in the unified form

$$a(k) = r_0 + \frac{1}{k}\arctan[k a_{res}/(1 + \tfrac{1}{2}k^2 r_0 a_{res}) \tag{3.155}$$

valid for both positive and negative a_{res}. Using the sign convention introduced above this becomes

$$a(k) = r_0 \pm \frac{1}{k}\arctan[k|a_{res}|/(1 \pm \tfrac{1}{2}k^2 r_0 |a_{res}|)]. \tag{3.156}$$

3.4.10 S matrix for s-wave resonance near threshold

Rather than expanding the arctangent we also consider the S matrix and separate the background contribution r_0 from the resonant contribution a_{res} by factorization. For a strongly enhanced scattering length ($|a| \gg r_0$) the S matrix can be factorized to the form [1]

$$S_0(k) = e^{2i\eta_0} = e^{-2ikr_0}\frac{1 - ika_{\mathrm{res}}}{1 + ika_{\mathrm{res}}} \tag{3.157}$$

and subsequently expand the background contribution to second order,

$$S_0(k) = (1 - 2ikr_0 - 2k^2 r_0^2 + \cdots)\frac{1 - ika_{\mathrm{res}}}{1 + ika_{\mathrm{res}}}, \tag{3.158}$$

which valid for $kr_0 \ll 1$. The real and imaginary parts of S_0 become

$$\mathrm{Re}\,S_0(k) = 1 - \frac{2k^2 a^2 + \cdots}{1 + k^2 (a - r_0)^2} \tag{3.159a}$$

$$\mathrm{Im}\,S_0(k) = -2ka + \cdots , \tag{3.159b}$$

---

[1] Here we use the logarithmic representation of the arctangent with a real argument α,

$$\arctan\alpha = \frac{i}{2}\ln\frac{1 - i\alpha}{1 + i\alpha}.$$

where we used $a = r_0 + a_{\rm res}$ and neglected terms of power k^3 or higher. We return to the S matrix in Chapter 4.

Following up on the discussion of Section 3.2.1.1 the resonant behavior can be studied by analytic continuation of the S matrix into the complex $\bar{k}$ plane, where $\bar{k} = k' + ik''$. In this way Eq. (3.157) can be rewritten in the form

$$S_0(\bar{k}) = e^{2i\eta_0} = e^{-2i\bar{k}r_0}\frac{\bar{k} + i/a_{\rm res}}{\bar{k} - i/a_{\rm res}}. \tag{3.160}$$

In this notation the resonance is associated with a pole in the complex plane at $\bar{k} = i/a_{\rm res}$. For bound states we have $1/a_{\rm res} > 0$, which corresponds to a pole at $\bar{k} = i\kappa$, where $\kappa = 1/a_{\rm res}$; i.e., on the *positive* imaginary axis in the complex $\bar{k}$ plane. The corresponding complex energy is real and negative, $\bar{\varepsilon} = \bar{k}^2 = -\kappa^2$, and is represented by a point on (the negative real axis of) the *first* Riemann sheet (the physical sheet) of the complex energy plane. For virtual levels we have $1/a_{\rm res} < 0$, which corresponds to a pole on the *negative* imaginary axis in the complex $\bar{k}$ plane, which we denote by $\bar{k} = -i\kappa_{vs}$, with $\kappa_{vs} > 0$. The corresponding complex energy is real and negative $\bar{\varepsilon} = \bar{k}^2 = -\kappa_{vs}^2$ and is represented by a point on (the negative real axis of) the *second* Riemann sheet. As in both cases the energy is negative these poles cannot be reached in a scattering experiment since the energy of continuum states is positive, $k^2 > 0$. Mathematically the complex notation has the advantage that the annoying divergences of the argument of the arctangent are avoided.

The above discussion was specialized to the universal regime near the threshold. More generally, in the presence of a weakly bound or virtual level, the phase shift is given by the boundary condition (3.93) and the expression for the S matrix becomes

$$S_0(k) = e^{2i\eta_0} = e^{-2i\bar{k}r_0}\frac{\bar{K}\cot\bar{K}r_0 + i\bar{k}}{\bar{K}\cot\bar{K}r_0 - i\bar{k}}, \tag{3.161}$$

where $\bar{K}^2 = \kappa_0^2 + \bar{k}^2$. In this case poles are found at

$$\bar{k} = -i\bar{K}\cot\bar{K}r_0. \tag{3.162}$$

Let us first analyze the properties of a pole on the *positive* imaginary axis, $\bar{k} = i\kappa$ with $\kappa > 0$. In this case $\bar{K}^2$ is real and the following equations are simultaneously satisfied,

$$\bar{K}\cot\bar{K}r_0 = -\kappa, \quad \bar{K}^2 = \kappa_0^2 - \kappa^2 = K_-^2. \tag{3.163}$$

Note that these expressions correspond to the boundary conditions for a bound state as obtained in Section 3.4.3. Thus we identify a pole of the S matrix on the *positive* imaginary axis with a *bound state*. Equally well we can identify a *zero* of the S matrix on the *negative* imaginary axis with a bound state.

Next we analyze the properties of a pole on the *negative* imaginary axis, $\bar{k} = -i\kappa_{vs}$ with $\kappa_{vs} > 0$. Also in this case $\bar{K}^2$ is real. Furthermore, the following equations are simultaneously satisfied,

$$\bar{K}\cot\bar{K}r_0 = \kappa_{vs}, \quad \bar{K}^2 = \kappa_0^2 - \kappa_{vs}^2 = K_-^2. \tag{3.164}$$

Note that these expressions correspond to the boundary conditions for a virtual level as obtained in Eqs. 3.142 and 3.143. Thus we identify a pole of the S matrix on the *negative* imaginary axis with a *virtual* level. Equivalently we can identify a *zero* of the S matrix on the *positive* imaginary axis with a *virtual* level.

3.4.11 Zero-range potentials

An important model potential is obtained by considering a spherical well in the zero-range limit $r_0 \to 0$. As illustrated in Fig. 3.17 it is possible to construct a zero-range well in such a way that

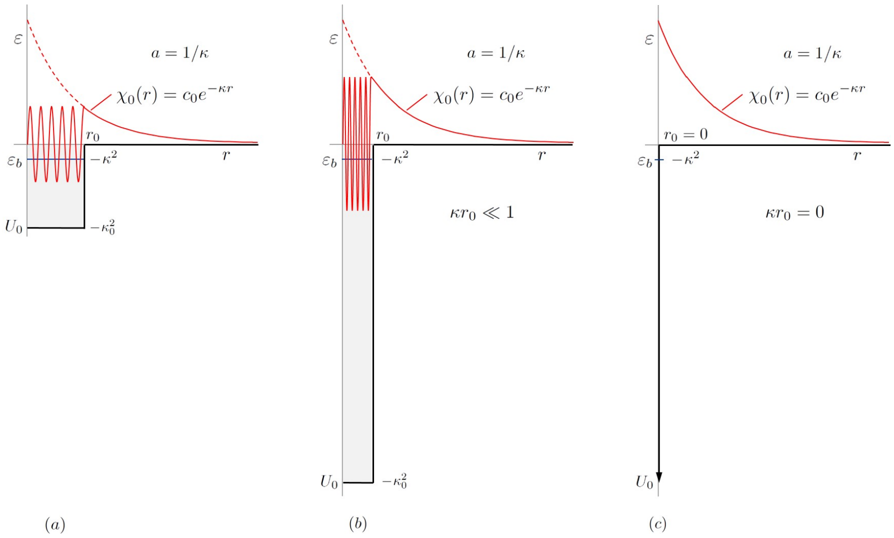


Figure 3.17: Wavefunctions corresponding to the *same* binding energy ($\varepsilon = -\kappa^2$) plotted for three different values of r_0. Outside r_0 the wavefunctions fall off exponentially, always with the same decay exponent κ; this is the essence of the Bethe-Peierls boundary condition. The dashed lines show the extrapolation for $r \to 0$. (a) reference case; (b) for $\kappa r_0 \ll 1$ most of the probability density of a bound state is found outside the well (halo state); (c) for zero-range potentials ($\kappa r_0 = 0$) the oscillating part of the wavefunction is compressed into a delta function and only the decaying exponent remains (universal limit). Note that these wavefunctions do not share the same normalization.

the long-range properties of the wavefunction are unaffected; i.e., the scattering length a and the binding energy $\varepsilon = -\kappa^2$ of the *least-bound* state remain unchanged.

For $E < 0$ this can be demonstrated with the aid of the boundary condition (3.82)

$$-\kappa = K_- \cot K_- r_0. \tag{3.165}$$

Reducing the radius r_0 the value of the binding energy $\varepsilon = -\kappa^2$, can be conserved by increasing κ_0. In the limit $r_0 \to 0$ the well depth should diverge in accordance with

$$-\frac{\kappa}{K_-} = \cot K_- r_0 \to 0. \tag{3.166}$$

This condition is satisfied for $K_- r_0 \simeq \pi/2$. To elucidate this point we consider the *least-bound* level with vibrational quantum number $v = v_{\max}$, for which $K_- r_0 = (v_{\max} + \frac{1}{2})\pi$. Reducing r_0 by a factor of 2 the wavenumber K_- has to be doubled to conserve the number of nodes in the wavefunction (i.e., to conserve $v_{\max}$). This means that the kinetic energy *inside the well* has to increases by a factor 4. Since for the *least-bound* level we have $K_- r_0 \simeq \gamma$, it means that in this case the binding energy can be conserved at *effectively constant* well parameter. Obviously, the freedom to conserve (for decreasing r_0) the binding energy of one of the levels can only be used once. It does *not* hold for the other levels because the level *separation* diverges with κ_0. In the zero range limit the potential only supports a single bound state and the wavefunction of that state is given by

$$R_0(r) = c_0 e^{-\kappa r}/r \qquad \text{for } r > 0 \tag{3.167}$$

and with $\kappa > 0$. Unit normalization, $\int r^2 R_0^2(r) dr = 1$, is obtained for $c_0 = \sqrt{2\kappa}$.

For $E > 0$ we can arrive at the same conclusion. The boundary condition for $k \to 0$ and given value of r_0 is given by Eq. (3.74), which we write in the form

$$\frac{1}{r_0 - a} = \kappa_0 \cot \kappa_0 r_0. \tag{3.168}$$

Reducing the radius r_0, the scattering length a can be conserved by increasing κ_0. In the limit $r_0 \to 0$ the well depth should diverge in accordance with

$$-\frac{1}{\kappa_0 a} = \cot \kappa_0 r_0 \to 0. \tag{3.169}$$

This is again satisfied for $\kappa_0 r_0 \simeq \pi/2$. In the zero-range limit the radial wavefunction for $k \to 0$ is given by

$$R_0(k,r) = \frac{1}{kr}\sin[k(r-a)] \qquad \text{for } r > 0, \tag{3.170}$$

which implies $R_0(k,r) \simeq 1 - a/r$ for $0 < r \ll 1/k$.

Bethe-Peierls boundary condition

Note that Eq. (3.167) is the solution for $E < 0$ of the 1D-Schrödinger equation in the zero-range approximation

$$\chi_0'' - \kappa^2 \chi_0 = 0 \qquad r > 0, \tag{3.171}$$

under the boundary condition

$$\chi_0'/\chi_0|_{r\to 0} = -\kappa. \tag{3.172}$$

The latter relation is called the *Bethe-Peierls boundary condition* and was first used to describe the *deuteron*, the weakly bound state of a *proton* with a *neutron* [6]. It shows that for weakly bound states the wavefunction has the *universal form* of a *halo state*, which only depends on the binding energy, $\varepsilon_b = -\kappa^2$ (see Fig. 3.17).

For $E > 0$ the 1D-Schrödinger equation in the zero-range approximation is given by

$$\chi_0'' + k^2 \chi_0 = 0 \quad (r > 0). \tag{3.173}$$

The general solution is $\chi_0(k,r) = c_0 \sin[kr + \eta_0]$. Using the Bethe-Peierls boundary condition we obtain

$$k \cot \eta_0(k) = -\kappa, \tag{3.174}$$

which yields after substituting $\eta_0(k \to 0) \simeq -ka$ the universal relation between the scattering length and the binding energy in the presence of a weakly bound s level, $\varepsilon_b = -\kappa^2 = -1/a^2$.

3.5 Spherical wells screened by a tunnel barrier

3.5.1 General

The third model potential to consider is the *spherical well* of range r_0 screened by a *deltafunction tunnel barrier* as sketched in Fig. 3.18,

$$U(r) = \begin{cases} -\kappa_0^2 + \kappa_1 \, \delta(r - r_0) & \text{for } r \le r_0 \\ 0 & \text{for } r > r_0. \end{cases} \tag{3.175}$$

This potential is a generalization of the spherical well introduced in Section 3.4. The well depth is again defined as a positive number, $|U_0| = \kappa_0^2$. The energy of the continuum states is denoted by $\varepsilon = k^2$ and the energy of the bound states is $\varepsilon_b = -\kappa^2$. Note that for $\kappa_1 = 0$ the barrier is absent and Eq. (3.175) reduces to Eq. (3.59). For $\kappa_1 \to \infty$ we regain the hard sphere (plus a disconnected well with only bound states). The presence of the barrier enhances the lifetime of the resonances which allows us to model narrow resonance features; e.g., s-wave Feshbach resonances.

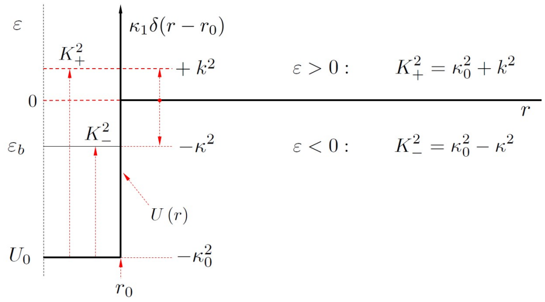


Figure 3.18: Sketch of spherical well with tunnel barrier.

3.5.2 s-wave resonances and scattering length for screened wells

For $l = 0$ and $E > 0$ the 1D-Schrödinger equation (3.9) for the radial motion is of the form

$$\chi_0'' + [k^2 - U(r)]\chi_0 = 0. \tag{3.176}$$

The solution is

$$\chi_0(k,r) = \begin{cases} C_0 \sin(K_+ r) & \text{for } \; r < r_0 \\ c_0 \sin(kr + \eta_0) & \text{for } \; r > r_0. \end{cases} \tag{3.177}$$

As the tunnel barrier is of zero width, the amplitude of $\chi_0(k,r)$ is conserved across the barrier. In contrast, the derivative $\chi_0'(k,r)$ changes step wise. The resulting boundary condition takes the form

$$\chi_0'/\chi_0|_{r=r_0} = K_+ \cot K_+ r_0 = k \cot(kr_0 + \eta_0) + \kappa_1. \tag{3.178}$$

To obtain the k dependence of the phase shift for large but otherwise arbitrary well parameter γ we rewrite the boundary condition (3.178) in the form - compare with Eq. (3.130)

$$a(k) = r_0 - \frac{1}{k} \arctan\left(\frac{kr_0}{K_+ r_0 \cot K_+ r_0 - \beta}\right), \tag{3.179}$$

where the quantity

$$\beta \equiv \kappa_1 r_0$$

is called the the barrier parameter. It is a measure for the coupling of the states across the barrier, large β corresponding to weak coupling. For $k \to 0$ this expression reduces to the following relation between the well parameter, the barrier parameter and the scattering length:

$$\gamma \cot \gamma = \frac{r_0}{r_0 - a} + \beta. \tag{3.180}$$

For potentials with $\gamma \gg 1$ the product $K_+ r_0$ is large,

$$K_+ r_0 = \kappa_0 r_0 (1 + k^2/\kappa_0^2)^{1/2} > \gamma \gg 1. \tag{3.181}$$

Therefore, the tangent of the resonant phase shift is typically small,

$$|\tan \eta_{res}| = \frac{k}{|K_+ \cot K_+ r_0 - \kappa_1|} \ll 1, \tag{3.182}$$

but diverges when $K_+ \cot K_+ r_0 - \kappa_1$ passes through zero; i.e., for

$$\cot K_+ r_0 = -\kappa_1 / K_+. \tag{3.183}$$

For $\kappa_1 r_0 \to 0$ this happens for $K_+ r_0 \simeq (\tilde{v} + \frac{1}{2})\pi$, where the integer $\tilde{v}$ is the *resonance index.* This is the result (3.97) as obtained for the Breit-Wigner s-wave resonance. For $\kappa_1 r_0 \to \infty$ the divergence occurs for $K_+ r_0 \simeq v\,\pi$, which is the boundary condition for level v in a closed box. To analyze then resonance corresponding to level v we expand $K_+ \cot K_+ r_0 - \kappa_1$ about the point of zero crossing. Note that this is only possible for $\kappa_v \geq \kappa_0$. For this purpose we introduce the notation

$$K_+ = [\kappa_0^2 + (\kappa_v + \delta k)^2]^{1/2} = K_v + \delta k\, \kappa_v / K_v + \cdots \,, \tag{3.184}$$

where $\delta k = k - \kappa_v$ is the *detuning* from resonance and κ_v^2 is the energy of level v with respect to the bottom of the well. Expanding $\cot K_+ r_0$ about the zero crossing at $K_+ r_0 = v\,\pi \geq \gamma$ and retaining only the linear term we obtain (See Problem 3.7)

$$K_+ \cot K_+ r_0 - \kappa_1 = -\delta k\, \kappa_v r_0 (\kappa_1/\kappa_0)^2, \tag{3.185}$$

where the factor K_+ in front of the cotangent was taken to be constant across the resonance, $K_+ \simeq K_v = (\kappa_0^2 + \kappa_v^2)^{1/2} \simeq \kappa_0$. Note that for a weak through the barrier ($\kappa_1 \gg \kappa_0$) the slope is enhanced by the factor $(\kappa_1/\kappa_0)^2$ with respect to the Breit-Wigner case. This narrows down the width of the resonance by the same amount (see Fig. 3.19). Approximating $K_v r_0 \simeq \gamma$, which is valid for the lowest few resonances above the threshold of a deep well, the boundary condition becomes

$$\tan \eta_v = \frac{k}{K_+ \cot K_+ r_0 - \kappa_1} \simeq -\frac{1}{\delta k\, r_0} \frac{\kappa_1^2}{\kappa_0^2} = \frac{-(k + \kappa_v)}{(k^2 - \kappa_v^2) r_0} \frac{\kappa_1^2}{\kappa_0^2} \simeq \frac{\kappa_v / R^*}{\varepsilon - \varepsilon_v}, \tag{3.186}$$

where, for narrow resonances ($\kappa_1 \gg \kappa_0$),

$$R^* = \tfrac{1}{2} r_0 (\kappa_1/\kappa_0)^2, \tag{3.187}$$

which is a measure for the resonance width. The above expansion is valid over the full range of the resonant phase change provided the following condition holds:

$$\delta k \ll \kappa_0 / \kappa_v. \tag{3.188}$$

Excluding a possible resonance near threshold, this condition is satisfied for resonances above threshold as long as the well parameter is sufficiently large ($\gamma \gg \kappa_v r_0$). As long as $\delta k \ll \kappa_v$ we may further approximate $k \simeq \kappa_v$. With these approximations and after restoring the dimensions, Eq. (3.103) can be written as a function of the energy $E = \hbar^2 k^2 / 2m_r$,

$$\tan \eta_v = \frac{k}{K_+ \cot K_+ r_0 - \kappa_1} \simeq \frac{-\Gamma/2}{E - E_v}, \tag{3.189}$$

where

$$\Gamma = (\hbar^2/m_r)(2\kappa_v/R^*) \tag{3.190}$$

is the *spectral width* of the resonance.

Problem 3.7. Derive the expansion (3.185)

Solution. We calculate the derivative at $K_+ r_0 \simeq v\pi$, where $\cos^2 K_+ r_0 \simeq 1$. Starting from Eq. (3.183) we obtain with the aid of the expansion (3.184) for resonances near threshold (i.e., $K_v \simeq \kappa_0$)

$$\left. \frac{d\,(K_v \cot K_+ r_0 - \kappa_1)}{d\,\delta k} \right|_{K_+ r_0 \simeq v\pi} = - \left. \frac{\kappa_v \cot^2 K_+ r_0}{\cos^2 K_+ r_0} \right|_{K_+ r_0 \simeq \tilde{v}\pi} = -\kappa_v r_0 (\kappa_1/\kappa_0)^2.$$

Multiplying the derivative with δk we obtain the desired result. □

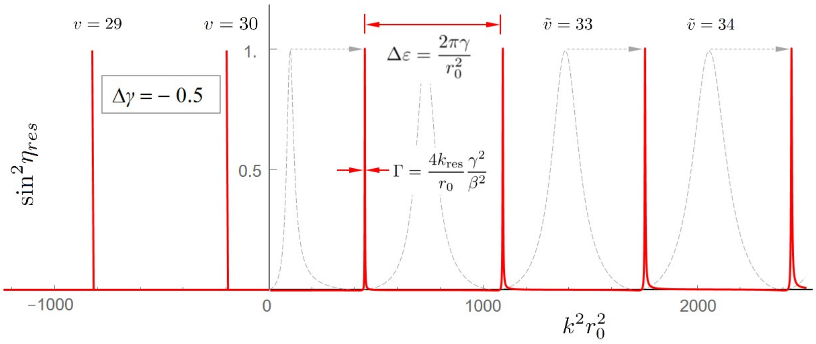


Figure 3.19: Crossover from bound states to *narrow* s-wave resonances (red solid line) plotted for $\Delta\gamma = -0.5$ with respect to the well parameter $\gamma = 98.960169$ (see Fig. 3.12). The bound states are indicated as zero-width spikes at energies $\varepsilon = -\kappa^2$, with κ following from Eq. (3.82). For $\varepsilon > 0$ the plot is based on Eq. (3.179). The width of the resonances increases with the square root of the energy. Note that the resonances are shifted with respect to the corresponding Breit-Wigner resonances as a result of the different boundary condition.

3.5.3 Effective-range expansion for screened wells

The leading energy dependence of the phase shift is obtained by applying the angle-addition formula of the tangent to the r.h.s. of Eq. (3.179) and expanding $\tan kr_0$ in (odd) powers of k,

$$k\cot\eta_0 = \frac{(K_+\cot K_+r_0 - \kappa_1) + k^2r_0 + \cdots}{1 - r_0\left(1 + \frac{1}{3}k^2r_0^2 + \cdots\right)(K_+\cot K_+r_0 - \kappa_1)}. \tag{3.191}$$

In view of the expansion, the validity of this expression is restricted to $kr_0 \ll 1$. Next we expand K_+r_0 in even powers of k,

$$K_+r_0 = \kappa_0r_0[1 + k^2/\kappa_0^2]^{1/2} = \gamma + \tfrac{1}{2}k^2r_0^2/\gamma + \cdots, \tag{3.192}$$

which is valid for $\gamma \gtrsim 1$, and using the angle-addition formula for the cotangent we find

$$K_+r_0\cot K_+r_0 - \beta = (\gamma\cot\gamma - \beta) - \tfrac{1}{2}k^2r_0^2\left[1 + (1 - \tan\gamma/\gamma)\cot^2\gamma\right] + \cdots. \tag{3.193}$$

Substituting Eq. (3.193) into Eq. (3.191) and subsequently use Eq. (3.180) we arrive after some calculus at the *effective-range expansion* in powers of k,

$$k\cot\eta_0 = -\frac{1}{a} + \tfrac{1}{2}k^2r_e + \cdots, \tag{3.194}$$

and

$$r_e = r_0\left(1 - \frac{3ar_0 + \gamma^2r_0^2 - 3\beta(a^2 - r_0^2) + 3\beta^2(a - r_0)^2}{3a^2\gamma^2}\right) \tag{3.195}$$

is called the *effective range*. In view of the derivation this expansion is valid for $kr_0 \ll 1$ and $\gamma \gtrsim 1$. For $\gamma \to \infty$ the effective range becomes

$$r_e = r_0(1 - \tfrac{1}{3}r_0^2/a^2). \tag{3.196}$$

Resonance near threshold

For finite γ we consider two limiting cases for a resonance near threshold ($-a \gg r_0$):

- *broad resonance.* For $|\beta/\gamma| \ll 1$ we have *strong coupling* across the boundary and regain the open channel result (3.114),
$$r_e = r_0\left(1 - \frac{3ar_0 + \gamma^2 r_0^2}{3a^2\gamma^2}\right) = r_0\left(1 - \frac{r_0}{a\gamma^2} - \frac{r_0^2}{3a^2}\right) \simeq r_0\,. \tag{3.197}$$
- *narrow resonance.* For $|\beta/\gamma| \gg 1$ we have *weak coupling* across the boundary and obtain
$$r_e \simeq -r_0\frac{\beta^2}{\gamma^2}\frac{(a-r_0)^2}{a^2} = -r_0\frac{\beta^2}{\gamma^2}\left(1 - 2\frac{r_0}{a} + \frac{r_0^2}{a^2}\right) \simeq -2R^*. \tag{3.198}$$

  This expression shows that the effective range is large and *negative* in the limit of *weak* coupling through the barrier.

3.5.4 Narrow versus broad resonances

As a measure for the width of a scattering resonance Dmitry Petrov introduced the resonance range parameter [55]
$$R^* = -\tfrac{1}{2}r_e. \tag{3.199}$$
In terms of this parameter the effective range expansion takes the form
$$k\cot\eta_0 = -\frac{1}{a} - k^2R^*. \tag{3.200}$$
For *narrow* resonances ($\beta^2/\gamma^2 \gg 1$), R^* is *large* (with respect to r_0) and *positive*,
$$R^* \simeq \tfrac{1}{2}r_0\frac{\beta^2}{\gamma^2}. \tag{3.201}$$
For *increasing* resonance width, R^* *decreases* until the open channel result (3.113) is reached as its limiting value,
$$R^* = -\tfrac{1}{2}r_0. \tag{3.202}$$
Note that this value is smaller than r_0 and *negative*.

To analyze narrow resonances we rewrite the effective-range expression (3.200) in the form of a universal expression for the the k dependence of the scattering length for a resonance near threshold,
$$a(k) = \frac{1}{k}\arctan\left[ka/(1+k^2R^*a)\right]. \tag{3.203}$$
Note that the limiting value is reached for $k^2R^*a \ll 1$. The expression (3.203) is plotted in Fig. 3.20 for two values of the resonance range. For $R^* = -\frac{1}{2}r_0$ we regain the conditions of the s-wave resonance near threshold as discussed in Section 3.4.9. For $R^* = 100\,r_0$ the resonant enhancement is narrowed down to a small spectral region. For $a > 0$ this region is below threshold and acts as a weakly bound level giving rise to an enhanced scattering length $a \gg r_0$ for $kr_0 \ll 1$. In the limit of vanishing coupling, $R^* \to \infty$, this enhancement vanishes. For $a < 0$ the resonant region is above threshold. It shows up as a spectral feature at $-k^2R^*a \simeq 1$; i.e., the resonance energy is found near
$$\kappa_v^2 \simeq -\frac{1}{R^*a}. \tag{3.204}$$

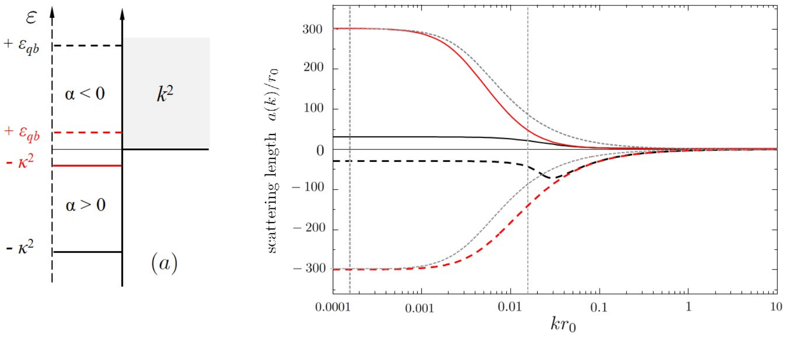


Figure 3.20: (a) Bound/quasi-bound levels (solid/dashed lines) in a (screened or open) flat-bottom well; (b) Narrow resonances ($R^* = 100\, r_0$ - red and black solid and dashed curves) compared with open s-wave resonances near threshold ($R^* = -\frac{1}{2}r_0$ - dashed grey curves). With respect to the open s-wave resonance we find for the same resonant enhancement: for positive/negative scattering length the enhancement is pulled/pushed to lower/higher energy by coupling to a bound state below/above threshold. The red solid and dashed curves were plotted for the same (positive or negative) scattering-length enhancement near threshold (i.e., for the same detuning of resonance from threshold - see left). For $a < 0$ the resonance shows up as a spectral feature at $k = k_{res} = (-a_{res}R^*)^{-1/2}$ (vertical dashed lines).

If the resonance width is much smaller than the resonance energy; i.e., for $k_v/R^* \ll k_v^2 \Leftrightarrow k_v \gg 1/R^*$, the resonance is visible as a spectral feature in the continuum.

In view of the expressions (5.49) and (5.53) the argument of the arctangent is equivalent to

$$\frac{ka_{res}}{1 + k^2 R^* a_{res}} = -\frac{k\gamma_{res}}{\varepsilon_v - \varepsilon_0 - k^2}. \tag{3.205}$$

From this expression we see that the resonance condition is given by

$$k^2 = \varepsilon_v - \varepsilon_0 \equiv \varepsilon_{res}. \tag{3.206}$$

In terms of this quantity the universal expression for $a(k)$ becomes

$$a(k) = a_{bg} - \frac{1}{k}\arctan\left[k\gamma_{res}/(\varepsilon_v - \varepsilon_0 - k^2).\right] \tag{3.207}$$

and the scattering length is given by

$$a = \lim_{k\to 0} a(k) = a_{bg} + a_{res} = a_{bg} - \frac{1}{R^*(\varepsilon_v - \varepsilon_0)}. \tag{3.208}$$

3.6 Arbitrary short-range potentials

The results obtained above for the spherical well are typical for so called *short-range potentials.* Such potentials have the property that they may be neglected beyond a certain *radius of action* r_0, the *range* of the potential. This holds manifestly for model potentials like the hard sphere or the spherical well but is in general not obvious or simply not true. Heuristically, one may argue that an arbitrary potential $\mathcal{V}(r)$ may be neglected at distances $r \gg r_0$ if the kinetic energy of confinement within a sphere of radius $r \gg r_0$ (i.e., the zero-point energy $\sim \hbar^2/2m_r r^2$) largely exceeds the potential energy $|\mathcal{V}(r)|$ *outside* that sphere. If this is the case, the potential is apparently so weak that it cannot confine the mass m_r and being small even in comparison to the lowest energy scale (the zero-point motion) means that it can be neglected. Estimating r_0 as the distance where the two contributions are equal,

$$|\mathcal{V}(r_0)| = \hbar^2/2m_r r_0^2, \tag{3.209}$$

it is obvious that the potential has to fall off faster than $1/r^2$ to be negligible at long distance. For $\mathcal{V}(r) = -C_6/r^6$ the range is called the *Van der Waals range* and we find

$$r_0 \simeq [2m_r C_6/\hbar^2]^{1/4}. \tag{3.210}$$

A more detailed analysis will show that the potential has to fall off faster than $1/r^s$ with $s > 2l+3$ for a finite range r_0 to exist; i.e., for s waves faster than $1/r^3$ (cf. Sections 3.6.2 and 3.7.1). For the time being we shall simply presume that a finite range exist and show that the scattering length, the effective range and resonant enhancement by a weakly bound s-level are typical phenomena for any short-range potential.

3.6.1 Scattering lengths for arbitrary l

For short-range potentials and distances $r \gg r_0$ the radial wave equation (3.7) reduces to the spherical Bessel differential equation

$$R_l'' + \frac{2}{r}R_l' + \left[k^2 - \frac{l(l+1)}{r^2}\right] R_l = 0. \tag{3.211}$$

Thus, for $r \gg r_0$ we have free atomic motion and the general solution for the radial wave functions of angular momentum l is given by Eq. (3.19),

$$R_l(k,r) \underset{r\gg r_0}{\simeq} c_l[\cos\eta_l\, j_l(kr) + \sin\eta_l\, n_l(kr)]. \tag{3.212}$$

For any finite value of k this expression has for $r \gg 1/k$ the asymptotic form

$$R_l(k,r) \underset{r\gg 1/k}{\simeq} \frac{c_l}{kr}\sin(kr + \eta_l - \frac{1}{2}l\pi), \tag{3.213}$$

thus regaining the appearance of a phase shift like in the previous sections.

For $kr \ll 1$ and $r \gg r_0$ equation (3.212) reduces with the aid of Eq. (C.107) to the form

$$R_l(kr) \simeq c_l \cos\eta_l \frac{(kr)^l}{(2l+1)!!} + c_l \sin\eta_l \frac{(2l+1)!!}{2l+1}\left(\frac{1}{kr}\right)^{l+1} \quad \text{for } r_0 \ll r \ll 1/k. \tag{3.214}$$

To determine η_l we are looking for a boundary condition. For this purpose we derive a second expression for $R_l(r)$, which is valid in the range of distances $r_0 \ll r \ll 1/k$ where *both* $\mathcal{V}(r)$ *and* k^2 may be neglected in the radial wave equation, which in this case reduces to

$$R_l'' + \frac{2}{r}R_l' = \frac{l(l+1)}{r^2}R_l. \tag{3.215}$$

For $l \geq 1$ the validity of this approximation is evident by comparing k^2 to the rotational barrier; for $l = 0$ we recall Eq. (3.78), which shows that also $R_0(r)$ is k independent on the interval $r_0 \ll r \ll 1/k$. The general solution of Eq. (3.233) is

$$R_l(r) = A_l\, r^l + B_l/r^{l+1}. \tag{3.216}$$

Comparing Eqs. (3.214) and (3.216) we find

$$c_l \cos\eta_l \underset{k\to 0}{\simeq} A_l(2l+1)!!k^{-l}; \quad c_l \sin\eta_l \underset{k\to 0}{\simeq} B_l \frac{2l+1}{(2l+1)!!}k^{l+1}. \tag{3.217}$$

Writing $a_l^{2l+1} = -B_l/A_l$ we find

$$\tan\eta_l \underset{k\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}\,(ka_l)^{2l+1}. \tag{3.218}$$

Remember that this expression is *only valid for short-range interactions.* The constant a_l is referred to as the l-wave *scattering length.* For the s-wave scattering length it is convention to suppress the subscript to avoid confusion with the Bohr radius a_0.

With Eq. (3.218) we have regained the form of Eq. (3.47). This is not surprising because a hard-sphere potential is of course a short-range potential. By comparing Eqs. (3.218) and (3.47) we see that for hard spheres all scattering lengths are equal to the diameter of the sphere, $a_l = a$. Eq. (3.218) also applies to other short-range potentials like the spherical well and for potentials exponentially decaying with increasing interatomic distance.

In particular, for the s-wave phase shift ($l = 0$) we find with Eq. (3.218)

$$\tan\eta_0 \underset{k\to 0}{\simeq} -ka \;\Leftrightarrow\; k\cot\eta_0 \underset{k\to 0}{\simeq} -\frac{1}{a}, \tag{3.219}$$

and since $\tan\eta_0 \to \eta_0$ for $k \to 0$ this result coincides with the hard-sphere result (3.54), $\eta_0 = -ka$. The p-wave phase shift ($l = 1$) vanishes in the limit $k \to 0$ in accordance with

$$\tan\eta_1 \underset{k\to 0}{\simeq} -\frac{1}{3}\left(ka_1\right)^3 \Leftrightarrow k\cot\eta_1 \underset{k\to 0}{\simeq} -\frac{3}{a_1^3k^2}. \tag{3.220}$$

For any finite value of k the radial wavefunction (3.213) has the asymptotic form

$$R_0(k,r) \underset{k\to 0}{\simeq} \frac{c_0}{kr}\sin(kr+\eta_0) = \frac{c_0}{kr}\sin\left[k(r-a)\right]. \tag{3.221}$$

As follows from Eq. (3.216), for the range of distances $r_0 \ll r \ll 1/k$ the radial wavefunction behaves asymptotically like

$$R_0(r) \underset{k\to 0}{\sim} 1-\frac{a}{r} \qquad \text{for } r_0 \ll r \ll 1/k. \tag{3.222}$$

This is an important result. Exactly as in the case of the spherical well the wavefunction of an general short-range potential is found to be constant throughout space (in the limit $k \to 0$) except for a small region of radius a around the potential center. For a *positive* scattering length we regain the characteristic node in the s wave at $r = a$; for *negative* scattering length we regain the *virtual* node. This result also confirms that the smallness of the gas parameter, $na^3 \ll 1$, is the prime indicator for the weakly interacting gas.

3.6.2 Existence of the finite range

Thus far we assumed that for distances $r \gg r_0$ the interaction potential could be neglected. In the present section we ask ourselves when this is justified. For this purpose we write the radial wave equation (3.7) in the form

$$R_l'' + \frac{2}{r}R_l' + \left[k^2 - \frac{l(l+1)}{r^2}\right]R_l = U(r)R_l. \tag{3.223}$$

Considering the zero energy limit ($k \to 0$) this relation reduces to

$$R_l'' + \frac{2}{r}R_l' - \frac{l(l+1)}{r^2}R_l = U(r)R_l. \tag{3.224}$$

This equation is valid for $r \ll 1/k \to \infty$. If the potential may be neglected the solution is given by Eq. (3.216). This shows that the condition

$$U(r)\left\{c_{1l}r^l + c_{2l}(\frac{1}{r})^{l+1}\right\} \sim c_{1l}r^{l-s} \to 0 \tag{3.225}$$

should hold for $r \to \infty$ provided $l < s$. However, the solution to Eq. (3.216) shows that the contribution

$$c_{2l} \frac{l(l+1)}{r^2} (\frac{1}{r})^{l+1}$$

has to remain significant, also in the presence of a short-range potential. This gives rise to the condition

$$c_{1l} r^{l-s} \ll c_{2l} (\frac{1}{r})^{l+3} \quad \text{for}\, r \to \infty. \tag{3.226}$$

Note that this condition is satisfied if the potential decays sufficiently fast,

$$l < \frac{1}{2}(s-3).$$

This shows that the range only exists if the potential decays faster than $1/r^3$.

3.6.3 Effective-range

In the previous section we restricted ourselves to the $k \to 0$ limit by using Eq. (3.215) to put a boundary condition on the general solution (3.212) of the radial wave equation. We can do better and explore the region of small k with the aid of the Wronskian Theorem. We demonstrate this for the case of s waves by comparing the regular solutions of the 1D-Schrödinger equation with and without potential,

$$\chi_0'' + [k^2 - U(r)]\chi_0 = 0 \quad \text{and} \quad y_0'' + k^2 y_0 = 0. \tag{3.227}$$

Clearly, for $r \gg r_0$, where the potential may be neglected, the solutions of both equations may be chosen to coincide. Rather than using the normalization to unit asymptotic amplitude ($c_0 = 1$) we turn to the normalization $c_0 = 1/\sin\eta_0(k)$,

$$y_0(k,r) = \cot\eta_0(k)\sin(kr) + \cos(kr) \underset{r \gg r_0}{\simeq} \chi_0(k,r), \tag{3.228}$$

which is well-defined except for the special case of a vanishing scattering length ($a = 0$). For $r \ll 1/k$ we have $y_0(k,r) \simeq 1 + kr\cot\eta_0$, which implies for the origin $y_0(k,0) = 1$ and $y_0'(k,0) = k\cot\eta_0(k)$. This allows us to express the phase shift in terms of a Wronskian of $y_0(k,r)$ at $k_1 = k$ and $k_2 \to 0$. For this we first write the Wronskian of $y_0(k_1,r)$ and $y_0(k_2,r)$,

$$W[y_0(k_1,r), y_0(k_2,r)]\,|_{r=0} = k_2\cot\eta_0(k_2) - k_1\cot\eta_0(k_1). \tag{3.229}$$

Then we specialize to the case $k_1 = k$ and obtain by using Eq. (3.219) in the limit $k_2 \to 0$

$$W[y_0(k_1,r), y_0(k_2,r)]\,|_{r=0} = -1/a - k\cot\eta_0(k). \tag{3.230}$$

To employ this Wronskian we apply the Wronskian Theorem twice in the form (C.147) with $k_1 = k$ and $k_2 = 0$,

$$W[y_0(k,r), y_0(0,r)]\,|_0^b = k^2 \textstyle\int_0^b y_0(k,r) y_0(0,r) dr \tag{3.231}$$

$$W[\chi_0(k,r), \chi_0(0,r)]\,|_0^b = k^2 \textstyle\int_0^b \chi_0(k,r) \chi_0(0,r) dr. \tag{3.232}$$

Since $\chi_0(k,0) = 0$ we have $W[\chi_0(k_1,r), \chi_0(k_2,r)]\,|_{r=0} = 0$. Furthermore, we note that for $b \gg r_0$ we have $W[\chi_0(k_1,r), \chi_0(k_2,r)]\,|_{r=b} = W[y_0(k_1,r), y_0(k_2,r)]\,|_{r=b}$. Thus subtracting Eq. (3.232) from Eq. (3.231) we obtain the Bethe formula [7]

$$1/a + k\cot\eta_0(k) = k^2 \textstyle\int_0^b [y_0(k,r)y_0(0,r) - \chi_0(k,r)\chi_0(0,r)]\, dr \equiv \frac{1}{2} r_e(k) k^2. \tag{3.233}$$

In view of Eq. (3.228) only the region $r \lesssim r_0$ (where the potential may not be neglected) contributes to the integral and we may extend $b \to \infty$. The quantity $r_e(k)$ is the *effective range* of the interaction. Replacing $r_e(k)$ by its $k \to 0$ limit,

$$r_e = 2\textstyle\int_0^\infty \left[y_0^2(0,r) - \chi_0^2(0,r)\right] dr, \tag{3.234}$$

where $y_0(0,r) = 1 - r/a$, the phase shift may be expressed as

$$k \cot \eta_0(k) \underset{k\to 0}{=} -\frac{1}{a} + \tfrac{1}{2} r_e k^2 + \cdots . \tag{3.235}$$

Comparing the first two terms in Eq. (3.235) we find that the $k \to 0$ limit is reached for

$$k^2 \left|a\right| r_e \ll 1. \tag{3.236}$$

As we derived an expression for the effective range of an arbitrary short range potential, we should be able to reproduce the results obtained for the rectangular potentials. For the hard sphere we have $\chi_0(0,r) = 1 - r/a$ for $r > a$. Substituting this into Eq. (3.234) we calculate

$$r_e = 2\textstyle\int_0^a (1 - r/a)^2 dr = \tfrac{2}{3} a, \tag{3.237}$$

which indeed coincides with the value obtained from expansion (3.58). Similarly we can reproduce the expression for the effective range of a spherical well (see Problem 3.8). In analogy with Eq. (3.120) we can also derive for the general case a power-law expansion of the effective hard-sphere diameter (see Problem 3.9)

$$a(k) = a[1 - \tfrac{1}{3} k^2 a^2 (1 - \tfrac{3}{2} r_e/a)]. \tag{3.238}$$

Note that substituting Eq. (3.124) for r_e of the spherical well we reproduce Eq. (3.120). Eq. (3.238) is valid for all values of a provided both $k\left|a\right| \ll 1$ and $k\left|r_e\right| \ll 1$.

With the above derivation we regained for an arbitrary short-range potential the main conclusions obtained in Section 3.4.9 for a spherical well: for ordinary quantum gases (large well parameters and scattering length not anomalously small or resonantly enhanced) we may approximate $|a| \simeq r_0$ and find that the k^2 term becomes important only for $kr_0 \gtrsim 1$. Since $kr_0 \ll 1$ in all quantum gases, this means that the effective hard sphere diameter has reached its limiting value $a(k) \simeq a$. The leading curvature of the function $a(k)$ becomes zero for $r_e = \frac{2}{3}a$ and changes sign when further increasing the well depth. In this case of resonant enhancement near threshold the k^2 term in Eq. (3.120) may only be neglected for the lowest values of k; i.e., for $k\left|a\right| \ll 1 \Leftrightarrow kr_0 \ll r_0/\left|a\right|$.

A famous example of an anomalously small scattering length is given by two hydrogen atoms in the electronic ground state interacting via the triplet interaction. In this case we have $a = 1.22\, a_0$ and $r_e = 348\, a_0$, where a_0 is the *Bohr radius [34]*. This case is anomalous for several reasons. The scattering length a is positive but the potential does not support even a single bound state. The effective range is large as expected for an anomalously small a but the sign of r_e is positive. The range r_0 is not determined by the Van der Waals interaction but by the exchange. These anomalies show that for shallow potentials the intuitive picture offered by the spherical well breaks down and one should integrate the Bethe formula (3.233) to obtain r_e. This requires the knowledge of the distorted waves $\chi_0(k,r)$, which are obtained by numerical integration of the 1D Schrödinger equation for the best available potential and also provide the value of a.

Problem 3.8. Show that the effective range of a spherical well of depth $-\kappa_0^2$ and radius r_0 is given by

$$r_e = 2r_0 \left[1 - \frac{r_0}{a} + \frac{1}{3}\left(\frac{r_0}{a}\right)^2 + \frac{1}{2}\left(\frac{\cot \kappa_0 r_0}{\kappa_0 r_0} - \frac{1}{\sin^2 \kappa_0 r_0}\right)\left(1 - \frac{r_0}{a}\right)^2\right].$$

Note that this equation can be rewritten in the form (3.114).

Solution. Substituting $y_0(0,r) = (1 - r/a)$ and $\chi_0(0,r) = (1 - r_0/a)\sin\kappa_0 r/\sin\kappa_0 r_0$ into Eq. (3.234) the effective range is given by

$$r_e = 2\int_0^{r_0}\left[(1 - r/a)^2 - \frac{\sin^2\kappa_0 r}{\sin^2\kappa_0 r_0}(1 - r_0/a)^2\right]dr.$$

Evaluating the integral results the desired expression. □

Problem 3.9. Show that the following expansion is valid

$$a(k) = a[1 - \tfrac{1}{3}k^2a^2(1 - \tfrac{3}{2}r_e/a)].$$

Note that for the r_e of a spherical well this equation results in Eq. (3.120).

Solution. Using the expansion (3.118) we have

$$\frac{1}{k}\tan ka(k) = -\frac{1}{k\cot\eta_0(k)} = \frac{a}{1 - \frac{1}{2}k^2ar_e + \cdots} = a + \tfrac{1}{2}k^2a^2r_e + \cdots .$$

Thus, $a(k)$ follows from the arctangent,

$$ka(k) = \arctan[a + \tfrac{1}{2}k^2a^2r_e + \cdots],$$

which leads to the desired expression by expansion to third order in k. □

3.6.4 Weakly bound s level

The analysis of the previous section can be extended to obtain the relation between the effective range and the binding energy of a weakly bound s level, $E_b = -\hbar^2\kappa^2/2m_r$, with $\kappa r_0 \ll 1$. In particular the relation between scattering length and κ can be determined. In this case four 1D Schrödinger equations are relevant to calculate the phase shift:

$$\begin{aligned} &\chi_0'' + [k^2 - U(r)]\chi_0 = 0 \qquad && y_0'' + k^2 y_0 = 0 \\ &B_0'' - [\kappa^2 + U(r)]B_0 = 0 \qquad && B_a'' - \kappa^2 B_a = 0. \end{aligned} \tag{3.239}$$

The first two equations are the same as the ones in the previous section and yield the continuum solutions (3.228). The second couple of equations deal with the bound state, with $B_a(r) = e^{-\kappa r}$. Like the continuum solutions they can be made to overlap asymptotically, $B_a(r) \underset{r\gg r_0}{\simeq} B_0(r)$. Hence, we have

$$\begin{aligned} B_a(0) &= 1 \qquad & B_a'(0) &= -\kappa \\ y_0(k,0) &= 1 \qquad & y_0'(k,0) &= k\cot\eta_0(k). \end{aligned} \tag{3.240}$$

As in the previous section we apply the Wronskian Theorem in the form (C.147) to the cases with and without potential.

$$W[B_0(r),\chi_0(k,r)]\,|_0^b = -\left(\kappa^2 + k^2\right)\textstyle\int_0^b B_0(r)\chi_0(k,r)dr \tag{3.241a}$$

$$W[B_a(r),y_0(k,r)]\,|_0^b = -\left(\kappa^2 + k^2\right)\textstyle\int_0^b B_a(r)y_0(k,r)dr. \tag{3.241b}$$

Subtracting these equations, noting that $\chi_0(0) = B_0(0) = 0$ and hence $W[B_0(r),\chi_0(k,r)]\,|_{r=0} = 0$, and further that $W[B_0(r),\chi_0(k,r)]\,|_{r=b} = W[B_a(r),y_0(k,r)]\,|_{r=b}$ for $b \gg r_0$ we obtain

$$W[B_a(r),y_0(k,r)]\,|_{r=0} = \left(\kappa^2 + k^2\right)\textstyle\int_0^b[B_a(r)y_0(k,r) - B_0(r)\chi_0(k,r)]\,dr. \tag{3.242}$$

Using $W\left[B_a(r), y_0(k,r)\right]|_{r=0} = k\cot\eta_0(k) + \kappa$ we obtain for $\kappa r_0 \ll 1$ in the limit $k \to 0$

$$k\cot\eta_0(k) \underset{\kappa r_0 \ll 1}{\simeq} -\kappa + \tfrac{1}{2}\left(\kappa^2 + k^2\right) r_e' + \cdots, \tag{3.243}$$

where

$$r_e' = 2\textstyle\int_0^b \left[B_a(r)y_0(0,r) - B_0(r)\chi_0(0,r)\right] dr \tag{3.244}$$

is the effective range for this case. Note that this integral differs from the one obtained for r_e by analysis of the continuum and is only valid for $\kappa r_0 \ll 1$ but r_e' should coincide with r_e in the limit $\kappa \to 0$. Comparing Eq. (3.243) with Eq. (3.235) we find that the scattering length can be written as

$$-\frac{1}{a} \underset{\kappa r_0 \ll 1}{\simeq} -\kappa + \tfrac{1}{2}\kappa^2 r_e. \tag{3.245}$$

Note that in the limit $\kappa \to 0$ the scattering length has the *positive* value $a \simeq 1/\kappa$ and the binding energy can be expressed in terms of the scattering length and the effective range as

$$E_b = -\frac{\hbar^2\kappa^2}{2m_r} \underset{\kappa r_0 \ll 1}{\simeq} -\frac{\hbar^2}{2m_r}\frac{1}{(a-\frac{1}{2}r_e)^2} \underset{\kappa \to 0}{\simeq} -\frac{\hbar^2}{2m_r a^2}. \tag{3.246}$$

For the case of a square well potential we have $r_e \simeq r_0$ for $a \to \infty$ and the above result coincides with the expression obtained for halo states in Section 3.4.4.

3.7 Power-law potentials

The general results obtained in the previous sections presumed the existence of a finite range of interaction, r_0. Thus far this presumption was based only on the heuristic argument presented in Section 3.6. To derive a proper criterion for the existence of a finite range and to determine its value r_0 we have to analyze the asymptotic behavior of the interatomic interaction [52]. For this purpose we consider potentials of the power-law type,

$$\mathcal{V}(r) = -\frac{C_s}{r^s}, \tag{3.247}$$

where $C_s = \mathcal{V}_0 r_c^s$ is the power-law coefficient, with $\mathcal{V}_0 \equiv |\mathcal{V}(r_c)| \equiv \hbar^2\kappa_c^2/2m_r$ the well depth. These power-law potentials are important from the general physics point of view because they capture major features of interparticle interactions.

For power-law potentials, the radial wave equation (3.7) takes the form

$$R_l'' + \frac{2}{r}R_l' + \left[k^2 + \frac{\kappa_c^2 r_c^s}{r^s} - \frac{l(l+1)}{r^2}\right] R_l = 0. \tag{3.248}$$

Because this equation can be solved analytically in the limit $k \to 0$ it is ideally suited to analyze the conditions under which the potential $\mathcal{V}(r)$ may be neglected and thus to determine r_0.

To solve Eq. (3.248) we look for a clever substitution of the variable r and the function $R_l(r)$ to optimally exploit the known r dependence of the potential in order to bring the differential equation in a well-known form. To leave flexibility in the transformation we search for functions of the type

$$G_l(x) = r^{-\nu} R_l(r), \tag{3.249}$$

where the power ν is to be selected in a later stage. Turning to the variable $x = \beta r^{(2-s)/2}$ with $\beta = \kappa_c r_c^{s/2}[2/(s-2)]$ (excluding the case $s = 2$) the radial wave equation (3.248) can be written as (cf. Problem 3.10)

$$G_l'' + \frac{2\,(2 - s/2 + 2\nu)}{(2-s)\,x} G_l' + \left[1 - \frac{l(l+1) - \nu\,(\nu+1) - k^2 r^2}{(2-s)^2}\frac{4}{x^2}\right] G_l = 0. \tag{3.250}$$

Choosing $\nu = -\frac{1}{2}$ we obtain for $kr \ll \frac{1}{2} \Leftrightarrow x \gg x_k = (2kr_c)^{s/2-1}\,\kappa_c r_c\, 2/(s-2)$ the Bessel differential equation (C.113),

$$G_n'' + \frac{1}{x}G_n' + \left(1 - \frac{n^2}{x^2}\right) G_n = 0, \tag{3.251}$$

where $n = (2l+1)/(s-2)$. In the limit $k \to 0$ the validity of this equation extends over all space and its general solution is given by Eq. (C.114a). Substituting the general solution into Eq. (3.249) with $\nu = -\frac{1}{2}$, the general solution for the radial wave equation of a power-law potential in the $k \to 0$ limit is given by

$$R_l(r) = r^{-1/2}\left[AJ_n(x) + BJ_{-n}(x)\right], \tag{3.252}$$

where the coefficients A and B are to be fixed by a boundary condition and the normalization.

Problem 3.10. Show that the radial wave equation (3.248) can be written in the form

$$G_l'' + \frac{2\,(2 - s/2 + 2\nu)}{(2-s)\,x}G_l' + \left[\frac{k^2}{\kappa_c^2}\frac{r^s}{r_c^s} + 1 - \frac{[l(l+1) - \nu\,(\nu+1)]}{(2-s)^2}\frac{4}{x^2}\right] G_l = 0,$$

where $x = \kappa_c r (r_c/r)^{s/2}[2/(s-2)]$ and $G_l(x) = r^{-\nu}R_l(r)$.

Solution. We first turn to the new variable $x = \beta r^\gamma$ by expressing R_l'', R_l' and R_l in terms of the function G_l and its derivatives

$$\begin{aligned}
R_l &= r^\nu G_l(x)\\
R_l' &= r^\nu G_l' x' + \nu r^{\nu-1}G_l = \gamma\beta r^{\gamma-1+\nu}G_l' + \nu r^{\nu-1}G_l\\
R_l'' &= \gamma^2\beta^2 r^{2\gamma-2+\nu}G_l'' + \gamma\,(\gamma - 1 + 2\nu)\,\beta r^{\gamma+\nu-2}G_l' + \nu\,(\nu-1)\,r^{\nu-2}G_l,
\end{aligned}$$

where $x' = dx/dr = \gamma\beta r^{\gamma-1}$. Combining the expressions for R_l'' and R_l' to represent part of the radial wave equation (3.248) we obtain

$$\begin{aligned}
R_l'' + \frac{2}{r}R_l' &= \gamma^2\beta^2 r^{2\gamma-2+\nu}G_l'' + \gamma\,(1+\gamma+2\nu)\,\beta r^{\gamma+\nu-2}G_l' + \nu\,(\nu+1)\,r^{\nu-2}G_l\\
&= \gamma^2\beta^2 r^{2\gamma-2+\nu}\left[G_l'' + \frac{(1+\gamma+2\nu)}{\gamma\beta r^\gamma}G_l' + \frac{\nu\,(\nu+1)}{\gamma^2\beta^2 r^{2\gamma}}G_l\right].
\end{aligned}$$

Now we use the freedom to choose β by setting $\gamma^2\beta^2 = \kappa_c^2 r_c^s$. Replacing twice βr^γ by x the radial wave equation (3.248) can be expressed in terms of $G(x)$ and its derivatives,

$$G_l'' + \frac{(1+\gamma+2\nu)}{\gamma x}G_l' + \frac{\nu\,(\nu+1)}{\gamma^2 x^2}G_l + \left[\frac{k^2}{\kappa_c^2} + \left(1 - \frac{l(l+1)(\beta^2/x^2)^{(1-s/2)/\gamma}}{\kappa_c^2 r_c^s}\right)\frac{r_c^s}{r^s}\right]\frac{r^s}{r_c^s}G_l = 0.$$

We collect the terms proportional to $G(x)$, with $x = [\kappa_c r_c^{s/2}/\gamma]r^\gamma$, and substitute the expression for β^2. Then we obtain the desired form by choosing $\gamma = (2-s)/2$ (which excludes the case $s = 2$), for which $x = \kappa_c r (r_c/r)^{s/2}[2/(s-2)]$. □

3.7.1 Existence of a finite range r_0

To establish whether the potential may be neglected at large distances we have to analyze the asymptotic behavior of the radial wavefunction $R_l(r)$ for $r \to \infty$. If the potential is to be neglected the radial wavefunction should be of the form

$$R_l(r) = A_l\, r^l + B_l/r^{l+1} \tag{3.253}$$

as was discussed in Section 3.6. The asymptotic behavior of $R_l(r)$ follows from the general solution (3.252) by using the expansion in powers of $(x/2)^2$ given by Eq. (C.115),

$$R_l(r) \sim r^{-1/2}\left[A_l\, x^n(1-\frac{x^2}{4(1+n)}+\cdots)+B_l\, x^{-n}(1-\frac{x^2}{4(1-n)}+\cdots)\right], \tag{3.254}$$

where $n=(2l+1)/(s-2)$. Substituting the definition $x=\beta r^{(2-s)/2}=\beta r^{(2l+1)/2n}$ with $\beta=\kappa_c r_c^{s/2}[2/(s-2)]$ we find for $r\to\infty$

$$R_l(r) \sim A_l\, r^l(1-a_1r^{2-s}+\cdots)+B_l\, r^{-l-1}(1-b_1r^{2-s}+\cdots), \tag{3.255}$$

where the coefficients a_p and b_p (with $p=1,2,3,\cdots$) are fully defined in terms of the potential parameters and l but not specified here. As before, the coefficients A_l and B_l depend on boundary condition and normalization. From Eq. (3.255) we notice immediately that in both expansions on the r.h.s. the leading terms are independent of the power s. Hence, for the r dependence of these terms the potential plays no role. If further also the second and higher terms of the left expansion may be neglected (for $r\to\infty$) compared to the first term of the right expansion the two leading terms of the asymptotic r dependence of $R_l(r)$ are independent of s and are of the form (3.253). This is the case for $l+2-s<-l-1$. Thus we have obtained that the potential may be neglected for

$$l<\tfrac{1}{2}(s-3)\Leftrightarrow 0\le n<1. \tag{3.256}$$

This shows that existence of a finite range depends on the angular momentum quantum number l; for s waves the potential has to fall off faster than $1/r^3$; for $1/r^6$ potentials the range does not exist for $l\ge 2$.

To obtain an expression for r_0 in the case of s waves we presume $n\ll 1$, which is valid for large values of s and even for $s=4$ not a bad approximation ($n=\frac{1}{2}$). With this presumption the inequality (3.256) may be rewritten in a form enabling the definition of the range r_0,

$$r^{2-s}\ll r_c^{2-s}(s-2)^2/(\kappa_c^2r_c^2)=r_0^{2-s}\Leftrightarrow r_0=r_c\left[\kappa_c r_c/(s-2)\right]^{2/(s-2)}. \tag{3.257}$$

In terms of the power-law coefficient this becomes

$$r_0=(s-2)^{2/(2-s)}\left[2m_rC_s/\hbar^2\right]^{1/(s-2)}. \tag{3.258}$$

In terms of the range r_0 the variable x is defined as

$$x=2\,(r_0/r)^{(s-2)/2}. \tag{3.259}$$

For $1/r^6$ potentials r_0 is called the *Van der Waals range*

$$r_{vdW}=\tfrac{1}{2}r_c[\kappa_c r_c]^{1/2}=\tfrac{1}{2}\left[2m_rC_s/\hbar^2\right]^{1/4}. \tag{3.260}$$

Note that this value agrees within a factor of 2 with the heuristic estimate (3.210).

3.7.2 Phase shifts for power-law potentials

To obtain an expression for the phase shift by a power-law potential of the type (3.247) we note that for $l<\frac{1}{2}(s-3)$ the range r_0 is well-defined and the short-range expressions must be valid,

$$\tan\eta_l \underset{kr\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}\,(ka_l)^{2l+1} \tag{3.261}$$

For $l\ge\frac{1}{2}(s-3)$ we have to adopt a different strategy to obtain an expression for the phase shifts. At distances where the potential may not be neglected but still is much smaller than the rotational barrier the radial wavefunction $R_l(k,r)$ will only be slightly perturbed by the presence of the potential; i.e., $R_l(k,r) \simeq j_l(kr)$. In this case the phase shift can be calculated perturbatively in the limit $k \to 0$ by replacing $\chi_l(k,r)$ with $krj_l(kr)$ in the integral expression (3.37) for the phase shift. This is known as the Born approximation. Its validity is restricted to cases where the vicinity of an l-wave shape resonance can be excluded. Thus we obtain for the phase shift by a power-law potential of the type (3.247)

$$\sin\eta_l \simeq \frac{\pi}{2}\int_0^\infty \frac{\kappa_c^2 r_c^s}{r^s}\left[J_{l+1/2}(kr)\right]^2 r dr. \tag{3.262}$$

Here we turned to Bessel functions of half-integer order using Eq. (C.111). To evaluate the integral we use Eq. (C.131) with $\lambda = s-1$ and $\mu = l+1/2$

$$\int_0^\infty \frac{1}{r^{s-1}}\left[J_{l+1/2}(kr)\right]^2 dr = \frac{k^{s-2}\Gamma(5)\,\Gamma\left(\frac{2l+3-s}{2}\right)}{2^{s-1}\left[\Gamma(3)\right]^2\Gamma\left(\frac{2l+7}{2}\right)} = 6k^{s-2}\frac{(2l+3-s)!!}{(2l+5)!!}.$$

This expression is valid for $1 < s < 2l+3$. Thus the same k dependence is obtained for all angular momentum values $l > \frac{1}{2}(s-3)$,

$$\sin\eta_l \underset{k\to 0}{\simeq} \kappa_c^2 r_c^2 \frac{3\pi(2l+3-s)!!}{(2l+5)!!}(kr_c)^{s-2}. \tag{3.263}$$

Note that the same k dependence is obtained as long as the wavefunctions only depend on the product kr. However, in general $R_l(k,r) \neq R_l(kr)$, with the cases $\mathcal{V}(r) = 0$ and $s = 2$ as notable exceptions.

3.7.3 Van der Waals potentials

A particularly important interatomic interaction in the context of the quantum gases is the Van der Waals interaction introduced in Section 1.4.3.1. It may be modeled by a potential consisting of a hard core and a $-1/r^6$ long-range tail (see Fig. 1.4),

$$\mathcal{V}(r) = \begin{cases} \infty & \text{for } r \le r_c \\ -C_6/r^6 & \text{for } r > r_c. \end{cases} \tag{3.264}$$

where $C_6 = \mathcal{V}_0 r_c^6$ is the Van der Waals coefficient, with $\mathcal{V}_0 = \hbar^2\kappa_c^2/2m_r$ the well depth. For this model potential the radial wavefunctions $R_l(r)$ are given by the general solution (3.252) for power-law potentials in the $k \to 0$ limit for the case $s = 6$. Choosing $l = 0$ we find for radial s waves,

$$R_0(r) = r^{-1/2}\left[AJ_{1/4}(x) + BJ_{-1/4}(x)\right], \tag{3.265}$$

where we used $n = (2l+1)/(s-2) = \frac{1}{4}$ and $x = 2\left(r_0/r\right)^2$, with r_0 being the range of the Van der Waals potential as given in Eq. (3.260). In Table 3.1 some values for C_6 and r_0 are listed for hydrogen [66] and the alkali atoms [17].

Imposing the boundary condition $R_0(r_c) = 0$ with $r_c \ll r_0$ (i.e., $x_c = 2\left(r_0/r_c\right)^2 \gg 1$) we calculate for the ratio of coefficients

$$\frac{A}{B} = -\frac{J_{-1/4}(x_c)}{J_{1/4}(x_c)} \underset{x_c\to\infty}{\simeq} -\frac{\cos\left(x_c - 3\pi/8 + \pi/4\right)}{\cos\left(x_c - 3\pi/8\right)} = -2^{-1/2}\left[1 - \tan\left(x_c - 3\pi/8\right)\right]. \tag{3.266}$$

An expression for the scattering length is obtained by analyzing the long-range ($r \gg r_0$) behavior of the wavefunction with the aid of the short-range ($x \ll 1$) expansion (C.118) for the Bessel function.

Table 3.1: Van der Waals C_6 coefficients and the corresponding ranges for alkali-alkali interactions. D^* is the maximum dissociation energy of the last bound state.

	C_6(Hartree a.u.)	$r_0(a_0)$	D^*(K)
^{1}H-^{1}H	6.49	5.2	249
^{6}Li-^{6}Li	1389	31	1.16
^{6}Li-^{23}Na	1467	36	0.565
^{6}Li-^{40}K	2322	41	0.391
^{6}Li-^{87}Rb	2545	43	0.335
^{23}Na-^{23}Na	1556	45	0.146
^{23}Na-^{40}K	2447	54	0.081
^{23}Na-^{87}Rb	2683	58	0.056
^{40}K-^{40}K	3897	65	0.040
^{40}K-^{87}Rb	4274	72	0.024
^{87}Rb-^{87}Rb	4691	83	0.011
^{133}Cs-^{133}Cs	6851	101	0.005

Choosing $B = r_0^{1/2}\Gamma(3/4)$ the zero-energy radial wavefunction is asymptotically normalized to unity and of the form (3.222),

$$R_0(r) \underset{x\ll 1}{\simeq} Br^{-1/2}\left[\frac{A}{B}\frac{(x/2)^{1/4}}{\Gamma(5/4)} + \frac{(x/2)^{-1/4}}{\Gamma(3/4)}\right] = 1 - \frac{a}{r}. \tag{3.267}$$

where

$$a = \bar{a}\,[1 - \tan(x_c - 3\pi/8)]\,, \tag{3.268}$$

with $\bar{a} = r_0 2^{-1/2}\Gamma(3/4)/\Gamma(5/4) \simeq 0.956\,r_0$ is identified as the scattering length. The parameter $\bar{a}$ has been referred to as the *"average" scattering length.*[1]

It is interesting to note the similarities between Eq. (3.268) and the result obtained for square well potentials given by Eq. (3.75). In both cases the typical size of the scattering length is given by the range r_0 of the interaction. Also the resonant structure is similar. The scattering length diverges for $x_c - 3\pi/8 = (p + 1/2)\pi$ with $p = 0, 1, 2, \cdots$. However, whereas the scattering length is almost always positive for deep square wells, for Van der Waals potentials this is the case over 3/4 of the free phase interval of π, with $-\pi/2 < x_c - 3\pi/8 - p\pi < \pi/4$. For arbitrary x_c this means that in 25% of the cases the scattering length will be negative.

3.7.4 Asymptotic bound states in Van der Waals potentials

The weakly bound states in a molecular potential are also known under the name *Asymptotic Bound States* (ABS). The least-bound of these states is a halo state if most of its probability density is found outside the potential well; i.e., if the classical turning point r_{cl} is located at distances where the potential may be neglected, $r_{cl} \gg r_0$. In the limit of zero binding energy the halo state can be regarded either as a *resonant bound states* or as a *zero-energy resonance.* In Fig. 3.21 we show the radial wavefunction $R_0(r)$ of such a resonant bound state for the case $x_c = (p + 7/8)\pi$ with $p = 15$ in a Van der Waals model potential of the type (3.264). As for such states the scattering length diverges the radial wavefunction (3.265) must be of the analytic form

$$R_0(r) \sim r^{-1/2} J_{1/4}(2r_0^2/r^2). \tag{3.269}$$

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[1] See G.F. Gribakin and V.V. Flambaum, Phys. Rev. A **48**, 546 (1993).

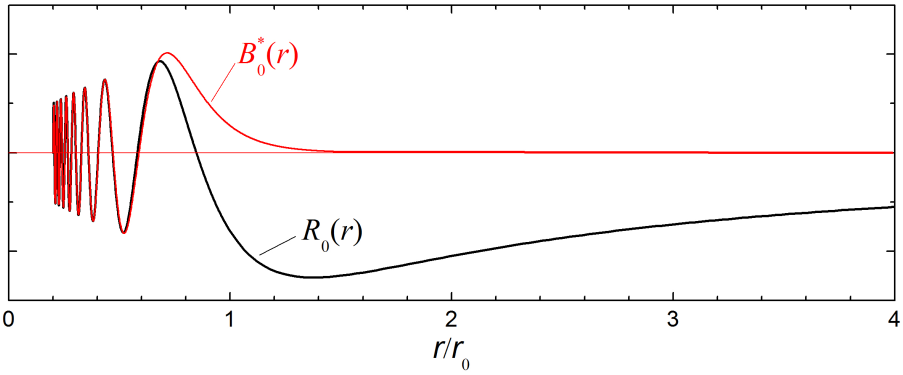

Figure 3.21: $R_0(r)$: radial wavefunction of a *resonant bound state* (diverging scattering length) in a Van der Waals potential; $B_0(r)$: corresponding first *regular* bound state (least-bound state for the same potential parameters). Its classical outer turning point lies close to the position of the last node of $R_0(r)$. Note the $1/r$ long-range behavior typical for resonant bound states.

The least-bound s level for the same values of r_c and C_0 can be obtained by numerical integration of the Schrödinger equation from r_c outward. The wavefunction of this state is denoted by $B_0^*(r)$ in Fig. 3.21, its binding energy E_b^* corresponds to the largest binding energy a least-bound state can have for this potential. The position of the outer classical turning point r_{cl}^* is found by equating the numerically determined E_b^* with the potential energy curve, $E_b^* = -C_6/r_{cl}^{*6}$. Using Eq. (3.258) this procedure yields $r_{cl}^* = 0.860\,r_0$. Thus the largest possible *dissociation energy* $D^* = -E_b^*$ of the least-bound $l = 0$ state is readily calculated if C_6 and m_r are known,

$$D^* \simeq 2.474\,C_6/r_0^6. \tag{3.270}$$

The D^* values are also included in Table 3.1. Comparing $D^*/k_B = 249$ K for hydrogen with the actual dissociation energy $D_{14,0}/k_B \approx 210$ K of the highest zero-angular-momentum bound state $|v = 14; J = 0\rangle$ (see Fig. 3.1) we notice that indeed $D_{14,0} \leq D^*$, in accordance with the definition of D^* as an upper limit. Since for halo states the condition $r_{cl}^* \gg r_0$ is satisfied these states necessarily have a dissociation energy $D \lll D^*$.

The expression for D^* was obtained starting from the boundary condition $R_0(r_c) = 0$. This forces all continuum and bound-state wavefunctions to have the same phase at $r = r_c$. Importantly, for distances $r_c \ll r \ll r_\phi \equiv |C_6/E|^{1/6}$, where $E = \hbar^2k^2/2m_r$, the phase development of both bound and continuum states is determined by the interaction potential. This can be seen in Fig. 3.21. Note that the result $r_{cl}^* = 0.860\,r_0$ coincides to within 1.5% with the value $r_{cl}^* = 0.848\,r_0$ obtained from the last node of $R_0(r)$; i.e., from the condition $J_{1/4}(x^*) = 0$, where $x^* \equiv 2r_0^2/r^{*2} \approx 2.778$ is the smallest (non-zero) node of the Bessel function $J_{1/4}(x)$. Similarly, the subsequent nodes of $J_{1/4}(x)$ correspond to the turning points of the next bound states in the Van der Waals potential and provide their binding energies. The expression (3.270) for D^* is valid for all potentials with a long-range Van der Waals tail as long as the phase of the wavefunction accumulated in the motion from the inner turning point to a point $r = r_\phi$ is to good approximation independent of E.

The concept of the *accumulated phase* is at the basis of semi-empirical precision descriptions of collisional phenomena in ultracold gases [51]. In a semi-classical approximation the turning points a and b of the v-th bound state (energy $E_v = -D$, with $v = 0, 1, \cdots$) are defined by the phase condition

$$\phi = (v + \tfrac{1}{2})\pi = \int_a^b K_v dr, \tag{3.271}$$

where $K_v \equiv [2m_r[E_v - \mathcal{V}(r)]/\hbar^2]^{1/2}$, with $\mathcal{V}(r)$ being the best available scattering potential for a given pair of atoms. For the spherical well $K_v = [\kappa_0^2 - \kappa_v^2]^{1/2}$, $a = 0$ and $b = r_0$; for the Van der

Waals model potential $\kappa_v^2 = 2m_rC_6/\hbar^2 r_v^6$, $a = r_c$ and $b = r_v$ and we find [43]

$$K_v = [2m_rC_6/\hbar^2 r^6 - \kappa_v^2]^{1/2} = \kappa_v [r_v^6/r^6 - 1]^{1/2}.$$

Turning to the new variable $y = r_v/r$ the integral becomes

$$(v + \tfrac{1}{2})\pi = \kappa_v r_v \textstyle\int_1^{r_v/r_c} [1 - 1/y^6]^{1/2} y dy.$$

In cases where the scattering length is known we can derive an expression for the effective range of Van der Waals potentials in the $k \to 0$ limit using the integral expression (3.234),

$$r_e = 2\textstyle\int_0^\infty \left[y_0^2(r) - \chi_0^2(r) \right] dr, \tag{3.272}$$

where $y_0(r) = 1 - r/a$. The wavefunction $\chi_0(r)$ corresponds to Eq. (3.265), normalized to the asymptotic form $\chi_0(r) \simeq 1 - r/a$. Using Eqs. (3.268) and (3.266) and turning to the dimensionless variable $\rho = r/r_0$ the function $\chi_0(r)$ takes the form

$$\chi_0(\rho) = \rho^{1/2} \left[\Gamma(5/4)\, J_{1/4}(2/\rho^2) - (r_0/a)\, \Gamma(3/4)\, J_{-1/4}(2/\rho^2) \right]. \tag{3.273}$$

Substituting this expression into Eq. (3.272) we obtain for the effective range[1]

$$\begin{aligned} r_e/2r_0 &= I_0 - 2\,(r_0/a)\, I_1 + I_2\,(r_0/a)^2 &\quad (3.274)\\ &= \frac{16}{3\pi} \left[[\Gamma(5/4)]^2 - \frac{\pi}{2}(r_0/a) + [\Gamma(3/4)]^2 (r_0/a)^2 \right]. &\quad (3.275) \end{aligned}$$

Substituting numerical values the expression (3.235) for the s-wave phase shift becomes

$$k \cot \eta_0 = -\frac{1}{a} + \frac{1}{2} r_0 k^2 \times 2.789 \left[1 - 1.912\,(r_0/a) + 1.828\,(r_0/a)^2 \right]. \tag{3.276}$$

Note that in the presence of a weakly bound state ($a \to \infty$) the effective range converges to the value $r_e = 2.789\, r_0$, which is somewhat larger than in the case of the spherical well.

3.8 Pseudo potentials

As in the low-energy limit ($k \to 0$) the scattering properties only depend on the asymptotic phase shift it is a good idea to search for the simplest mathematical form that generates this asymptotic behavior. The situation is similar to the case of *electrostatics*, where a spherically symmetric charge distribution generates the same far field as a properly chosen *point charge* in its center. Not surprisingly, the suitable mathematical form is a *point interaction.* It is known as the *pseudo potential* and serves as an important theoretical *Ansatz* at the two-body level for the description of interacting many-body systems [32]. The existence of such pseudo potentials is not surprising in view of the zero-range square well solutions discussed in Section 3.4.11.

As the pseudo potential cannot be obtained at the level of the radial wave equation we return to the full 3D Schrödinger equation for a pair of free atoms

$$\left(\Delta + k^2 \right) \psi_k(\mathbf{r}) = 0, \tag{3.277}$$

---

[1] Here we use the following definite integrals:

$$I_2 = \textstyle\int_0^\infty \varrho^2 \left[1 - \left[\Gamma(3/4)\, J_{-1/4}(x) \right]^2 / \varrho \right] d\varrho = [\Gamma(3/4)]^2\, 16/3\pi$$

$$I_1 = \textstyle\int_0^\infty \varrho \left[1 - \Gamma(3/4)\, J_{-1/4}(x) \Gamma(5/4)\, J_{1/4}(x) \right] d\varrho = 4/3$$

$$I_0 = \textstyle\int_0^\infty \left[1 - \varrho \left[\Gamma(5/4)\, J_{1/4}(x) \right]^2 \right] d\varrho = [\Gamma(5/4)]^2\, 16/3\pi.$$

where $k = [2m_r E]^{1/2}/\hbar$ is the wave number for the relative motion (cf. Section 3.2.1). The general solution of this homogeneous equation can be expressed in terms of the complete set of eigenfunctions $R_l(k,r)Y_l^m(\hat{\mathbf{r}})$,

$$\psi_k(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm} R_l(k,r) Y_l^m(\hat{\mathbf{r}}). \tag{3.278}$$

In this section we restrict ourselves to the s-wave limit (i.e., choosing $c_{lm} = 0$ for $l \geq 1$) where $\eta_0 = -ka$. We are looking for a pseudo potential that will yield a solution of the type (3.221) *throughout* space,

$$\psi_k(\mathbf{r}) = \frac{c_0}{kr} \sin(kr + \eta_0), \tag{3.279}$$

where the contribution of the spherical harmonic $Y_0^0(\hat{\mathbf{r}})$ is absorbed into the proportionality constant. The difficulty of this expression is that it is irregular in the origin. We claim that the operator

$$-\frac{4\pi}{k \cot \eta_0} \delta(\mathbf{r}) \frac{\partial}{\partial r} r \tag{3.280}$$

is the s-wave pseudo potential $U(\mathbf{r})$ that has the desired properties; i.e.,

$$\left(\Delta + k^2 + \frac{4\pi}{k \cot \eta_0} \delta(\mathbf{r}) \frac{\partial}{\partial r} r \right) \psi_k(\mathbf{r}) = 0. \tag{3.281}$$

The presence of the delta function makes the pseudo potential act as a boundary condition at $r = 0$,

$$\frac{4\pi\delta(\mathbf{r})}{k \cot \eta_0} \left[\frac{\partial}{\partial r} r \psi_k(\mathbf{r}) \right]_{r=0} = 4\pi\delta(\mathbf{r}) \frac{c_0}{k} \sin \eta_0 = -4\pi\delta(\mathbf{r}) \frac{c_0}{k} \sin(ka) \underset{k \to 0}{\simeq} -4\pi a c_0 \delta(\mathbf{r}), \tag{3.282}$$

where we used the expression for the s-wave phase shift, $\eta_0 = -ka$. This is the alternative boundary condition we were looking for. Substituting this into Eq. (3.281) we obtain the inhomogeneous equation

$$\left(\Delta + k^2 \right) \psi_k(\mathbf{r}) \underset{k \to 0}{\simeq} 4\pi a c_0 \delta(\mathbf{r}). \tag{3.283}$$

This inhomogeneous equation has the solution (3.279) as demonstrated in Problem 3.11.

For functions $f(\mathbf{r})$ with regular behavior in the origin we have

$$\left[\frac{\partial}{\partial r} r f(\mathbf{r}) \right]_{r=0} = f(\mathbf{r}) + \left[r \frac{\partial}{\partial r} f(\mathbf{r}) \right]_{r=0} = f(\mathbf{r}) \tag{3.284}$$

and the pseudo potential takes the form of a *delta function potential*[1]

$$U(\mathbf{r}) = -\frac{4\pi}{k \cot \eta_0} \delta(\mathbf{r}) \underset{k \to 0}{\simeq} 4\pi a\, \delta(\mathbf{r}) \tag{3.285}$$

or, equivalently, restoring the dimensions

$$\mathcal{V}(\mathbf{r}) = g\, \delta(\mathbf{r}) \quad \text{with } g = \left(2\pi\hbar^2/m_r \right) a\,. \tag{3.286}$$

This expression, for $na^3 \ll 1$ valid in the zero energy limit, is convenient for calculating the interaction energy as will be shown in Section 3.9.7.

---

[1] Note that the dependence on the relative position vector $\mathbf{r}$ rather than its modulus r is purely formal as the delta function restricts the integration to only zero-length vectors. This notation is used to indicate that normalization involves a 3-dimensional integration, $\int \delta(\mathbf{r})\, d\mathbf{r} = 1$. Pseudo potentials do not carry physical significance but are mathematical constructions that can chosen such that they provide wavefunctions with the proper phase shift.

Problem 3.11. Verify the equation

$$\left(\Delta + k^2\right) \psi_k\left(\mathbf{r}\right) = 4\pi\delta(\mathbf{r})\frac{1}{k}\sin\eta_0 \tag{3.287}$$

by direct substitution of the solution (3.279) setting $c_0 = 1$.

Solution. Integrating Eq. (3.283) by over a small sphere V of radius ϵ about the origin we have

$$\int_V \left(\Delta + k^2\right)\frac{1}{kr}\sin(kr+\eta_0)d\mathbf{r} = -\frac{4\pi}{k}\sin\eta_0 \tag{3.288}$$

Here we used $\int_V \delta\left(\mathbf{r}\right)d\mathbf{r} = 1$ for an arbitrarily small sphere about the origin. The second term on the l.h.s. of Eq. (3.288) vanishes,

$$4\pi k \lim_{\epsilon\to 0}\int_0^{\epsilon} r\sin(kr+\eta_0)dr = 4\pi k\sin(\eta_0)\lim_{\epsilon\to 0}\epsilon = 0.$$

The first term follows with the divergence theorem (Gauss theorem)

$$\begin{aligned}\lim_{\epsilon\to 0}\int_V \Delta\frac{1}{kr}\sin(kr+\eta_0)d\mathbf{r} &= \lim_{\epsilon\to 0}\oint_S d\mathbf{S}\cdot\boldsymbol{\nabla}\frac{1}{kr}\sin(kr+\eta_0)\\ &= \lim_{\epsilon\to 0} 4\pi\epsilon^2\left(\frac{1}{\epsilon}\cos(k\varepsilon+\eta_0) - \frac{1}{k\epsilon^2}\sin(k\varepsilon+\eta_0)\right)\\ &= -\frac{4\pi}{k}\sin\eta_0.\end{aligned}$$

□

3.9 Impurity model for pair interactions

3.9.1 Introduction

How do interatomic interactions affect the energy of the individual atoms in a gas? To answer this question we start by considering an ultracold gas of N non-interacting atoms of mass m contained in a spherical volume of radius R. To include the interaction we add a probe particle to the system which interacts with all atoms of the gas. The interaction is modeled by a spherically symmetric potential of finite range r_0 as introduced in Section 3.5. For simplicity we fix the potential at the center of the sphere. Physically this corresponds to introducing an impurity atom of infinite mass into the gas; i.e., the reduced mass equals the mass of the gas atoms, $m_r = m$. The radius of the container, R, will be chosen larger than all relevant length scales in the system; in particular, $R \gg a$.

In view of the central symmetry we search for the eigenstates of the atoms in the spherical basis,

$$\psi_{nlm}(\mathbf{r}) = c_{nlm}Y_l^m(\hat{\mathbf{r}})R_{nl}(r), \tag{3.289}$$

where c_l is a normalization constant and depends on R. Most of these states are not affected by the interaction because for an ultracold gas ($kr_0 \ll 1$) only the s-wave channel gives rise to scattering. Therefore, we focus on the s waves; i.e., the $l = 0$ wavefunctions inside the sphere,

$$\psi_n(\mathbf{r}) = Y_0^0(\hat{\mathbf{r}})R_0(k_n, r), \tag{3.290}$$

where $Y_0^0(\hat{\mathbf{r}}) = (4\pi)^{-1/2}$ represents the $l = 0$ rotational state and $R_0(k_n, r)$ is the radial wavefunction for energy $\varepsilon_n = k_n^2$, with n being the quantum number for the radial motion. For $n = 1$ we obtain the motional ground state of the atoms in the spherical box.

3.9.2 Fermions - not interacting with impurity

In the absence of the interaction we denote the full wavefunction by $\varphi_n(\mathbf{r})$ and the radial wavefunction is of the form

$$R_0^{(0)}(k_n, r) = c_n \frac{\sin[k_n r]}{r}. \tag{3.291}$$

The normalization constant c_n follows from the boundary condition that the wavefunction vanish at the surface of the spherical container, $R_0^{(0)}(k_n, R) = 0$. For the wavefunction (3.291) this condition becomes

$$\frac{c_n}{R}\sin[k_n R] = 0 \;\Leftrightarrow\; k_n = n\frac{\pi}{R} \quad \text{with } n \in \{1, 2, \cdots\}. \tag{3.292}$$

In Fig. 3.22 this is illustrated for the motional ground state of the atoms. Integrating over the angles the normalization of $\varphi_n(\mathbf{r})$ follows from the radial integral,

$$1/c_n^2 = \int_0^R dr \sin^2[k_n r] = \frac{R}{2} \quad \Leftrightarrow \quad c_n = \sqrt{\frac{2}{R}}. \tag{3.293}$$

Thus the normalized radial wavefunction is

$$R_0^{(0)}(k_n, r) = \sqrt{\frac{2}{R}} \frac{\sin[k_n r]}{r}. \tag{3.294}$$

Let us now specialize to a fermionic quantum gas and suppose that the Fermi energy is given by

$$\varepsilon_F = k_F^2 = n_F^2 \frac{\pi^2}{R^2}. \tag{3.295}$$

How many particles in the spherical volume correspond to this Fermi energy for given value of R? For a homogeneous gas the Fermi energy is given by

$$\varepsilon_F = (6\pi^2 n_0)^{2/3} = [\tfrac{9}{2}\pi N/R^3]^{2/3} \tag{3.296}$$

For k_F and n_F this yields

$$k_F R \approx 2.4\, N^{1/3} \Leftrightarrow n_F \approx 0.77\, N^{1/3}. \tag{3.297}$$

Hence, for a million atoms only some 100 radial s levels are occupied.

3.9.3 Fermions interacting with impurity

Let us turn on the interactions. As we found in this chapter, the presence of interaction gives rise to an l-dependent phase shift $\eta_l(k)$. So the perturbed $l = 0$ radial wavefunction of the atom can be written in the form

$$R_0(k_n', r) \underset{r>r_0}{=} \frac{c_n'}{r} \sin[k_n' r + \eta_0(k_n')], \tag{3.298}$$

where $\eta_0(k_n') = -k_n' a(k_n')$ is the s-wave phase shift at radial wavenumber k_n'. For this wavefunction the boundary condition becomes

$$\frac{c_{n'}}{R}\sin\left[k_n'(R-a)\right] = 0 \;\Leftrightarrow\; k_n' = n\frac{\pi}{(R-a)} \quad \text{with } n \in \{1, 2, \cdots\}. \tag{3.299}$$

Expressing k_n' in terms of k_n we find to leading order in the phase shift

$$k_n' = k_n \frac{1}{(1 - a/R)} = k_n \left[1 + a(k_n')/R + \cdots\right]. \tag{3.300}$$

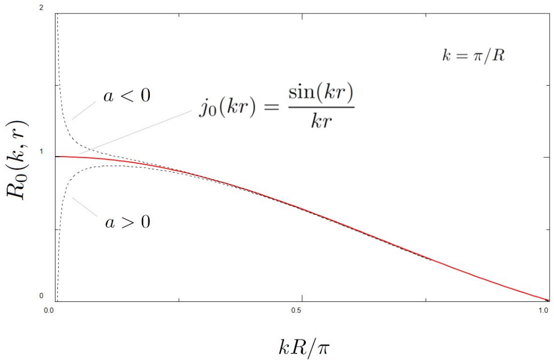

Figure 3.22: Ground state radial wavefunctions satisfying the boundary condition of zero amplitude at the surface of a spherical quantization volume of radius R. In this example $|a/R| = 0.1$. Note that for positive scattering length the wavefunction is suppressed for distances $r \lesssim a$ as expected for repulsive interactions. The oscillatory behavior of the wavefunction in the core region cannot be seen on this length scale (i.e., $r_0 \ll a$ in this example).

Substituting (3.300) into (3.298) we obtain, to leading order in the phase shift, for the radial wavefunction [2][1]

$$R_0(k_n, r) \underset{r>r_0}{=} \frac{c'_n}{r} \sin[k_n r + \eta_0(k_n)(1 - r/R)]. \tag{3.301}$$

Here we approximate $a(k'_n) \simeq a(k_n)$, which is always allowed for sufficiently large R. Extending Eq. (3.298) to $r = 0$ we obtain, with the aid of the boundary condition (3.299), an approximate expression for the normalization integral,

$$\begin{aligned} 1/c'^2_n &= \int_0^R dr \sin^2\left[k'_n R + \eta_0(k'_n)\right] \\ &= \frac{1}{2}\int_0^R dr[1 - \cos[2k'_m r + 2\eta_0(k'_m)]. \end{aligned} \tag{3.302}$$

The oscillatory term can be made arbitrarily small by choosing R sufficiently large. To demonstrate this we evaluate the integral; using the boundary condition (3.299) we obtain

$$1/c'^2_n = \frac{R}{2}\left[1 + \frac{\sin[2\eta_0(k'_n)]}{2k'_n R}\right]. \tag{3.303}$$

As the sine is bounded the second term can indeed be made arbitrarily small by choosing R sufficiently large. Hence, to a good approximation the normalization constant is conserved by switching on the interaction if R is chosen sufficiently large,

$$c'_n = c_n \text{ for } R \to \infty. \tag{3.304}$$

This is a remarkable result because it shows that for $a/R \ll 1$ the short range physics drops out of the normalization,

$$R_0(k'_n, r) \simeq \sqrt{\frac{2}{R}} \frac{\sin[k_n r + \eta_0(k_n)(1 - r/R)]}{r}. \tag{3.305}$$

---

[1] Note that Anderson uses a different sign convention for the phase shift.

3.9.4 Energy shift - repulsive versus attractive interaction

What happens to the energy of the atoms if we adiabatically apply the interaction? To first order in $a(k)/R$ we find for the shift in wavenumber

$$\delta k_n = k_n' - k_n = k_n a(k_n)/R + \cdots . \tag{3.306}$$

This fixes the energy shifts of all levels. For the n^{th} radial state the energy shift is given by

$$\delta E = \frac{\hbar^2}{2m}\left(k_n'^2 - k_n^2\right) = \frac{\hbar^2}{2m} 2k_n^2 [a(k_n)/R + \cdots] \simeq n^2 \frac{\hbar^2}{m}\frac{\pi^2}{R^3} a(k_n)\,, \tag{3.307}$$

For the motional ground state ($n = 1$) we have $k_1 \to 0$ and $a(k_1)$ approaches the scattering length, $a(k_1) \to a$. Thus the change in ground-state energy as a result of the interaction is

$$\delta E = \frac{\hbar^2}{2m}\left(k_1'^2 - k_1^2\right) \simeq \frac{\hbar^2}{m}\frac{\pi^2}{R^3} a\,, \tag{3.308}$$

where m is the mass of the gas atoms. Note that for $a > 0$ the energy increases by the presence of the interaction (*effective repulsion*). Likewise, for $a < 0$ the energy decreases (*effective attraction*). The energy shift δE is known as the *interaction energy* of the interacting pair (atom plus impurity). Apart from the s-wave scattering length it depends on the mass of the atoms and scales inversely proportional to the volume of the quantization sphere; i.e., linearly proportional to the mean probability density of the pair. The linear dependence in a is only accurate to first order in the expansion in powers of a/R. Most importantly, note that the shift δE only depends on the value of a and not on the details of the oscillatory part of the wavefunction in the core region.

3.9.5 Analysis of orthonormality between perturbed and unperturbed states

Let us investigate the overlap between the unperturbed wavefunctions $\alpha(k_i, \mathbf{r})$ and the perturbed wavefunctions $\beta(k_i', \mathbf{r})$. The overlap integral is given by

$$\langle \alpha_i | \beta_j \rangle = \frac{2}{R}\int_0^R dr \sin[k_i r] \sin[k_j' r + \eta_0(k_j')], \tag{3.309}$$

where we used the same normalization for the perturbed and unperturbed states - see Eq. (3.304). The overlap can be rewritten in the form

$$\langle \alpha_i | \beta_j \rangle = \frac{1}{R}\int_0^R dr \left\{\cos[k_i r - k_j' r - \eta_0(k_j')] - \cos[k_i r + k_j' r + \eta_0(k_j')]\right\}. \tag{3.310}$$

For $k_i - k_j' \ll k_i + k_j'$ the second term oscillates faster than the first one and becomes negligible for $R \to \infty$. This holds in particular for states close to the Fermi level. Integrating the first term we obtain

$$\langle \alpha_i | \beta_j \rangle = \int_0^{(k_i - k_j')R} dx \frac{\cos[x - \eta_0(k_j')]}{(k_i - k_j')R} = \frac{\sin[\eta_0(k_j')] + \sin[(k_i - k_j')R - \eta_0(k_j')])}{(k_i - k_j')R}. \tag{3.311}$$

Recalling the boundary condition (3.299) we find

$$\sin[k_i R - k_j' R - \eta_0(k_j')] = 0, \tag{3.312}$$

and using the approximation (3.300) the overlap integral simplifies to [2][1]

$$\langle \alpha_i | \beta_j \rangle = \frac{\sin[\eta_0(k_j)]}{(i-j)\pi + \eta_0(k_j)}. \tag{3.313}$$

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[1] Note that this is the same expression as given by Anderson but we started from different sign conventions. The result given here is correct as, for $i = j$, the overlap should go to unity for vanishing phase shift.

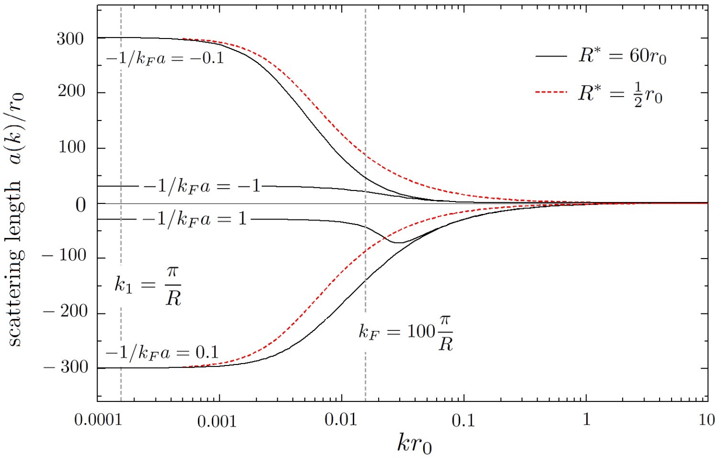

Figure 3.23: Black curves: the k dependence of the scattering length for resonances with a resonance-range $R^* = 60\,r_0$ and 30-fold/300-fold resonant enhancement of the scattering length ($k_Fa = \pm 1$ / $k_Fa = \pm 10$). Red curve: comparison with the k dependence of a Breit-Wigner resonance near threshold ($R^* = r_0/2$) with the a resonant enhancement of 300. In all cases the r_0 is taken as the background scattering length, $a_{bg} = r_0$. Note the asymmetry of the narrow resonance.

For sufficiently large R this approximation is valid to first order in the phase shift. The result shows that for $i = j$ the overlap is unity for zero phase shift and decreases like a spherical Bessel function with phase shift. Just as one expects for a weak perturbation *the overlap is close to unity if the perturbation is small.* Returning to the second term of Eq. (3.310) we find that it evaluates to

$$\frac{\sin[\eta_0(k_j)]}{(i+j)\pi - \eta_0(k_j)}. \tag{3.314}$$

Comparing with (3.313) shows that this term is indeed negligible if $j\pi \gg \eta_0(k_j)$, which can always be satisfied by making R sufficiently large.

3.9.6 Examples

Let us look at a few examples. We consider the ^{6}Li-^{40}K interaction with a range $r_0 = 40\,a_0 \simeq 2\,\text{nm}$ and a spherical volume of radius $R = 50\,\mu\text{m} = 2.5 \times 10^4 r_0$. For this system the ground state wavenumber is $k_1 = \pi/R \to k_1r_0 = 1.3 \times 10^{-4}$. The Fermi wavenumber for $N = 10^6$ atoms inside the sphere is $k_F = N^{1/3}\pi/R = 100\,k_1$. For atom-impurity interactions with a regular scattering length, $|a| \approx r_0$, we have $|\eta_0(k)| \approx kr_0 \ll 1$ and the overlap is close to unity up to the Fermi level. For cases with a moderately enhanced positive scattering length, $k_Fa = 1$, the resonant enhancement is 30 fold, $a = 30\,r_0$ and $a(k_F) \approx 15\,r_0$. Thus the phase shift is $\eta_0(k_F) = -k_Fa(k_F) \approx 1500\,k_1r_0 \approx 0.2$ and we calculate for the overlap $\langle\alpha_{n_F}|\beta_{n_F}\rangle \approx 1$. For a strong enhancement, $k_Fa = 10$, the resonant enhancement is 300 fold, $a = 300\,r_0$ and $a(k_F) \approx 50\,r_0$. Thus the phase shift is $\eta_0(k_F) = -k_Fa(k_F) \approx 5000\,k_1r_0 \approx 0.65$ and we find for the overlap $\langle\alpha_{n_F}|\beta_{n_F}\rangle \approx 0.93$.

We analyze the resonance conditions for these examples. For an s-wave resonance close to threshold, the k dependence of the total scattering length $a(k)$ can be written in the universal form

$$a(k) = a_{bg} + \frac{1}{k}\arctan\left[ka_{res}/(1 + k^2R^*a_{res})\right]. \tag{3.315}$$

The expression is called universal because the spectral width of the resonance can be varied independently from the resonant enhancement $(a_{res} + a_{bg})/r_0$ and the background contribution a_{bg}/r_0.

The variation of the width is done by variation of the resonance range R^*. In Feshbach resonances R^* is a measure for the coupling between the open and the closed channel. For a resonance with $R^* = 60\,r_0$ ($k_F R^* = 1$) the k dependence of the scattering length is shown as the black curves in Fig. 3.23. For comparison also the behavior of the corresponding Breit-Wigner resonance near threshold is shown. Note that for the ground state the scattering-length limit is reached. As we are dealing with an ultracold gas and in the presence of at most one resonance we can put a bound on the phase shift,

$$|\eta_0(k_F)| \lesssim \pi. \tag{3.316}$$

3.9.7 Energy shift obtained with pseudo potentials

The method used above to calculate the interaction energy δE of the reduced mass m_r in a spherical volume of radius R has the disadvantage that it relies on the boundary condition at the surface of the volume. It would be hard to extend this method to non-spherical volumes or to calculate the interaction energy of a gas of N atoms because only one center of mass of a collisional pair can be put in the center of the quantization volume. Therefore we look for a different boundary condition that does not have this disadvantage. The pseudo potentials introduced in Section 3.8 provide this boundary condition.

With the delta function potential (3.285) we can readily regain the interaction energy (3.307) using first order in perturbation theory

$$\delta E = \frac{\langle \varphi_k | \mathcal{V}(r) | \varphi_k \rangle}{\langle \varphi_k | \varphi_k \rangle}, \tag{3.317}$$

where

$$\varphi_k(\mathbf{r}) = c_0 Y_0^0(\hat{\mathbf{r}}) j_0(kr) \tag{3.318}$$

is the wavefunction for the *unperturbed* relative motion of two atoms,with $Y_0^0(\hat{\mathbf{r}})$ being the lowest order spherical harmonic and $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$ the unit vector in the radial direction (θ, ϕ). The normalization condition is $1 = \langle \varphi_k | \varphi_k \rangle = \int_V [c_0 Y_0^0(\hat{\mathbf{r}}) j_0(kr)]^2 d\mathbf{r}$ with $kR = \pi$. Rewriting the integral in terms of the variable $\varrho \equiv kr$ we find after integration and choosing the wavevector used in the previous section ($k = \pi/R$)

$$\frac{1}{c_0^2} = \frac{1}{k^2} \int_0^R \sin^2(kr) dr = \frac{1}{k^3} \int_0^\pi \sin^2(\varrho) d\varrho = \frac{R^3}{\pi^3} \frac{\pi}{2}. \tag{3.319}$$

Then, to first order in perturbation theory the interaction energy is given by

$$\delta E \underset{k \to 0}{\simeq} \frac{\hbar^2}{2m_r} \int 4\pi a\, \delta(\mathbf{r})\, \varphi_k^2(\mathbf{r}) d\mathbf{r} = \frac{\hbar^2}{2m_r} a c_0^2 \left[\frac{\sin^2(kr)}{k^2 r^2} \right]_{r \to 0} = \frac{\hbar^2}{m_r} \frac{\pi^2}{R^3} a\,, \tag{3.320}$$

which is seen to coincide with Eq. (3.307). This expression is accurate only as long as we can *restrict ourselves to first order in perturbation theory*; the pseudo potential is constructed such that it provides the correct value for the interaction energy but the actual correlations between the colliding atoms are neglected.

3.9.8 Interaction energy of two unlike atoms

Let us consider two unlike atoms in a cubic box of length L and volume $V = L^3$ interacting via the central potential $\mathcal{V}(r)$. The hamiltonian of this two-body system is given by [1]

$$\mathcal{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + \mathcal{V}(r). \tag{3.321}$$

---

[1] In this description we leave out the internal states of the atoms (including spin).

In the absence of the interaction the pair wavefunction of the two atoms is given by the product wavefunction

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V} e^{-i\mathbf{k}_1\cdot\mathbf{r}_1} e^{-i\mathbf{k}_2\cdot\mathbf{r}_2}$$

with the wavevector of the atoms $i, j \in \{1,2\}$ subject to the same boundary conditions as above, $k_{i\alpha} = (2\pi/L)\, n_{i\alpha}$. The interaction energy is calculated by first-order perturbation theory using the delta function potential $\mathcal{V}(\mathbf{r}) = g\,\delta(\mathbf{r})$ with $\mathbf{r} = |\mathbf{r}_1 - \mathbf{r}_2|$,

$$\delta E = \frac{\langle \mathbf{k}_1,\mathbf{k}_2 | \mathcal{V}(\mathbf{r}) | \mathbf{k}_1,\mathbf{k}_2\rangle}{\langle \mathbf{k}_1,\mathbf{k}_2 | \mathbf{k}_1,\mathbf{k}_2\rangle} = \frac{g}{V}. \tag{3.322}$$

This result follows in two steps. The norm is given by

$$\begin{aligned}\langle \mathbf{k}_1,\mathbf{k}_2 | \mathbf{k}_1,\mathbf{k}_2\rangle &= \iint_V |\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)|^2\, d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{V^2}\int_V |e^{-i\mathbf{k}_1\cdot\mathbf{r}_1}|^2 d\mathbf{r}_1 \int_V |e^{-i\mathbf{k}_2\cdot\mathbf{r}_2}|^2 d\mathbf{r}_2 = 1, \end{aligned} \tag{3.323}$$

because $\left|e^{-i\alpha}\right|^2 = 1$. As the plane waves are regular in the origin we can indeed use the delta function potential (3.286) to approximate the interaction

$$\begin{aligned}\langle \mathbf{k}_1,\mathbf{k}_2 | \mathcal{V}(r) | \mathbf{k}_1,\mathbf{k}_2\rangle &= \frac{g}{V^2}\iint_V \delta(\mathbf{r}_1 - \mathbf{r}_2)\left|e^{-i\mathbf{k}_1\cdot\mathbf{r}_1}e^{-i\mathbf{k}_2\cdot\mathbf{r}_2}\right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \qquad (3.324)\\ &= \frac{g}{V^2}\int_V |e^{-i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_1}|^2 d\mathbf{r}_1 = g/V.\end{aligned}$$

Like in Eq. (3.307) the interaction energy depends on the reduced mass of the atoms and scales inversely proportional to the quantization volume.

3.9.9 Interaction energy of two identical bosons

Let us return to the calculation of the interaction energy but now for the case of identical bosonic atoms. As in Section 3.9.8 we shall use first-order perturbation theory and the delta function potential

$$\mathcal{V}(r) = g\,\delta(\mathbf{r}) \quad \text{with } g = \left(4\pi\hbar^2/m\right) a, \tag{3.325}$$

where m is the atomic mass (the reduced mass equals $m_r = m/2$ for particles of equal mass).

First we consider two atoms in the same state and wavevector $\mathbf{k} = \mathbf{k}_1 = \mathbf{k}_2$. In this case the wavefunction is given by

$$\psi_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V} e^{i\mathbf{k}\cdot\mathbf{r}_1} e^{i\mathbf{k}\cdot\mathbf{r}_2}, \tag{3.326}$$

with $\langle \mathbf{k},\mathbf{k} | \mathbf{k},\mathbf{k}\rangle = 1$. Thus, to first order in perturbation theory the interaction energy is given by

$$\begin{aligned}\delta E = g\,\langle \mathbf{k},\mathbf{k}|\,\delta(\mathbf{r})\,|\mathbf{k},\mathbf{k}\rangle &= \frac{g}{V^2}\iint_V \delta(\mathbf{r}_1 - \mathbf{r}_2)\left|e^{-i\mathbf{k}\cdot\mathbf{r}_1}e^{-i\mathbf{k}\cdot\mathbf{r}_2}\right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{g}{V^2}\int_V \left|e^{-i2\mathbf{k}\cdot\mathbf{r}_1}\right|^2 d\mathbf{r}_1 = g/V.\end{aligned} \tag{3.327}$$

We notice that we have obtained exactly the same result as in Section 3.9.8.

For $\mathbf{k}_1 \neq \mathbf{k}_2$ the situation is different. The pair wavefunction is given by

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V}\sqrt{\tfrac{1}{2!}}\left(e^{i\mathbf{k}_1\cdot\mathbf{r}_1}e^{i\mathbf{k}_2\cdot\mathbf{r}_2} \pm e^{i\mathbf{k}_2\cdot\mathbf{r}_1}e^{i\mathbf{k}_1\cdot\mathbf{r}_2}\right). \tag{3.328}$$

with norm $\langle \mathbf{k}_1, \mathbf{k}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle = 1$. To first order in perturbation theory we obtain in this case

$$\begin{aligned}
\delta E &= g \langle \mathbf{k}_1, \mathbf{k}_2 | \, \delta(\mathbf{r}) \, | \mathbf{k}_1, \mathbf{k}_2 \rangle \\
&= \frac{1}{2} \frac{g}{V^2} \iint_V \delta \left(\mathbf{r}_1 - \mathbf{r}_2 \right) \left| \mathrm{e}^{-i\mathbf{k}_1 \cdot \mathbf{r}_1} \mathrm{e}^{-i\mathbf{k}_2 \cdot \mathbf{r}_2} + \mathrm{e}^{-i\mathbf{k}_2 \cdot \mathbf{r}_1} \mathrm{e}^{-i\mathbf{k}_1 \cdot \mathbf{r}_2} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{1}{2} \frac{g}{V^2} \int_V [|\mathrm{e}^{-i(\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{r}_1}|^2 + |\mathrm{e}^{-i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}_1}|^2 + |\mathrm{e}^{i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}_1}|^2 + |\mathrm{e}^{i(\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{r}_1}|^2] d\mathbf{r}_1 \\
&= 2g/V.
\end{aligned} \tag{3.329}$$

Thus the interaction energy between two bosonic atoms in same state is seen to be twice as small as for the same atoms in ever so slightly different states! Clearly, in the presence of repulsive interactions the interaction energy can be minimized by putting the atoms in the same state.

4

Elastic scattering of neutral atoms

4.1 Introduction

To gain insight in the *collisional properties* of dilute quantum gases it is important to understand the *elastic scattering* of atoms under the influence of an interatomic potential. For dilute gases the interest primarily concerns binary collisions; by elastic we mean that the energy of the relative motion is the same before and after the collisions. Important preparatory work has already been done. In Chapter 3 we showed how to obtain the radial wavefunctions necessary to describe the relative motion of a pair of atoms moving in a central interaction potential. In the present chapter we search for the relation between these wavefunctions and the scattering properties in binary collisions. This is more subtle than it may seem at first sight because in quantum mechanics the scattering of two particles does not only depend on the interaction potential but also on the intrinsic properties of the particles.[1] This has to do with the concept of *indistinguishability of identical particles.* We must assure that the pair wavefunction of two colliding atoms has the proper symmetry with respect to the interchange of its constituent elementary particles. We start the discussion in Section 4.2 with the elastic scattering of two atoms of different atomic species. The atoms of such a pair are called *unlike* or *distinguishable*. In Section 4.3 we turn to the case of identical (*indistinguishable*) atoms. These are atoms of the same isotopic species. First we discuss the case of identical atoms in the same atomic state (Section 4.3.1). This case turns out to be relatively straightforward. More subtle questions arise when the atoms are of the same isotopic species but in different atomic states (Section 4.4). In the latter case we can distinguish between the states but not between the atoms. Many option arise depending on the spin states of the colliding atoms. In the present chapter we focus on the principal phenomenology for which we restrict the discussion to atoms with only a nuclear spin degree of freedom. In Chapter 5 collisions between atoms in arbitrary hyperfine states will be discussed.

We derive for all mentioned cases the probability amplitude of scattering and the corresponding differential and total cross sections. As it turns out the expressions that are obtained hold for *elastic* collisions at any non-relativistic velocity. In Section 4.3.2 we specialize to the case of slow collisions. At low collision energy the scattering amplitude is closely related to the scattering length. Important differences between the collisions of identical bosons and fermions are pointed out. At the end of the chapter the origin of Ramsauer-Townsend minima in the elastic scattering cross section is discussed.

4.2 Distinguishable atoms

We start this chapter with the scattering of two atoms of different atomic species (which includes the case of two different isotopes of the same element). These atoms are called *distinguishable* because

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[1] N.F. Mott, *Proc. Roy. Soc.* A**126**, 259 (1930).

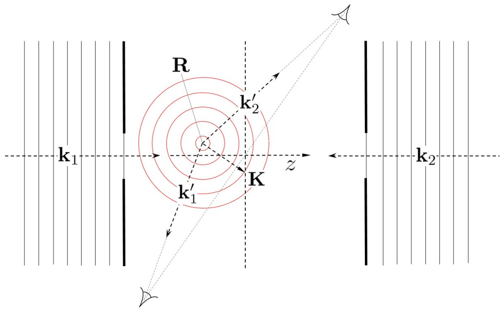

Figure 4.1: Scattering configuration.

they have a different composition of elementary particles and consequently lack a prescribed overall exchange symmetry and may be labeled 1 and 2. Let us presume that, long before the collision, the atoms are in momentum eigenstates close to $\mathbf{k}_1$ and $\mathbf{k}_2$ the pair wavefunction can be expressed as a product of plane wave eigenfunctions,[1]

$$\psi_{in}\left(\mathbf{r}_1, \mathbf{r}_2\right) = e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2}. \tag{4.1}$$

To describe this collision we turn to center-of-mass and relative coordinates,

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r} \text{ and } \mathbf{r}_2 = \mathbf{R} - \frac{m_1}{M}\mathbf{r}, \tag{4.2}$$

where $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$ is the position of the center of mass and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ the position of particle 1 relative to particle 2 (see Appendix A.7). In terms of the new coordinates we have

$$\psi_{in}\left(\mathbf{R}, \mathbf{r}\right) = e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} e^{i(m_2\mathbf{k}_1 - m_1\mathbf{k}_2)\cdot\mathbf{r}/M} = e^{i\mathbf{K}\cdot\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{4.3}$$

where $\mathbf{P} = \hbar\mathbf{K} = \hbar(\mathbf{k}_1 + \mathbf{k}_2)$ is the center-of-mass momentum and

$$\mathbf{p} = m_r(\mathbf{v}_1 - \mathbf{v}_2) = m_r\mathbf{v} = \hbar\mathbf{k} \tag{4.4}$$

the relative momentum. In the presence of the interaction, the relative motion is completely determined by the Schrödinger equation (3.2). As, by definition, the potential center is located at relative position $\mathbf{r} = 0$, each collision event also fixes a *scattering center* (the position $\mathbf{R}$ of the center of mass at the time of the event), which differs from event to event within the limits set by the uncertainty in $\mathbf{K}$. In the presence of a *central* potential $\mathcal{V}(|\mathbf{r}_1 - \mathbf{r}_2|)$ the wavefunction for the relative motion is distorted by the interaction and can be written is the form

$$\psi\left(\mathbf{R}, \mathbf{r}\right) = e^{i\mathbf{K}\cdot\mathbf{R}}\left[\psi_{in}\left(\mathbf{r}\right) + \psi_{sc}\left(\mathbf{r}\right)\right], \tag{4.5}$$

were $\psi_{in}\left(\mathbf{r}\right)$ is referred to as the *incident wave* and $\psi_{sc}\left(\mathbf{r}\right)$ as the *scattered wave*, in reference to freely propagating waves in axial/radial direction, long before/after a collision. The actual positions $\mathbf{R}$ remain undetermined in a typical scattering experiment, where the scattering products are detected in the far field. In experiments the quantum mechanical uncertainty in $\mathbf{R}$ depends on the practical realization of the plane wave $e^{i\mathbf{K}\cdot\mathbf{R}}$.

$$\mathbf{k}_1 = \frac{m_1}{M}\mathbf{K} + \mathbf{k} \text{ and } \mathbf{k}_2 = \frac{m_2}{M}\mathbf{K} - \mathbf{k}. \tag{4.6}$$

To be specific we consider the crossed atomic beam scattering configuration sketched in Fig. 4.1. Two atomic beams are crossed after collimation, with the wavevectors of the atoms chosen to be

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[1] To promote a transparent notation the normalization volume is chosen to be unity ($V = 1$).

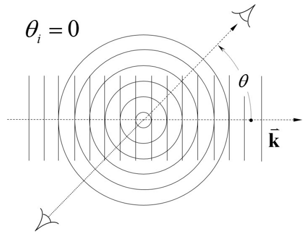

Figure 4.2: Schematic drawing of the scattering of a matter wave at a spherically symmetric scattering center in the center-of-mass coordinate system. Indicated are the wavevector $\mathbf{k}$ of the incident wave, representing the reduced mass μ moving in the positive z-direction ($\theta_i = 0$), as well as the scattering angle $\vartheta = \theta$, which can take values in the interval $0 \leq \vartheta \leq \pi$.

equal and opposite along the z axis; i.e., $\mathbf{k}_2 = -\mathbf{k}_1$, up to the limits of diffraction posed by the collimation slits. In this arrangement the center of mass is approximately at rest ($|\mathbf{K}| \ll |\mathbf{k}_1|$). Before discussing the scattering we estimate the uncertainty in $\mathbf{K}$.

In view of the central symmetry the variables for the radial and angular motion separate (see Section 2.1.6) and far from the scattering center the scattered wave can be represented by the stationary solution of an *outgoing* spherical wave,

$$\psi_{sc}(\mathbf{r}) \underset{r\to\infty}{\simeq} f(\theta)\frac{e^{ikr}}{r}. \tag{4.7}$$

As required for elastic scattering the modulus of the relative wave vector $k = |\mathbf{k}|$ is conserved. The current density falls off asymptotically as $1/r^2$, as expected for a spherically expanding wave. The prefactor $f(\theta)$ is called the *scattering amplitude* and represents the probability amplitude for scattering of the reduced mass in the direction (θ, ϕ). Here ϕ defines the *scattering plane* and θ the *scattering angle*. As the direction of incident motion is chosen along the positive z axis and the potential is central the scattering amplitude is independent of the orientation of the scattering plane; i.e., independent of ϕ. Combining the expressions for the incident and the scattered wave we obtain the *distorted wave* describing the relative motion of the interacting pair,

$$\psi = \psi_{in} + \psi_{sc} \underset{r\to\infty}{\simeq} e^{ikz} + f(\theta)\frac{e^{ikr}}{r}. \tag{4.8}$$

Note that this is an axially symmetric solution of the Schrödinger equation (3.2).

The scattering of the reduced mass (in the center-of-mass-fixed frame) is illustrated in Fig. 4.2. Particle 1 is moving from left to right and scatters over the angle $\vartheta = \theta$ in the direction (θ, ϕ), while particle 2 moves from right to left and scatters also over the angle $\vartheta = \theta$ in the opposite direction $(\pi - \theta, \pi + \phi)$. Experimentally, this can be arranged by providing the colliding atoms in opposing atomic beams. A pair of mass spectrometers would be an appropriate (atom selective) detector in this (spin-independent) case as with these instruments we can determine the direction of scattering (θ, ϕ) of the individual atoms.

4.2.1 Scattered waves - partial wave expansion of the scattering amplitude

It is the goal of this section to derive an expression for the scattering amplitude. Knowing the angular and radial eigenfunctions $Y_l^m(\theta, \phi)$ and $R_l(k, r)$, the general solution for a particle in a central potential field $\mathcal{V}(r)$ can be expressed as a linear combination of the eigenstates,

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm} R_l(k, r) Y_l^m(\theta, \phi), \tag{4.9}$$

where $\mathbf{r} \equiv (r, \theta, \phi)$ is the position vector relative to the scattering center. This important expression is known as the *partial-wave expansion.* The coefficients c_{lm} depend on the particular choice of coordinate axes. Our interest concerns the wave functions with axial symmetry along the z axis, which are ϕ independent. Hence, all coefficients c_{lm} with $m \neq 0$ must be zero. Accordingly, for axial symmetry about the z axis the partial wave expansion (4.9) can be written in the form

$$\psi = \sum_{l=0}^{\infty} (2l+1) i^l c_l R_l(k,r) P_l(\cos\theta), \tag{4.10}$$

where the $P_l(\cos\theta)$ are Legendre polynomials and the $R_l(k,r)$ satisfy the radial wave equation (3.7).

It is our task to choose the coefficients c_l such that at large distances the partial-wave expansion has the asymptotic form given by Eq. (4.8). For this purpose we note that in the absence of scattering the distorted wave ψ reduces to the unperturbed plane wave ψ_{in}. Hence, the radial wavefunction $R_l(k,r)$ reduces to the spherical Bessel function $j_l(kr)$ and the partial-wave expansion becomes (see Problem 4.1)

$$e^{ikz} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\cos\theta). \tag{4.11}$$

Comparison of Eqs. (4.10) and (4.11) shows that the form (4.10) was chosen such that $c_l = 1$ in the absence of scattering. To obtain the desired asymptotic behavior for the distorted wave ψ the coefficient c_l should be chosen such that the scattered wave is asymptotically of the form (4.7); i.e., represents a pure outgoing spherical wave. Subtracting the incident wave from the general solution for the distorted wave the partial-wave expansion of the scattered wave is found to be

$$\psi - \psi_{in} = \psi_{sc} = \sum_{l=0}^{\infty} (2l+1) i^l Q_l(k,r) P_l(\cos\theta), \tag{4.12}$$

where

$$Q_l(k,r) \equiv c_l R_l(k,r) - j_l(kr) \tag{4.13}$$

represents the scattered part of the radial wave. For short-range potentials, the asymptotic forms of both $R_l(k,r)$ and $j_l(kr)$ should satisfy the spherical Bessel equation (3.14); i.e., be of the asymptotic form (3.24). Thus we have

$$\begin{aligned} Q_l(k,r) &\underset{r\to\infty}{\simeq} \frac{1}{kr}\left[c_l \sin(kr + \eta_l - \tfrac{1}{2}l\pi) - \sin(kr - \tfrac{1}{2}l\pi)\right] \\ &\underset{r\to\infty}{\simeq} \frac{1}{2ikr}\left[i^{-l}e^{ikr}e^{i\eta_l}c_l - i^l e^{-ikr}e^{-i\eta_l}c_l - i^{-l}e^{ikr} + i^l e^{-ikr}\right]. \end{aligned} \tag{4.14}$$

This expression represents an outgoing spherical wave if the terms proportional to e^{-ikr} vanish, which is the case for $c_l = e^{i\eta_l}$. Note that in this case we have $c_l \to 1$ for $\eta_l \to 0$, which means that $c_l = 1$ in the absence of scattering, as it should. The coefficient c_l is obtained by analyzing the long-range behavior but once it is known it can be used in Eq. (4.13) to represent the *full* solution of the scattered wave,

$$\psi_{sc}(r,\theta) = \sum_{l=0}^{\infty} (2l+1) i^l \left[e^{i\eta_l} R_l(k,r) - j_l(kr)\right] P_l(\cos\theta), \tag{4.15}$$

which includes the distortion of the wave close to the scattering center.

4.2.1.1 Partial wave expansion

Many features of elastic scattering can be understood by analyzing the asymptotic behavior of the scattered wave. Therefore, it is important to derive an expression for the scattering amplitude. Substituting $c_l = e^{i\eta_l}$ into Eq. (4.14) the scattered part of the radial wave takes the asymptotic form

$$Q_l(k,r) \underset{r\to\infty}{\simeq} \frac{e^{ikr}}{2ikr} i^{-l}(e^{2i\eta_l}-1). \tag{4.16}$$

Substituting this expression into Eq. (4.12) we obtain

$$\psi_{sc} \underset{r\to\infty}{\simeq} \frac{e^{ikr}}{r}\frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)(e^{2i\eta_l}-1)P_l(\cos\theta) \tag{4.17}$$

and comparing this equation with the asymptotic expression (4.7) we find that the scattering amplitude is given by

$$f(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)(e^{2i\eta_l}-1)P_l(\cos\theta). \tag{4.18}$$

This expression is know as the partial wave decomposition of the scattering amplitude.

Problem 4.1. Show that the partial wave expansion of the plane wave e^{ikz}, describing the motion of a free particle in the positive z direction, is given by

$$e^{ikz} = \sum_{l=0}^{\infty}(2l+1)i^l j_l(kr)P_l(\cos\theta).$$

Solution. For configurations with axial symmetry the partial wave expansion is of the general form

$$\psi = \sum_{l=0}^{\infty} c_l R_l(k,r)P_l(\cos\theta), \tag{a}$$

where $R_l(k,r)$ is the radial wavefunction for partial waves of angular momentum l, $P_l(\cos\theta)$ the Legendre polynomial of order l, and c_l the expansion coefficient. For a free particle the radial wavefunction $R_l(k,r)$ must be a regular solution of the spherical Bessel equation. So we choose $R_l(k,r)$ equal to the spherical Bessel function $j_l(kr)$ (see Section C.12.1). The remaining task is to determine the coefficients c_l. Expanding e^{ikz} in powers of $kz = kr\cos\theta$ we find

$$e^{ikz} = \sum_{l=0}^{\infty}\frac{(ikr\cos\theta)^l}{l!}. \tag{b}$$

Turning to the r.h.s. of Eq. (a) we obtain

$$\sum_{l=0}^{\infty} c_l j_l(kr)P_l(\cos\theta) \underset{r\to 0}{\simeq} \sum_{l=0}^{\infty} c_l \frac{(kr)^l}{(2l+1)!!}\frac{1}{2^l l!}\frac{(2l)!}{l!}(\cos\theta)^l. \tag{c}$$

Here we used the expansion of the Bessel function $j_l(kr)$ in powers $(kr)^l$ as given by Eq. (C.106b),

$$j_l(kr) \underset{r\to 0}{\simeq} \frac{(kr)^l}{(2l+1)!!}(1+\cdots),$$

and used Eq. (C.37) to find the term of order $(\cos\theta)^l$ in the expansion of $P_l(u)$ with $u \equiv \cos\theta$,

$$P_l(u) = \frac{1}{2^l l!}\frac{d^l}{du^l}(u^2-1)^l = \frac{1}{2^l l!}\frac{d^l}{du^l}\left(u^{2l}+\cdots\right) = \frac{1}{2^l l!}\frac{(2l)!}{l!}(u^l+\cdots).$$

Thus, equating the terms of order $(kr\cos\theta)^l$ in Eqs. (a) and (b), we obtain for the coefficients [1]

$$c_l = i^l(2l+1)!!\frac{2^l l!}{(2l)!} = i^l(2l+1),$$

which leads to the desired result after substitution into Eq. (a). □

4.2.2 Scattered waves - the method of Green's functions

The formal theory of scattering is based on exact integral expressions for the scattered wave. As the goal of this introductory text is to emphasize the physics rather than formalism formal theory is avoided as much as possible. In this section we make an exception and show (as an intermezzo) how an exact integral expression for the scattered wave is obtained with the method of Green's functions. For this purpose we start at the Schrödinger equation for an interacting pair of atoms,

$$\left[-\frac{\hbar^2}{2m_r}\Delta + \mathcal{V}(r)\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{4.19}$$

where $\mathcal{V}(r)$ is the potential energy curve describing the interaction between the two atoms. Introducing the wavenumber notation, $k = [2m_rE/\hbar^2]^{1/2}$ and defining $U(r) \equiv (2m_r/\hbar^2)\mathcal{V}(r)$, for positive energy $(E>0)$ this expression can be written in the form

$$\left(\Delta + k^2\right)\psi(\mathbf{r}) = U(r)\psi(\mathbf{r}). \tag{4.20}$$

The general solution of this equation can be written in the form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \psi_{sc}(\mathbf{r}) \tag{4.21}$$

where $e^{i\mathbf{k}\cdot\mathbf{r}}$ is an arbitrary solution of the homogeneous equation $\left(\Delta + k^2\right)\psi(\mathbf{r}) = 0$ and

$$\psi_{sc}(\mathbf{r}) \sim \frac{e^{ikr}}{r} \tag{4.22}$$

is a particular solution of Eq. (4.20) representing an outgoing spherical wave.

Particular solutions of Eq. (4.20) can be expressed in the form (see Problem 4.2)

$$\psi_{sc}(\mathbf{r}) = -\frac{1}{4\pi}\int G(\mathbf{r},\mathbf{r}')U(r')\psi_{sc}(\mathbf{r}')d\mathbf{r}', \tag{4.23}$$

where $G(\mathbf{r},\mathbf{r}')$ is a solution of the equation

$$\left(\Delta + k^2\right)G(\mathbf{r},\mathbf{r}') = -4\pi\delta(\mathbf{r}-\mathbf{r}'). \tag{4.24}$$

Here the choice of the prefactor -4π is based on insider knowledge of the final result for $G(\mathbf{r},\mathbf{r}')$. Eq. (4.24) is solved by Fourier transformation

$$G(\mathbf{r},\mathbf{r}') = \int g(\mathbf{k}')e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')}d\mathbf{k}' \tag{4.25}$$

and by using the well-known relation for the delta function

$$\delta(\mathbf{r}-\mathbf{r}') = \frac{1}{(2\pi)^3}\int e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')}d\mathbf{k}'. \tag{4.26}$$

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[1] Note that $(2n)!/(2n-1)!! = (2n)!! = 2^n n!$

Substituting these expressions into Eq. (4.24) we obtain

$$\left(\Delta + k^2\right) \int g(\mathbf{k}') e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{k}' = -\frac{4\pi}{(2\pi)^3} \int e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{k}', \tag{4.27}$$

which is satisfied for

$$\left(k^2 - k'^2\right) g(\mathbf{k}') = -\frac{4\pi}{(2\pi)^3}. \tag{4.28}$$

After substitution of $g(\mathbf{k}')$ into Eq. (4.25) we obtain for the Green's function

$$G(\mathbf{r}-\mathbf{r}') = -\frac{4\pi}{(2\pi)^3} \int \frac{e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')}}{k^2 - k'^2} d\mathbf{k}'. \tag{4.29}$$

To evaluate the integral we first rewrite it in the form (see Problem 4.3)

$$G(\mathbf{r}) = -\frac{4\pi}{(2\pi)^3} \int \frac{e^{i\mathbf{k}'\cdot\mathbf{r}}}{k^2 - k'^2} d\mathbf{k}' = -\frac{1}{\pi r} \frac{d}{dr} \int_{-\infty}^{+\infty} \frac{e^{ik'r}}{k'^2 - k^2} dk'. \tag{4.30}$$

What remains to be done is to evaluate an integral with a complex argument. The integral leads to a class of solutions for $G(\mathbf{r})$, each corresponding to a particular solution of the Schrödinger equation (4.20). In Problem 4.4 it is shown that *one* of the results is of the desired form of an outgoing spherical wave,

$$G(\mathbf{r}-\mathbf{r}') = \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}. \tag{4.31}$$

The expression for the scattered wave becomes

$$\psi_{sc}(\mathbf{r}) = -\frac{1}{4\pi} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} U(r') \psi_{sc}(\mathbf{r}') d\mathbf{r}'. \tag{4.32}$$

Problem 4.2. Show that

$$\psi(\mathbf{r}) = -\frac{1}{4\pi} \int G(\mathbf{r}, \mathbf{r}') U(r') \psi(\mathbf{r}') d\mathbf{r}'$$

is a solution of the equation $\left(\Delta + k^2\right) \psi(\mathbf{r}) = U(r)\psi(\mathbf{r})$.

Solution. By substitution we have

$$\begin{aligned}\left(\Delta + k^2\right) \psi(\mathbf{r}) &= -\frac{1}{4\pi} \int \left(\Delta + k^2\right) G(\mathbf{r}, \mathbf{r}') U(r') \psi(\mathbf{r}') d\mathbf{r}' \\ &= \int \delta(\mathbf{r}-\mathbf{r}') U(r') \psi(\mathbf{r}') d\mathbf{r}' = U(r)\psi(\mathbf{r}).\end{aligned}$$

□

Problem 4.3. Derive the following expression

$$\int \frac{e^{i\mathbf{k}'\cdot\mathbf{r}}}{k^2 - k'^2} d\mathbf{k}' = -\frac{2\pi}{r} \frac{d}{dr} \int_{-\infty}^{+\infty} \frac{e^{ik'r}}{k^2 - k'^2} dk'.$$

Solution. First we rewrite the integral in polar coordinates

$$\int \frac{e^{i\mathbf{k}'\cdot\mathbf{r}}}{k^2 - k'^2} d\mathbf{k}' = \int \frac{e^{ik'r\cos\theta}}{k^2 - k'^2} k'^2 \sin\theta d\theta d\varphi dk'$$

where we chose to define the angle θ with respect to the direction $\mathbf{r}$. Since $\sin\theta d\theta = -d\cos\theta$ the integral can be written in the form

$$\begin{aligned}\int \frac{e^{i\mathbf{k}'\cdot\mathbf{r}}}{k^2 - k'^2} d\mathbf{k}' &= -\frac{2\pi}{r} \int_0^{\infty} \frac{e^{ik'r} - e^{-ik'r}}{k^2 - k'^2} ik' dk' \\ &= -\frac{2\pi}{r} \frac{d}{dr} \int_0^{\infty} \frac{e^{ik'r} + e^{-ik'r}}{k^2 - k'^2} dk'.\end{aligned}$$

The latter expression is readily rewritten in the desired form. □

Problem 4.4. Show that $G(\mathbf{r}) = e^{ikr}/r$ is one of the solutions for the Green's function

$$G(\mathbf{r}) = -\frac{1}{\pi r}\frac{d}{dr}\int_{-\infty}^{+\infty}\frac{e^{ik'r}}{k'^2 - k^2}dk'.$$

Solution. To search for solutions we replace the linear integral by a contour integral in the upper half of the complex $\bar{k}$ plane,

$$\int_{-\infty}^{+\infty}\frac{e^{ik'r}}{k'^2 - k^2}dk' = \lim_{\eta\to 0}\oint_\gamma \frac{e^{i\bar{k}r}}{\bar{k}^2 - (k+i\eta)^2}d\bar{k}$$

where $\bar{k} = |\bar{k}|e^{i\phi} = |\bar{k}|\cos\phi + i|\bar{k}|\sin\phi$. The poles of the integrand are shifted over a small distance $i\eta$ into the complex plane to assure that the contour is void of singularities. The result depends on the contour chosen, each contour corresponding to a particular solution. As we are looking for a particular solution in the form of an outgoing spherical wave, e^{ikr}/r, we choose to close the contour along the path γ in the upper half of the complex plane where $e^{i\bar{k}r} = e^{i|\bar{k}|r\cos\phi}e^{-|\bar{k}|r\sin\phi} \to 0$ for $|\bar{k}| \to \infty$. The integrand has poles for $\bar{k} = \pm(k+i\eta)$. Hence, for $\eta > 0$ the contour encloses the pole $\bar{k} = k + i\eta$ and the integral evaluates to

$$\oint_\gamma \frac{e^{i\bar{k}r}}{\bar{k}^2 - (k+i\eta)^2}d\bar{k} = 2\pi i \operatorname*{Res}_{\bar{k}=k+i\eta}\frac{e^{i\bar{k}r}}{\bar{k}^2 - (k+i\eta)^2} = 2\pi i\frac{e^{i(k+i\eta)r}}{2(k+i\eta)} \tag{4.33}$$

and the Green's function becomes

$$G(\mathbf{r}) = -\frac{i}{r}\frac{d}{dr}\lim_{\eta\to 0}\frac{e^{i(k+i\eta)r}}{(k+i\eta)} = \frac{e^{ikr}}{r}. \qquad \square$$

4.2.3 Partial-wave scattering amplitudes and forward scattering

For future convenience we rewrite the partial-wave expansion of the scattering amplitude, see Eq. (4.18), in the more compact form

$$f(\theta) = \sum_{l=0}^{\infty}(2l+1)f_l P_l(\cos\theta), \tag{4.34}$$

where the contribution f_l of the partial wave with angular momentum l can be written in several equivalent forms

$$f_l = \frac{1}{2ik}(e^{2i\eta_l} - 1) \tag{4.35a}$$
$$= k^{-1}e^{i\eta_l}\sin\eta_l \tag{4.35b}$$
$$= \frac{1}{k\cot\eta_l - ik} \tag{4.35c}$$
$$= k^{-1}\left(\sin\eta_l\cos\eta_l + i\sin^2\eta_l\right). \tag{4.35d}$$

Each of these expressions has its specific advantage. In particular we draw the attention to the last expression, which shows that the imaginary part of the scattering amplitude f_l is given by

$$\operatorname{Im} f_l = \frac{1}{k}\sin^2\eta_l. \tag{4.36}$$

Specializing Eq. (4.34) to the case of forward scattering and summing over all partial waves we obtain an important expression that relates the forward scattering to the phase shifts,

$$\operatorname{Im} f(0) = \sum_{l=0}^{\infty}(2l+1)\operatorname{Im} f_l\, P_l(1) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\sin^2\eta_l. \tag{4.37}$$

This expression shows that in general the scattering amplitude is not real and $\operatorname{Im} f(0)$ is always positive. Quantum gases in the s-wave regime form an exception to this rule because for $k \to 0$ the imaginary part vanishes proportional to k.

4.2.4 Partial wave scattering amplitudes for power-law potentials

Let us turn now to power-law potentials for which we derived in Section 3.7.2 explicit expressions for the phase shifts in the limit $k \to 0$:

- For $l < \frac{1}{2}(s-3)$ a short range r_0 can be defined and the limiting phase shifts are given by Eq. (3.261). As this is an expression for $\tan \eta_l$ we use Eq. (4.35c) and obtain

$$f_l = \frac{1}{k} \frac{\tan \eta_l}{1 - i \tan \eta_l} \underset{k \to 0}{\simeq} -a_l \frac{2l+1}{\left[(2l+1)!!\right]^2} (ka_l)^{2l} . \tag{4.38}$$

  We see that for $ka_l \ll 1$ all partial-wave amplitudes f_l with $l \neq 0$ are small in comparison to the s-wave scattering amplitude f_0, demonstrating again that in the low-energy limit only s waves contribute to the scattering of atoms which may be traced back to the presence of the rotational barrier for all scattering processes with $l > 0$ (see Section 3.2.1). For Van der Waals potentials we find for $l = 0, 1$

$$f_0 \underset{k \to 0}{\simeq} -a \, ; \qquad f_1 \underset{k \to 0}{\simeq} -a_1 \tfrac{1}{3} k^2 a_1^2 . \tag{4.39}$$

- For $l \geq \frac{1}{2}(s-3)$ the limiting phase shifts are given by Eq. (3.263). As this is an expression for $\tan \eta_l$ we use Eq. (4.35c) and obtain

$$f_l = k^{-1} e^{i\eta_l} \sin \eta_l \underset{k \to 0}{\simeq} k^{-1} \kappa_c^2 r_c^2 \frac{3\pi(2l+3-s)!!}{(2l+5)!!} (kr_c)^{s-2} . \tag{4.40}$$

  For Van der Waals potentials ($s = 6$) we find for $l = 2$

$$f_2 \underset{k \to 0}{\simeq} r_c \tfrac{1}{100} k^3 r_c^3 \, \kappa_c^2 r_c^2 . \tag{4.41}$$

4.2.5 s-wave scattering amplitude - effective range expansion

To analyze the k dependence for scattering in the s-wave regime we use expression (4.35c) to write the s-wave scattering amplitude in the form

$$f_0 = \frac{1}{k \cot \eta_0 - ik} . \tag{4.42}$$

For (unscreened) short-range potentials we may substitute the effective range expansion for $kr_0 \ll 1$,

$$f_0 = \frac{1}{-1/a + \frac{1}{2} r_e k^2 - ik} = -\frac{a}{1 - \frac{1}{2} k^2 r_e a + ika} , \tag{4.43}$$

with r_e given by Eq. (3.234), which corresponds to Eq. (3.114) for the spherical square well. For a narrow resonance near threshold this expression becomes

$$f_0 = \frac{-1}{1/a + R^* k^2 + ik} . \tag{4.44}$$

4.2.5.1 Existence of a finite range r_0 for s-wave scattering

In this section we derive a criterion for the existence of a finite range r_0 for s-wave scattering by power-law potentials (see Section 3.7). It differs from the derivation of Section 3.7.1 because it is based on the requirement of a vanishing contribution to the scattering amplitude of distances $r > r_0$ when using the integral expression for the phase shift. We start by combining Eqs. (4.35b) and (3.37) to obtain the integral expression for the s-wave scattering amplitude,

$$f_0 = k^{-1} e^{i\eta_0} \sin\eta_0 = -k^{-1} e^{i\eta_0} \int_0^\infty U(r)\chi_0(kr) j_0(kr) r dr. \tag{4.45}$$

For the finite range to exist we require the contribution Δf_0 of distances larger than a radius r_0 to the s-wave scattering amplitude f_0 to vanish for $k \to 0$. Substituting Eq. (3.228) into Eq. (4.45) this contribution can be written as

$$\begin{aligned} \Delta f_0 &= k^{-1} (kr_c)^s e^{i\eta_0} \left(U_0/k^2\right) \int_{kr_0}^\infty \frac{1}{\varrho^s} \left[\sin\eta_0 \cos\varrho + \cos\eta_0 \sin\varrho\right] \sin\varrho d\varrho \\ &= k^{s-3} e^{i\eta_0} U_0 r_c^s \int_{kr_0}^\infty \frac{1}{\varrho^s} \left[\cos\eta_0 - \cos(2\varrho + \eta_0)\right] d\varrho. \end{aligned} \tag{4.46}$$

where $U_0 \equiv U_0(r_c) = \kappa_c^2$. Because the integral in Eq. (4.46) converges for $s > 1$, we see that the zero-energy limit of Δf_0 is determined by the prefactor k^{s-3} in front of the integral. This implies that, for s waves in the limit $k \to 0$, the contribution of distances $r > r_0$ to the scattering amplitude vanishes provided $s > 3$, which agrees with the result obtained in Section 3.7.

4.2.6 Scattering amplitudes - relation with S matrix

The S matrix was introduced in Section 3.2.3 as the ratio (apart from the sign) of the phase factors of the outgoing over the incoming spherical wave. Using Eq. (4.35a) the l-wave contribution to the S matrix can be expressed in the form

$$S_l \equiv e^{2i\eta_l} = 1 + 2ikf_l. \tag{4.47}$$

This is one of the fundamental relations of scattering theory. An important feature of the S matrix is that it enables to separate different contributions to the phase shift and to approximate these separately. Substituting Eq. () we obtain

$$S_l = 1 + \frac{2ik}{k\cot\eta_l - ik}$$

the the expression As the total phase shift is given by $\eta = \eta_0 + \eta_1 + \eta_2 + \cdots$, the S matrix can be factorized and becomes

$$S = S_0 S_1 S_2 \cdots . \tag{4.48}$$

With regard the point of implementing approximations we consider the s-wave resonance structure analyzed in Section 3.4 where we have two contributions to the phase shift, $\eta_0 = \eta_{bg} + \eta_{\text{res}}$, and the S matrix takes the form

$$S = e^{2i\eta_0} = e^{2i\eta_{bg}} e^{2i\eta_{\text{res}}} \equiv S_{bg} S_{\text{res}}. \tag{4.49}$$

Recalling the expression for the resonant phase shift - see Eq. (3.105),

$$\eta_{\text{res}} = -\arctan\left[\frac{\Gamma/2}{E - E_{\text{res}}}\right], \tag{4.50}$$

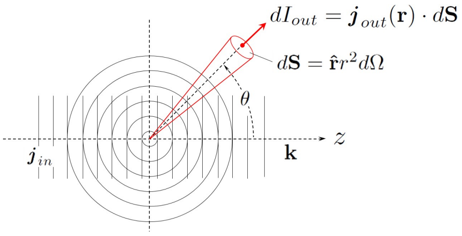

Figure 4.3: A fraction of the probability current is scattered in the direction $\hat{\mathbf{r}} = (\theta, \phi)$.

the S matrix becomes[1]

$$S_{\text{res}} = e^{2i\eta_{\text{res}}} = \frac{E - E_{\text{res}} - i\Gamma/2}{E - E_{\text{res}} + i\Gamma/2} = 1 - \frac{i\Gamma}{E - E_{\text{res}} + i\Gamma/2}. \tag{4.51}$$

Combining with Eq. (4.47) we find

$$f_{\text{res}} = -\frac{1}{k}\frac{\Gamma/2}{E - E_{\text{res}} + i\Gamma/2}. \tag{4.52}$$

The real and imaginary parts of S_{res} become

$$\operatorname{Re} S_{\text{res}}(E) = 1 - \frac{2\left(\Gamma/2\right)^2}{\left(E - E_{\text{res}}\right)^2 + \left(\Gamma/2\right)^2} \tag{4.53a}$$

$$\operatorname{Im} S_{\text{res}}(E) = -2\frac{\left(\Gamma/2\right)\left(E - E_{\text{res}}\right)}{\left(E - E_{\text{res}}\right)^2 + \left(\Gamma/2\right)^2}. \tag{4.53b}$$

In view of the derivation in Section 3.4 these expressions are valid across the low-energy resonances at energies $E = E_{\text{res}}$ for potentials with large resonance spacing ($\gamma \gg k_{\text{res}} r_0$).

Of particular importance for the quantum gases is the case of a s-wave resonance near threshold for which Eqs. (4.50)-(4.53) do *not* hold. These are the resonances caused by a weakly bound ($\kappa = \kappa_b$) or virtually bound ($\kappa = -\kappa_{vb}$) s level for which the phase shift is given by - see Section 3.4.5

$$\eta_0 = -kr_0 - \arctan ka_{\text{res}}. \tag{4.54}$$

Rather than expanding the arctangent we first factorize the S matrix and subsequently expand the background contribution to second power in k - see Eqs. (3.159). From this we find with the aid of Eq. (4.35a) for the s-wave scattering amplitude

$$f_0 = \frac{1}{2ik}\left[1 - S_0(k)\right] = -a\frac{1 + ika + \cdots}{1 + k^2\left(a - r_0\right)^2}. \tag{4.55}$$

In the limit $k \to 0$ this becomes

$$f_0 = -a. \tag{4.56}$$

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[1] Here we use the logarithmic representation of the arctangent with a real argument α,

$$\arctan \alpha = \frac{i}{2}\ln\frac{1 - i\alpha}{1 + i\alpha}.$$

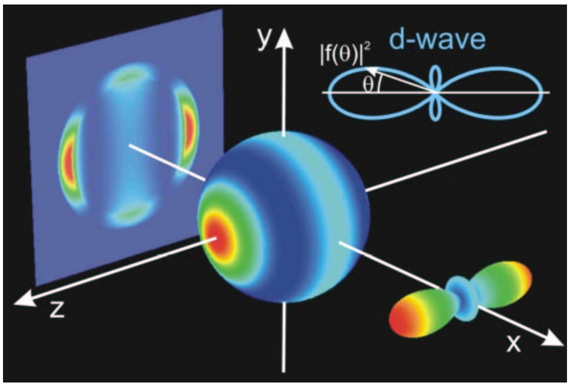

Figure 4.4: Schematic plot of a pure d-wave sphere emerging from a scattering center and its projection as can be observed with absorption imaging after collision of two ultracold clouds. Also shown are 2D and 3D angular plots of $|f(\theta)|^2$ where the length of the radius vector represents the probability of scattering in the direction of the radius vector. See further N.R. Thomas, N. Kjaergaard, P.S. Julienne, A.C. Wilson, PRL 93 (2004) 173201.

4.2.7 Differential and total cross section

To calculate the *partial cross-section* for scattering of the reduced mass within the cone of angles between θ and $\theta + d\theta$ we have to compare the probability current density $\boldsymbol{j}_{out}$ emerging from the scattering center in the direction $\hat{\mathbf{r}} = (\theta, \phi)$ with that of the incident wave j_{in}. Using the asymptotic expression for the scattered wave (4.7) the probability current density for the reduced mass at position $\mathbf{r} = (r, \theta, \phi)$ is given by (see Problem 4.5)

$$\boldsymbol{j}_{out}(\mathbf{r}) = |f(\theta)|^2 \frac{v}{r^2}\hat{\mathbf{r}}. \tag{4.57}$$

Hence, the probability current of reduced masses scattering through an infinitesimal surface element $d\mathbf{S} = \hat{\mathbf{r}}\, r^2 d\Omega$ is given by

$$dI_{out} = \boldsymbol{j}_{out}(\mathbf{r}) \cdot d\mathbf{S} = v\,|f(\theta)|^2\, d\Omega, \tag{4.58}$$

where $d\Omega$ is an infinitesimal solid angle around the direction $\hat{\mathbf{r}}$ (see Fig. 4.3). The ratio of the current $dI_{out}(\theta, \phi)$ to the current density $j_{in} = v$ of the incident wave defines the partial cross section,

$$d\sigma(\theta, \phi) = dI_{out}(\theta, \phi)/j_{in} = |f(\theta)|^2\, d\Omega, \tag{4.59}$$

for scattering in the direction (θ, ϕ). This expression can be rewritten as the cross section per unit solid angle for scattering in the direction (θ, ϕ)

$$\frac{d\sigma(\theta, \phi)}{d\Omega} = |f(\theta)|^2. \tag{4.60}$$

This quantity is called the *differential cross section.* For pure d-wave scattering we illustrate in Fig. 4.4 how this quantity can be measured by observing the radially expanding sphere of scattered atoms emerging from the scattering center after collision of two small atomic clouds. Note the characteristic d-wave distribution $|f(\theta)|^2 \sim |Y_2^0(\theta, \phi)|^2$ as follows from Eq. (4.34).

Expressing the solid angle in the form $d\Omega = \sin\theta d\theta d\phi$, the partial cross section for scattering of the reduced mass over an angle between θ and $\theta + d\theta$ is found to be

$$d\sigma(\theta) = 2\pi \sin\theta\, |f(\theta)|^2\, d\theta. \tag{4.61}$$

The circumstance that the quantity $d\sigma(\theta)/d\theta$ is zero in the forward direction, $d\sigma(\theta)/d\theta|_{\theta=0} = 0$, does not mean that there is no forward scattering; the differential cross section typically remains nonzero also in the forward direction, $d\sigma(\theta)/d\Omega|_{\theta=0} = |f(0)|^2$, as follows from Eq. (4.34). The total cross section is obtained by integration over all scattering angles,

$$\sigma = \int_0^\pi 2\pi \sin\theta \, |f(\theta)|^2 \, d\theta. \tag{4.62}$$

Substituting Eq. (4.34) for the scattering amplitude we find for the cross-section

$$\sigma = 2\pi \sum_{l,l'=0}^{\infty} (2l'+1)(2l+1) f_{l'}^* f_l \int_0^\pi P_{l'}(\cos\theta) P_l(\cos\theta) \sin\theta d\theta. \tag{4.63}$$

The cross terms drop due to the orthogonality of the Legendre polynomials,

$$\sigma = 2\pi \sum_{l=0}^{\infty} (2l+1)^2 |f_l|^2 \int_0^\pi [P_l(\cos\theta)]^2 \sin\theta d\theta, \tag{4.64}$$

which reduces with Eq. (C.46) to

$$\sigma = 4\pi \sum_{l=0}^{\infty} (2l+1)|f_l|^2 \equiv \sum_{l=0}^{\infty} \sigma_l, \tag{4.65}$$

where

$$\sigma_l = 4\pi(2l+1)|f_l|^2 \tag{4.66}$$

is called the partial cross section for l-wave scattering. Substituting Eq. (4.35b) the total cross section takes the form

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l. \tag{4.67}$$

In particular for pure s-wave scattering the cross section becomes

$$\sigma_0 = \frac{4\pi}{k^2} \sin^2 \eta_0. \tag{4.68}$$

4.2.7.1 Optical theorem and unitary limit

Substituting Eq. (4.37) into Eq. (4.67) we obtain the *optical theorem*

$$\sigma = \frac{4\pi}{k} \operatorname{Im} f(0). \tag{4.69}$$

This theorem shows that the imaginary part of the forward scattering amplitude is a measure for the loss of intensity of the incident wave as a result of the scattering. Clearly, conservation of probability assures that the scattered wave cannot represent a larger flux than the incident wave. Writing Eq. (4.67) as the sum of partial-wave cross sections, we note that the l-wave contribution to the cross section has an upper limit given by

$$\sigma_l \leq \frac{4\pi}{k^2}(2l+1). \tag{4.70}$$

This limit is called the *unitary limit*. It shows that even for a diverging scattering length the cross section remains *finite* (be it that it diverges for $k \to 0$).

Problem 4.5. Show that the current density of the scattered wave runs purely in the radial direction

$$\boldsymbol{j}_{out}(\mathbf{r}) = |f(\theta)|^2 \frac{\hbar k}{m_r r^2} \hat{\mathbf{r}} = |f(\theta)|^2 \frac{v}{r^2} \hat{\mathbf{r}}.$$

Solution. The asymptotic expression for the scattered wave is given by

$$\psi_{sc} \underset{r\to\infty}{\simeq} f(\theta)\frac{e^{ikr}}{r} \quad \text{with } 0 \leq \theta \leq \pi.$$

To calculate $\boldsymbol{j}_{out}(\mathbf{r})$ we use Eq. (2.14) for the gradient operator (note that ψ_{sc} does *not* depend on the ϕ angle),

$$\begin{aligned}\boldsymbol{j}_{out}(\mathbf{r}) &= \frac{i\hbar}{2m_r}\left(\psi_{sc}\boldsymbol{\nabla}\psi_{sc}^* - c.c.\right)\\ &= \frac{i\hbar}{2m_r}\left[\left(\frac{e^{ikr}}{r}\frac{\partial}{\partial r}\frac{e^{-ikr}}{r} - c.c.\right)|f(\theta)|^2\,\hat{\mathbf{r}} + \left(f(\theta)\frac{\partial}{\partial\theta}f^*(\theta) - c.c.\right)\frac{1}{r^3}\hat{\boldsymbol{\theta}}\right].\end{aligned}$$

The component in the $\hat{\mathbf{r}}$ direction immediately yields the desired result. To show explicitly that the component in the $\hat{\boldsymbol{\theta}}$ direction vanishes we substitute the expression for the scattering amplitude,

$$f(\theta)\frac{\partial}{\partial\theta}f^*(\theta) - c.c. = \sum_{l,l'=0}^{\infty}(2l+1)(2l'+1)P_l(\cos\theta)\frac{\partial}{\partial\theta}P_{l'}(\cos\theta)\left[f_l f_{l'}^* - f_l^* f_{l'}\right] = 0.$$

This contribution vanishes because all terms l, l' cancel against the terms l', l. □

4.2.8 s-wave cross section - dependence on scattering length

Using Eq. (4.35c) the total cross section takes the form

$$\sigma = 4\pi\sum_{l=0}^{\infty}\frac{(2l+1)}{k^2\cot^2\eta_l + k^2}. \tag{4.71}$$

Let us consider in particular the expression for the s-wave scattering cross section

$$\sigma_0 = 4\pi\frac{1}{k^2\cot^2\eta_0 + k^2}. \tag{4.72}$$

This form is particularly suited to analyze the low-energy k dependence using the effective range expansion for $k\cot\eta_0$ as expressed by Eq. (3.113),

$$\sigma_0 = 4\pi a^2\frac{1}{1 + k^2a^2(1 - r_e/a) + \cdots}. \tag{4.73}$$

Importantly, although the interaction energy (and therefore the *thermodynamics*) differs dramatically depending on the sign of the scattering length a (see Section 3.9) this has no consequences for the *collisional* aspects (such a the collision rate) because the cross section depends on the *square* of the scattering length.

4.2.8.1 Example: spherical square well

For a spherical square-well potential we obtain with the aid of Eqs. (3.128) − (3.125) for the cases $a = 0$, $a = \pm r_0$ and $|a| \gg r_0$ to leading order in kr_0 the following expressions:

- For $a = 0$ we use Eq. (3.128) and obtain for $k \to 0$ a vanishing cross section,

$$\sigma_0 = \frac{1}{12}\pi r_0^2(kr_0)^4 + \cdots. \tag{4.74}$$

- For $a = r_0$ we use $r_e = \frac{2}{3} r_0$ and obtain for $kr_0 \ll 1$ a constant cross section,

$$\sigma_0 = 4\pi a^2 \frac{1}{1 + \frac{1}{3} k^2 a^2 + \cdots} \underset{kr_0 \ll 1}{\simeq} 4\pi a^2. \tag{4.75}$$

- For $a = -r_0$ we use again $r_e = \frac{2}{3} r_0$ and obtain for $kr_0 \ll 1$ the same constant cross section,

$$\sigma_0 = 4\pi a^2 \frac{1}{1 + \frac{5}{3} k^2 a^2 + \cdots} \underset{kr_0 \ll 1}{\simeq} 4\pi a^2. \tag{4.76}$$

- For $|a| \gg r_0$ we use $r_e \simeq r_0$ and obtain for $k^2 a^2 \ll 1$ a cross section that diverges for $k \to 0$ in the limit $a \to \infty$,

$$\sigma_0 = 4\pi a^2 \frac{1}{1 + k^2 a^2 (1 - r_0/a) + \cdots} \underset{a \to \infty}{\simeq} \frac{4\pi}{k^2}. \tag{4.77}$$

  This means that, whatever the scattering length, the cross section cannot exceed the value $\sigma_0 = 4\pi/k^2$. This is the *unitarity* limited s-wave cross section.

4.2.9 s-wave cross section - relation with S matrix

Using Eq. (4.35a) we obtain for the total cross section

$$\sigma_l = \frac{\pi}{k^2}(2l+1)\left|1 - S_l(k)\right|^2. \tag{4.78}$$

Specializing to s waves this expression can be written as

$$\sigma_0 = \frac{2\pi}{k^2}\left[1 - \operatorname{Re} S_0(k)\right]. \tag{4.79}$$

For the case of a spherical square well with a resonance near threshold we substitute $\operatorname{Re} S_0$ from Eq. (3.159a) and obtain

$$\sigma_0 = 4\pi a^2 \frac{1}{1 + k^2 a^2 (1 - r_0/a)^2}. \tag{4.80}$$

For the other low-energy resonances we find with the aid of Eq. (4.53a) for the resonance contribution to the cross section

$$\sigma_0 = \frac{4\pi}{k_{\rm res}^2} \frac{(\Gamma/2)^2}{(E - E_{\rm res})^2 + (\Gamma/2)^2}. \tag{4.81}$$

Note that this expression is also obtained by using Eq. (4.68) for the cross section after substitution of the Breit-Wigner formula.

4.3 Identical atoms

In this section we turn to collisions between two atoms of the same atomic isotope. In this case the atoms are *identical* because they have the same composition of elementary particles, which implies that two conditions are satisfied:

1. it is impossible to construct a detector that can distinguish between the atoms,
2. the pair wavefunction must have a prescribed symmetry under exchange of the atoms.

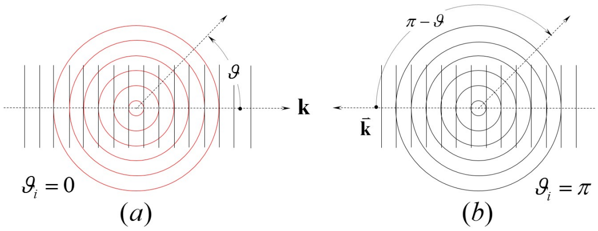

Figure 4.5: Schematic drawing of two indistinguishable scattering processes (a) and (b) for identical atoms. Indicated are the wavevectors $\mathbf{k}$ of the incident waves for the reduced mass μ moving in (a) the positive z-direction ($\theta_i = 0$) and scattering over the angle $\vartheta = \theta$; (b) the negative z-direction ($\theta_i = \pi$) and scattering over the angle $\vartheta = \pi - \theta$. The indistinguishability of the two possibilities restricts the range of distinguishable scattering angles to the interval $0 \leq \vartheta \leq \pi/2$.

Condition 1 is the same in classical physics. Condition 2 is specific for quantum mechanics: it is impossible to distinguish by position; the pair wavefunction is symmetric if the total spin of the pair is integer (bosons) and antisymmetric if the total spin of the pair is half-integer (fermions). At this point we recognize two more possibilities: the identical atoms can be in the same internal state or in different internal states. In the first case the total spin of the pair is necessarily integer and the wavefunction for the relative motion of the atoms must be either symmetric (for bosonic atoms) or anti-symmetric (for fermionic atoms). If the atoms are in different internal states neither symmetric nor anti-symmetric spin states can be excluded. The latter is a complicating factor and will be discussed in Section 4.4.

A special class of collisions between atoms in the same internal state concerns all bosonic atoms with a non-degenerate electronic ground state $^1S_0$ and zero nuclear spin; i.e., all *even* isotopes of closed shell atoms: ^{4}He, ^{20}Ne,^{22}Ne, ^{36}Ar, $\cdots$,^{40}Ar, ^{78}Kr, $\cdots$,^{86}Kr, ^{124}Xe, $\cdots$,^{134}Xe, the earth-alkalis ^{24}Mg,^{26}Mg, ^{40}Ca, $\cdots$,^{48}Ca, ^{78}Sr, $\cdots$,^{86}Sr, ^{130}Ba, $\cdots$,^{138}Ba, the transition elements ^{64}Zn, $\cdots$,^{70}Zn, ^{102}Pd, $\cdots$,^{110}Pd, ^{106}Cd, $\cdots$,^{114}Cd, ^{196}Hg, $\cdots$,^{204}Hg, and the rare earths ^{168}Yb, $\cdots$,^{176}Yb.

4.3.1 Identical atoms in the same internal state

We start the discussion of identical atoms with two of such atoms (classically we would call them 1 and 2) in the same internal state and moving freely in opposite directions with relative momentum k along the z direction as illustrated in Fig. 4.5. Since the atoms are identical and in an *eigenstate* of relative momentum their relative position is completely delocalized and we have no possibility to point to the atoms to identify them as atom 1 moving in the positive direction (to the right) and as atom 2 in the negative direction (to the left) or *vice versa.* Consequently, the direction of the reduced mass (defined for labeled atoms) can equally well be in the positive or negative z direction and probability amplitudes for these two options have to be added. In other words the wavefunction for the relative motion has to be symmetrized. As the atoms are in the same internal state, the internal state of the pair (*e.g.,* spin state) is symmetric under exchange of the atoms. In accordance, the wavefunction for the relative motion must be symmetric (+) under exchange of two bosonic atoms and anti-symmetric (−) in the case of fermionic atoms,[1]

$$\psi_{in} = e^{ikz} \pm e^{-ikz}. \tag{4.82}$$

---

[1] To keep the notation transparent we have chosen not to use the usual symmetrization prefactor $\sqrt{1/2}$. As we will do the same for subsequent symmetrization procedures concerning the relative motion this amounts to an overall change of normalization (current densities twice as large) that does not affect the results obtained for the differential and total cross section.

This corresponds to a choice of normalization in which the current density j_{in} *towards the scattering center* is equal to twice the relative velocity of the atoms, $j_{in} = 2v$, with half of j_{in} coming from the left and the other half from the right (note that the current density *with respect to the laboratory frame* is identically zero, as expected for stationary standing wave).

What happens in the presence of scattering? As long as the internal state of the atoms is conserved in the collision (i.e., for elastic collisions) we only have to consider the orbital part of the motion. When an atom is detected after scattering in the *direction* (θ, ϕ) with respect to the positive z axis (symmetry axis) it may be an atom coming from the left after scattering over the angles $\vartheta = \theta$ and $\varphi = \phi$ into the detector. Equally well it may be an atom coming from the right after scattering over the complementary angle, $\vartheta = \pi - \theta$ and $\varphi = \pi + \phi$. Since we cannot distinguish between these two processes the corresponding waves interfere and we have to add their amplitudes. In other words, in the collision we created an EPR pair.[1] As the operation $(\theta, \varphi) \to (\pi - \theta, \pi + \phi)$ amounts to interchange of the scattered atoms we require that the scattered wave is either symmetric (for bosons) or antisymmetric (for fermions) under this operation. Hence, the scattered wave must be of the following asymptotic form

$$\psi_{sc} \underset{r\to\infty}{\simeq} [f(\theta) \pm f(\pi - \theta)] e^{ikr}/r. \tag{4.83}$$

Formally the expression also depends on the position of the scattering center in the standing wave pattern but this is of no practical consequence as long as the scattering region is much larger than the de Broglie wavelength and one has to average over the pattern. This condition holds for typical scattering arrangements (for the hypothetical counter-propagating plane waves of Fig. 4.5 the scattering region even covers all space). Note that we can still use the positive exponent to define the outgoing spherical wave since (as for distinguishable atoms) both scattering partners emerge from the scattering center. Combining the symmetrized expressions for the incident and scattered wave we find for the asymptotic wavefunction of the relative motion for a pair of identical atoms

$$\psi \underset{r\to\infty}{\simeq} (e^{ikz} \pm e^{-ikz}) + [f(\theta) \pm f(\pi - \theta)] e^{ikr}/r, \tag{4.84}$$

with $+/-$ for bosonic/fermionic atoms.

Along the same lines of reasoning also the partial wave expansion for the wavefunction for the relative motion must be of the symmetrized form

$$\psi = \sum_{l=0}^{\infty} c_l (2l+1) i^l R_l(k,r) \left[P_l(\cos\theta) \pm P_l(-\cos\theta) \right], \tag{4.85}$$

again with $+/-$ for bosonic/fermionic atoms. Using the *parity rule* for the Legendre polynomials, $P_l(-u) = (-1)^l P_l(u)$ (*cf.* Section C.9), Eq. (4.85) takes the form

$$\psi = \sum_{l=0}^{\infty} c_l (2l+1) i^l R_l(k,r) \left[1 \pm (-1)^l\right] P_l(\cos\theta), \tag{4.86}$$

which corresponds to a summation over even/odd partial waves. In particular, the symmetrized incident wave can be written in the form

$$\psi_{in} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) [1 \pm (-1)^l] P_l(\cos\theta). \tag{4.87}$$

Repeating the procedure of Section 4.2 we choose the expansion coefficients c_l such that, asymptotically, the scattered wave represents a purely outgoing spherical wave. Subtracting the incident

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[1] A. Einstein, B. Podolski, N. Rosen, Phys. Rev. **47**, 777 (1935).

wave from the general solution for the distorted wave, the partial-wave expansion of the scattered wave becomes

$$\psi - \psi_{in} = \psi_{sc} = \sum_{l=0}^{\infty}(2l+1)i^l Q_l(k,r)\left[1 \pm (-1)^l\right] P_l(\cos\theta), \tag{4.88}$$

where $Q_l(k,r)$ is defined by Eq. (4.13) and takes the form of Eq. (4.16) when choosing $c_l = e^{i\eta_l}$. Being aware of the equivalent expressions (4.35) $Q_l(k,r)$ can be written as

$$Q_l(k,r) \underset{r\to\infty}{\simeq} i^{-l}k^{-1}e^{i\eta_l}\sin\eta_l\, e^{ikr}/r. \tag{4.89}$$

Substituting this equation into the partial wave expansion (4.88) we obtain for the scattered wave

$$\psi_{sc} \underset{r\to\infty}{\simeq} \frac{e^{ikr}}{kr}\sum_{l=0}^{\infty}(2l+1)e^{i\eta_l}\sin\eta_l\left[1 \pm (-1)^l\right] P_l(\cos\theta). \tag{4.90}$$

From a comparison of Eq. (4.90) with the asymptotic expression (4.83) we find that the scattering amplitude is given by a sum over even/odd partial waves for bosonic/fermionic atoms,

$$f_\pm(\theta) \equiv f(\theta) \pm f(\pi-\theta) = \frac{2}{k}\sum_{l=\text{even/odd}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l \qquad \text{(bosons/fermions)}. \tag{4.91}$$

In view of the parity of the Legendre polynomials we note that the terms of even l have even parity and the odd-l terms odd parity. Therefore, the parity of the orbital wavefunction is conserved in the collision as it should for a centrally symmetric potential.

4.3.2 Scattering amplitudes in the s-wave regime - comparing like and unlike atoms

Depending on the symmetry under permutation of the scattering partners Eq. (4.38) leads to the following expressions for the scattering amplitudes in the s-wave regime:

$$\text{unlike atoms:} \quad f(\theta) \simeq f_0 \simeq -a \tag{4.92a}$$

$$\text{identical bosons:} \quad f(\theta) + f(\pi-\theta) \simeq 2f_0 \simeq -2a \tag{4.92b}$$

$$\text{identical fermions:} \quad f(\theta) - f(\pi-\theta) \simeq 6f_1\cos\theta \simeq -2a_1\,(ka_1)^2\cos\theta. \tag{4.92c}$$

We notice that for bosons the scattering amplitude is closely related to the s-wave scattering length a introduced in Section 3.4.2. For fermions the lowest non-zero partial wave is the p-wave ($l=1$), which vanishes in the limit $k \to 0$. In practice this means that *fermionic quantum gases do not thermalize.*

4.3.3 Differential and total section

In the case of identical atoms the best we can do is determine the partial cross-section for scattering of *one of the atoms* over an angle between θ and $\theta + d\theta$. To analyze this case we start with Eq. (4.83) and calculate the asymptotic current density for the *reduced mass* to emerge from the scattering center in the direction $\hat{\mathbf{r}} = (\theta,\phi)$,

$$\frac{i\hbar}{2m_r}\left(\psi\boldsymbol{\nabla}\psi^* - \psi^*\boldsymbol{\nabla}\psi\right) = |f(\theta) \pm f(\pi-\theta)|^2\,\frac{v}{r^2}\hat{\mathbf{r}} \qquad (0 \le \theta \le \pi)\,. \tag{4.93}$$

Importantly, Eq. (4.93) gives us the correct expression for the probability current density of the reduced mass moving in the direction $\hat{\mathbf{r}}$ (taking into account that it may have come from the left or from the right). However, experimentally it is impossible to determine this direction as $\hat{\mathbf{r}} = (\theta,\phi)$

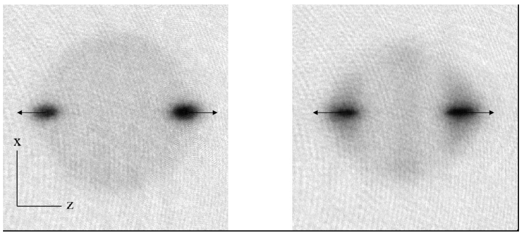

Figure 4.6: Absorption images of collision halo's of two ultracold clouds of ^{87}Rb atoms just after their collision. Left: collision energy $E/k_B = 138(4)\,\mu$K (mostly s-wave scattering), measured 2.4 ms after the collision (this corresponds to the $k \to 0$ limit discussed in this course); Right: idem but measured 0.5 ms after a collision at 1230(40) μK (mostly d-wave scattering). The field of view of the images is $\sim 0.7 \times 0.7$ mm^2. See further Ch. Buggle, *Thesis*, University of Amsterdam (2005).

and $-\hat{\mathbf{r}} = (\pi - \theta, \pi + \phi)$ are equivalent directions for identical particles. In both cases *one of the atoms* scatters in the direction $\hat{\mathbf{r}}$. Therefore, the best we can do is to determine the total current density for scattering of *one of the atoms* in the direction $\hat{\mathbf{r}}$. This quantity is obtained by adding the contributions for scattering in the directions $\hat{\mathbf{r}}$ and $-\hat{\mathbf{r}}$. To avoid double counting, the angle θ has to be restricted to the interval $0 \leq \theta \leq \pi/2$. Since $|f_\pm(\pi-\theta)|^2 = |f_\pm(\theta)|^2$ the total current density of scattered atoms at position $\mathbf{r} = (r, \theta, \phi)$ becomes

$$\boldsymbol{j}_{out}(\mathbf{r}) = 2\,|f(\theta) \pm f(\pi-\theta)|^2\,\frac{v}{r^2}\hat{\mathbf{r}} \qquad (0 \leq \theta \leq \pi/2)\,. \tag{4.94}$$

Hence, the probability current $dI_{out}(\theta,\phi) = \boldsymbol{j}_{out}(\mathbf{r}) \cdot d\mathbf{S}$ that one of the atoms scatters through a surface element $d\mathbf{S} = \hat{\mathbf{r}} r^2 d\Omega$ is given by $dI_{out}(\theta,\phi) = j_{out}(r,\theta,\phi)dS = 2v\,|f_\pm(\theta)|^2\,d\Omega$ and the partial cross section for one of the atoms to scatter in the direction (θ,ϕ) is given by

$$d\sigma_\pm\,(\theta,\phi) = dI_{out}\,(\theta,\phi)\,/j_{in} = |f(\theta) \pm f(\pi-\theta)|^2\,d\Omega, \tag{4.95}$$

where $j_{in} = 2v$ is the combined current density towards the scattering center originating from the two incident waves e^{ikz} and e^{-ikz}. Hence, the differential cross section for one of the atoms to scatter in the direction (θ,ϕ) is found to be

$$\frac{d\sigma_\pm\,(\theta,\phi)}{d\Omega} = |f(\theta) \pm f(\pi-\theta)|^2\,.$$

For the case of s-wave scattering, where $|f_+(\theta)|^2 \sim |Y_0^0(\theta,\phi)|^2 = 1/4\pi$, and for d-wave scattering, where $|f_+(\theta)|^2 \sim |Y_2^0(\theta,\phi)|^2$, this is illustrated in Fig. 4.6. For bosonic atoms p-wave scattering is absent because $f_+(\theta) = 0$ for $l = 1$.

The total cross section follows by integration over all scattering angles,

$$\sigma_\pm = \int_0^{\pi/2} 2\pi \sin\theta\,|f(\theta) \pm f(\pi-\theta)|^2\,d\theta, \tag{4.96}$$

where we used $d\Omega = 2\pi\sin\theta d\theta$. After substitution of the scattering amplitude (4.91), the cross section is given by

$$\sigma_\pm = 8\pi \sum_{l,l'=\text{even/odd}} (2l'+1)(2l+1) f_{l'}^* f_l \int_0^{\pi/2} P_{l'}(\cos\theta) P_l(\cos\theta) \sin\theta d\theta. \tag{4.97}$$

Using the orthogonality of the Legendre polynomials Eq. (4.97) becomes

$$\sigma_\pm = 8\pi \sum_{l=\text{even/odd}} (2l+1)^2 |f_l|^2 \int_0^{\pi/2} [P_l(\cos\theta)]^2 \sin\theta d\theta. \tag{4.98}$$

which reduces with Eq. (C.46) to

$$\sigma_{\pm} = 8\pi \sum_{l=\text{even/odd}} (2l+1)|f_l|^2 \equiv \sum_{l=\text{even/odd}} \sigma_l \ , \tag{4.99}$$

where

$$\sigma_l = 8\pi(2l+1)|f_l|^2 \tag{4.100}$$

is the partial cross section for l-wave scattering of identical atoms, with $|f_l|^2$ given by Eqs. (4.2.8). For a given value of l the partial cross section σ_l is found to be *either zero* or *twice as big* as for distinguishable atoms as determined by the statistical nature of the atoms. Substituting Eq. (4.35b) we obtain

$$\sigma_{\pm} = \frac{8\pi}{k^2} \sum_{l=\text{even/odd}} (2l+1)\sin^2\eta_l \qquad \text{(bosons/fermions)}. \tag{4.101}$$

4.3.4 Total cross section in the s-wave regime - comparing like and unlike atoms

In the absence of resonant enhancement the total cross-section for unlike atoms in the limit $k \to 0$ follows from Eq. (4.67) as

$$\sigma = \frac{4\pi}{k^2}\sin^2\eta_0 \underset{k\to 0}{\approx} 4\pi a^2. \tag{4.102}$$

Similar we find, starting from Eq. (4.101), for the cross section of bosons in the $k \to 0$ limit

$$\sigma = \frac{8\pi}{k^2}\sin^2\eta_0 \underset{k\to 0}{\approx} 8\pi a^2. \tag{4.103}$$

For fermions we find

$$\sigma = \frac{8\pi}{k^2}3\sin^2\eta_1 \underset{k\to 0}{\approx} 8\pi a_1^2\,(ka_1)^4\,. \tag{4.104}$$

With Eqs. (4.102)-(4.104) we have obtained the quantum mechanical underpinning of Eq. (1.3) for the zero temperature limit ($k \to 0$).

4.3.5 Ramsauer-Townsend effect

Whenever the phase of a partial wave has shifted by exactly π with respect to the phase in the plane wave expansion, the influence of the potential on the scattering pattern vanishes. This gives rise to minima in the total cross section. The contribution of the involved partial wave vanishes completely because $\sin\eta_l = 0$.

Let us look in particular to the case of bosons at relative energies such that all but the lowest two partial waves contribute. At the first s-wave Ramsauer minimum we have $\eta_0 = \pi$. Hence the d-wave contributes to the scattering in leading order. The differential cross-section becomes,

$$d\sigma(u) = \frac{8\pi}{k^2}\frac{25}{4}\sin^2\eta_2\,\left(3u^2-1\right)^2 du, \tag{4.105}$$

where we used the notation $u \equiv \cos\theta$ and substituted $P_2(u) = \left(3u^2-1\right)/2$. This expression demonstrates that the differential cross-section will vanish in directions where $u = \pm\sqrt{1/3}$; i.e., for scattering over $\theta \approx 53°$ or its complement with π. The total cross section is given by

$$\sigma = \frac{8\pi}{k^2}5\sin^2\eta_2. \tag{4.106}$$

Problem 4.6. Show that in the limit $k \to 0$ the cross-section of hard-sphere bosons of diameter a is given by $\sigma = 8\pi a^2$ and determine the value of k for which the first Ramsauer minimum is reached.

Solution. The cross-section for bosons is given by Eq. (4.101). For hard-sphere bosons the low energy phase shifts are given by Eq. (3.47),

$$\eta_l \underset{k\to 0}{\sim} -(ka)^{2l+1}.$$

Hence, for $ka \ll 1$ all but the $l=0$ phase shift vanish (to first order in ka) and

$$\sigma = \frac{8\pi}{k^2}\sin^2\eta_0 \underset{k\to 0}{\approx} 8\pi a^2. \tag{4.107}$$

For hard spheres the radius of action is the sphere diameter, $r_0 = a$, so we confirm that for $ka \ll 1$ we are in the s-wave regime. The Ramsauer minima are reached for $(\sin\eta_0)/k = 0$, i.e., for $ka = n\pi$, where $n \in \{1, 2, 3, \cdots\}$. So the lowest Ramsauer minimum is reached for $k = \pi/a$. □

Problem 4.7. Show that for low energies, where only the s-wave and d-wave contribute to the scattering of bosons in the same internal state, the partial cross section can be written in a quadratic form of the type

$$d\sigma(u) = \frac{8\pi}{k^2}\sin^2\eta_0\left[1 + 2\cos(\eta_0-\eta_2)\, f(\eta_0,\eta_2,u) + f^2(\eta_0,\eta_2,u)\right]\sin\theta d\theta,$$

where $u = \cos\theta$ with θ the scattering angle and

$$f(\eta_0,\eta_2,u) = \frac{5}{2}\frac{\sin\eta_2}{\sin\eta_0}(3u^2-1).$$

4.4 Identical atoms in different internal states

Arguably more subtle situations arise in the elastic scattering between atoms of the same isotopic species but in different atomic states. In the context of the quantum gases this usually means that both atoms are in their electronic ground state but in different hyperfine states. From a general point of view we know that the total angular momentum of the pair must be conserved in the collision. Neglecting spin-orbit interaction, this means that also the total spin must be conserved. This will be presumed throughout this section. But what is the total spin of the pair? For arbitrary hyperfine states the answer to this question can become rather elaborate. Therefore, this is postponed till Chapter 5. To reveal the essential physics we focus in the present chapter on the relatively simple case of fermionic atoms with a nuclear spin degree of freedom but in a $^1S_0$ electronic ground state (see Table 4.1). Interestingly, for atoms in different spin *eigenstates* the same expression for the elastic cross section is obtained as was found in Section 4.2.7 for distinguishable atoms. First we show this for the important case of spin-1/2 atoms (Section 4.4.1). In Section 4.4.3 it is generalized to the case of arbitrary half-integer nuclear spin.

4.4.1 Fermionic $^1S_0$ atoms in nuclear spin 1/2 eigenstates

We start with $^1S_0$ atoms with nuclear spin 1/2. The famous example is the inert gas ^{3}He but also the closed-shell rare earth ^{171}Yb and the 'group 12' atoms ^{199}Hg, ^{111}Cd and ^{113}Cd fall in this class. Let us consider collisions between two ^{3}He atoms in their electronic ground state, one with nuclear spin "up" and the other with nuclear spin "down"; i.e., in spin *eigenstates*. Experimentally, we can prepare ^{3}He pairs in such a way that the spin-up atoms always move in the positive z direction and the spin-down atoms always in the negative z direction. However, because the atoms are identical, for any pair of colliding atoms it is impossible to determine which atom carries the up spin and which the down spin. All we know is that the ^{3}He atoms are fermions and the pair wavefunction

Table 4.1: Nuclear spin of all stable isotopes of atoms with $^1S_0$ electronic ground state.

	$^1S_0$ atoms														
	He	Ne	Ar	Kr	Xe	Be	Mg	Ca	Sr	Ba	Zn	Pd	Cd	Hg	Yb
bosons	0	0	0	0	0		0	0	0	0	0	0	0	0	0
	1/2				1/2								1/2	1/2	1/2
		3/2			3/2	3/2				3/2				3/2	
fermions							5/2				5/2	5/2			5/2
								7/2							
				9/2					9/2						

must be anti-symmetric under exchange of complete atoms,[1]

$$\psi_{in} = e^{ikz}|\text{↟↡}) - e^{-ikz}|\text{↡↟}). \tag{4.108}$$

With this normalization the current density j_{in} towards the scattering center is again equal to the relative velocity of the atoms, $j_{in} = 2v$, with half of j_{in} coming from the incident wave $e^{ikz}|\text{↟↡})$ in which particle 1 carries an up spin to the right and the other half from the incident wave $e^{-ikz}|\text{↡↟})$ in which particle 1 carries a down spin to the left. To better reveal the relevant symmetries Eq. (4.108) is rewritten in the form

$$\psi_{in} = \tfrac{1}{\sqrt{2}}\left(e^{ikz} + e^{-ikz}\right)|0,0\rangle + \tfrac{1}{\sqrt{2}}\left(e^{ikz} - e^{-ikz}\right)|1,0\rangle, \tag{4.109}$$

where the state $|I, m_I\rangle$ represents the total nuclear spin state of the pair, with Clebsch-Gordan decomposition

$$|0,0\rangle = \tfrac{1}{\sqrt{2}}[|\text{↟↡}) - |\text{↡↟})]; \qquad |1,0\rangle = \tfrac{1}{\sqrt{2}}[|\text{↟↡}) + |\text{↡↟})]. \tag{4.110}$$

Note that - as expected for fermions - the symmetric spin state $|1,0\rangle$ combines with the anti-symmetric pair wavefunction for the end-over-end orbital motion and the anti-symmetric spin state $|0,0\rangle$ with the symmetric orbital pair wavefunction. We found that with two angular momenta $i_1 = i_2 = \frac{1}{2}$ the total spin $\mathbf{I} = \mathbf{i}_1 + \mathbf{i}_2$ can take the values $I \in \{0,1\}$ for "anti-parallel" and "parallel" coupling, respectively. Since the total spin of the pair is conserved in the collision this must also hold for the parity of the orbital part. Thus, the symmetric spin state $|1,0\rangle$ (anti-symmetric spin state $|0,0\rangle$) can only give rise to scattering into odd (even) partial waves and along the same lines of reasoning as developed in Section 4.3.1 we find for the corresponding scattering amplitudes

$$f_\pm(\theta) \equiv \begin{cases} f(\theta) + f(\pi - \theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{even}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I = 0) \\ f(\theta) - f(\pi - \theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{odd}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I = 1)\,. \end{cases} \tag{4.111}$$

The two scattering options are referred to as the singlet $(I = 0)$ and the triplet $(I = 1)$ channel. Note that the expression for the triplet scattering amplitude $f_-(\theta)$ coincides with the expression obtained in Section 4.3.1 for fermionic atoms in the same internal state. On closer inspection this is not surprising because two ^{3}He atoms in the same spin state carry total spin $I = 1$, $|\text{↟↟}\rangle = |1,1\rangle$ and $|\text{↡↡}\rangle = |1,-1\rangle$, which implies that these atoms also scatter through the triplet channel.

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[1] The curved brackets $|s_1, \cdots, s_N)$ are used for unsymmetrized many-body states with the convention of referring always in the same order to the states of particle $1, \cdots, N$. With the symbol ↟ we refer to a nuclear spin 1/2.

4.4.1.1 Differential and total cross section

For ^{3}He atoms in different spin states the pair-wavefunction for the scattered wave depends on the total spin I and is asymptotically given by

$$\psi_{sc} \underset{r\to\infty}{\sim} \sum_{I=0,1} \tfrac{1}{\sqrt{2}}[f(\theta) + (-1)^I f(\pi - \theta)]|I,0\rangle e^{ikr}/r, \tag{4.112}$$

From this equation the total current density of scattered atoms (in any spin state) at position $\mathbf{r} = (r, \theta, \phi)$ is found to be

$$\boldsymbol{j}_{out}(\mathbf{r}) = \sum_{I=0,1} \left| f(\theta) + (-1)^I f(\pi - \theta) \right|^2 \frac{v}{r^2} \hat{\mathbf{r}} \qquad (0 \leq \theta \leq \pi/2) \,. \tag{4.113}$$

The singlet-triplet cross terms drop due to the orthogonality of the singlet and triplet states. The probability current that one of the colliding atoms scatters through a surface element $d\mathbf{S} = \hat{\mathbf{r}} r^2 d\boldsymbol{\Omega}$ in the direction (θ, ϕ) is given by

$$dI_{out}\left(\theta, \phi\right) = j_{out}\left(r, \theta, \phi\right) dS = \sum_{I=0,1} v \left| f(\theta) + (-1)^I f(\pi - \theta) \right|^2 d\Omega.$$

The partial cross sections for scattering in the direction (θ, ϕ) is given by

$$d\sigma\left(\theta, \phi\right) = dI_{out}\left(\theta, \phi\right)/j_{in} = \tfrac{1}{2} \sum_{I=0,1} \left| f(\theta) + (-1)^I f(\pi - \theta) \right|^2 d\Omega, \tag{4.114}$$

where $j_{in} = 2v$ is the combined current density towards the scattering center originating from the two incident waves $e^{ikz}|\Uparrow\Downarrow\rangle$ and $e^{-ikz}|\Downarrow\Uparrow\rangle$. The total cross section is given by

$$\sigma = \tfrac{1}{2} \sum_{I=0,1} \sigma_I, \text{ where } \sigma_I = \int_0^{\pi/2} 2\pi \sin\theta \left| f(\theta) + (-1)^I f(\pi - \theta) \right|^2 d\theta. \tag{4.115}$$

Evaluating the integral like in Section 4.3.1 we obtain

$$\sigma_I = \begin{cases} \sigma_+ = \dfrac{8\pi}{k^2} \sum\limits_{l=\text{even}} (2l+1) \sin^2 \eta_l & (I = 0) \\ \sigma_- = \dfrac{8\pi}{k^2} \sum\limits_{l=\text{odd}} (2l+1) \sin^2 \eta_l & (I = 1) \,. \end{cases} \tag{4.116}$$

Thus the expression for the triplet $(I = 1)$ cross section $\sigma_I = \sigma_-$ is found to coincide with the expression obtained in Section 4.3.1 for two fermionic atoms in the same internal state. This is in line with the comment made below Eq. (4.111) where we point out that two ^{3}He atoms in the same spin state also carry total spin $I = 1$. Substituting Eq. (4.116) into Eq. (4.115) we establish that the elastic cross section for up-down pairs is given by the average of the even (σ_+) and odd (σ_-) parity contributions,

$$\sigma = \tfrac{1}{2}\left(\sigma_+ + \sigma_-\right) = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l. \tag{4.117}$$

Note that this expression coincides with the result obtained for distinguishable atoms. Thus we arrive at an important conclusion: in elastic collisions between identical atoms in different *eigenstates* of the nuclear spin the atoms can be treated *as if they are distinguishable by their nuclear spin state.*

4.4.2 Fermionic $^1S_0$ atoms in nuclear spin 1/2 spinor states

We continue with $^1S_0$ atoms with nuclear spin 1/2. Let us consider collisions between two ^{3}He atoms in their electronic ground state, one - as in the previous section - with nuclear spin up but the other in a given spinor state, the mixed state $\chi = a|⤉\rangle + b|⤈\rangle$, with $a = \cos\phi$ and $b = \sin\phi$. Note that the polarization direction of the mixed state is rotated by an angle 2ϕ with respect to the quantization axis. Since we are free to choose our quantization axis this case is equivalent with collisions where both atoms are in spinor states with an angle 2ϕ between their planes of polarization. Experimentally, we can prepare ^{3}He pairs in such a way that the spin up atoms always move in the positive z direction and the mixed state atoms always in the negative z direction. However, because the atoms are identical, for any pair of colliding atoms it is impossible to determine which atom carries the up spin and which the spinor. All we know is that the ^{3}He atoms are fermions and the pair wavefunction must be anti-symmetric under exchange of complete atoms,

$$\psi_{in} = e^{ikz}[a|⤉⤉) + b|⤉⤈)] - e^{-ikz}[a|⤉⤉) + b|⤈⤉)]. \tag{4.118}$$

To better reveal the relevant symmetries this expression can be rewritten in the form

$$\psi_{in} = a\left(e^{ikz} - e^{-ikz}\right)|1,1\rangle + \tfrac{1}{\sqrt{2}}b\left(e^{ikz} + e^{-ikz}\right)|0,0\rangle + \tfrac{1}{\sqrt{2}}b\left(e^{ikz} - e^{-ikz}\right)|1,0\rangle, \tag{4.119}$$

where the state $|I, m_I\rangle$ represents the total nuclear spin state of the pair. Note that the symmetric spin states $|1,1\rangle$ and $|1,0\rangle$ combine with the anti-symmetric pair wavefunction for the end-over-end orbital motion and the anti-symmetric spin state $|0,0\rangle$ with the symmetric orbital pair wavefunction. We found that with two angular momenta $i_1 = i_2 = \frac{1}{2}$ the total spin $\mathbf{I} = \mathbf{i}_1 + \mathbf{i}_2$ can take the values $I \in \{0,1\}$ for "anti-parallel" and "parallel" coupling, respectively. Since the total spin of the pair is conserved in the collision this must also hold for the parity of the orbital part. Thus, the symmetric spin states $|1,1\rangle$ and $|1,0\rangle$ (anti-symmetric spin state $|0,0\rangle$) can only give rise to scattering into odd (even) partial waves and along the same lines of reasoning as used in Section 4.3.1 we find for the corresponding scattering amplitudes

$$f_\pm(\theta) = \begin{cases} f(\theta) + f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{even}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I=0) \\ f(\theta) - f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{odd}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I=1)\,. \end{cases} \tag{4.120}$$

The two options are referred to in the present context as the singlet ($I = 0$) and the triplet ($I = 1$) channel. Note that the expression for the triplet scattering amplitude $f_-(\theta)$ coincides with the expression obtained in Section 4.3.1 for fermionic atoms in the same internal state. On closer inspection this is not surprising because two ^{3}He atoms in the same spin state carry total spin $I = 1$, $|⤉⤉\rangle = |1,1\rangle$ and $|⤈⤈\rangle = |1,-1\rangle$, which implies that these atoms also scatter through the triplet channel.

4.4.2.1 Differential and total cross section

For ^{3}He atoms in spin states of different polarizations the pair-wavefunction for the scattered wave is asymptotically given by

$$\begin{aligned}\psi_{sc} \underset{r\to\infty}{\sim} {} & a[f(\theta) - f(\pi-\theta)]|1,1\rangle e^{ikr}/r \\ & + b\sum_{I=0,1}\tfrac{1}{\sqrt{2}}[f(\theta) + (-1)^I f(\pi-\theta)]|I,0\rangle e^{ikr}/r \qquad (0 \le \theta \le \pi/2)\,.\end{aligned} \tag{4.121}$$

The total current density of scattered atoms (irrespective of the spin state) at position $\mathbf{r} = (r, \theta, \phi)$ is found to be

$$\boldsymbol{j}_{out}(\mathbf{r}) = \left(2a^2 + b^2\right) |f(\theta) - f(\pi - \theta)|^2 \frac{v}{r^2}\hat{\mathbf{r}} + b^2 |f(\theta) + f(\pi - \theta)|^2 \frac{v}{r^2}\hat{\mathbf{r}}, \tag{4.122}$$

with $0 \leq \theta \leq \pi/2$. The singlet-triplet cross terms drop due to the orthogonality of the singlet and triplet states. The probability current $dI_{out}(\theta, \phi) = j_{out}(r, \theta, \phi) dS$ that *any* of the colliding atoms scatters through a surface element $d\mathbf{S} = \hat{\mathbf{r}} r^2 d\Omega$ in the direction (θ, ϕ) is given by

$$dI_{out}(\theta, \phi) = \left(2a^2 + b^2\right) v \, |f(\theta) - f(\pi - \theta)|^2 \, d\Omega + b^2 v \, |f(\theta) + f(\pi - \theta)|^2 \, d\Omega. \tag{4.123}$$

The partial cross sections for scattering in the direction (θ, ϕ) is given by

$$\begin{aligned} d\sigma(\theta, \phi) &= dI(\theta, \phi) / j_z & (4.124)\\ &= \tfrac{1}{2}\left(2a^2 + b^2\right) |f(\theta) - f(\pi - \theta)|^2 \, d\Omega + \tfrac{1}{2} b^2 |f(\theta) + f(\pi - \theta)|^2 \, d\Omega, & (4.125) \end{aligned}$$

where $j_z = 2v$ is the total current density towards the scattering center of the incident wave. The total cross section between atoms in specified spinor states can be written as

$$\sigma = \tfrac{1}{2}(\sigma_{0,0} + \sigma_{1,1} + \sigma_{1,0}) = \tfrac{1}{4}(\sigma_+ + 3\sigma_-) + \tfrac{1}{4}(\sigma_- - \sigma_+) \cos 2\phi, \tag{4.126}$$

where $\sigma_\pm$ represents the cross sections defined by Eq. (4.96) and 2ϕ is the angle between the polarization planes of the two spinors. Using the procedure given in Section 4.3.1 we obtained $\sigma_{0,0} = \sigma_+ \sin^2 \phi$, $\sigma_{1,1} = \sigma_- \cos^2 \phi$ and $\sigma_{1,0} = \sigma_-$.

For parallel polarizations ($\phi = 0$) we regain the expression $\sigma = \sigma_-$ for scattering of atoms in the same spin state; for opposite polarizations ($2\phi = \pi$) we regain the expression $\sigma = \frac{1}{2}(\sigma_+ + \sigma_-)$ for scattering of atoms in opposite spin states; for perpendicular polarization ($2\phi = \pi/2$) we find

$$\sigma = \tfrac{1}{4}(\sigma_+ + 3\sigma_-). \tag{4.127}$$

The latter result is also obtained by averaging over all angles ($0 \leq 2\phi \leq 2\pi$). This is just the statistical average we expect for collisions in an unpolarized gas of spin 1/2 atoms, where we identify four possibilities for the initial spin configurations, $|\uparrow\uparrow\rangle, |\uparrow\downarrow), |\downarrow\uparrow)$ and $|\downarrow\downarrow\rangle$, each with equal probability. From these possibilities $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ manifestly represent triplet scattering; the other two cases yield 50/50 probability to scatter through the singlet/triplet channel. Together this results in 75% triplet and 25% singlet scattering events. Reasoning *verbatim* along these lines we find for an arbitrary angle 2ϕ between the polarization planes two possibilities, $\cos^2 \phi |\uparrow\uparrow\rangle$ and $\sin^2 \phi |\uparrow\downarrow)$. This means that the triplet and singlet scattering probabilities are given by $\sigma_- \cos^2 \phi + \frac{1}{2}\sigma_- \sin^2 \phi$ and $\frac{1}{2}\sigma_+ \sin^2 \phi$, respectively. For the cross section this yields

$$\sigma = \tfrac{1}{2}\sigma_- \left(1 + \cos^2 \phi\right) + \tfrac{1}{2}\sigma_+ \sin^2 \phi, \tag{4.128}$$

which is equivalent to Eq. (4.126), as it should.

4.4.3 Fermionic $^1S_0$ atoms with arbitrary half-integer nuclear spin

In this section we will generalize the discussion to collisions between fermionic $^1S_0$ atoms in arbitrary half-integer spin *eigenstates*.[1] Aside from the spin-1/2 systems ^{3}He, ^{111}Cd and ^{113}Cd, ^{129}Xe, ^{199}Hg and ^{171}Yb this class includes the spin-3/2 systems ^{9}Be, ^{21}Ne, ^{131}Xe, ^{135}Ba, ^{137}Ba and ^{201}Hg, the spin-5/2 systems ^{25}Mg, ^{67}Zn, ^{105}Pd and ^{173}Yb, the spin-7/2 system ^{43}Ca, and the spin-9/2 systems

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[1] All stable bosonic isotopes with $^1S_0$ electronic ground state have nuclear spin $I = 0$.

^{83}Kr and ^{87}Sr. As we are dealing with fermions the pair wavefunction must be anti-symmetric under exchange of complete atoms,

$$\psi_{in} \underset{r\to\infty}{\sim} e^{ikz}|m_1m_2) - e^{-ikz}|m_2m_1), \tag{4.129}$$

which can be rewritten in the form

$$\psi_{in} \underset{r\to\infty}{\sim} \tfrac{1}{2}\left(e^{ikz}+e^{-ikz}\right)[|m_1m_2) - |m_2m_1)] + \tfrac{1}{2}\left(e^{ikz}-e^{-ikz}\right)[|m_1m_2) + |m_2m_1)] \tag{4.130}$$

With two equal angular momenta ($i_1 = i_2$) the total spin $\mathbf{I} = \mathbf{i}_1 + \mathbf{i}_2$ takes the values $0 \leq I \leq I_{\max} = 2i_1$ and using a Clebsch-Gordan decomposition we obtain (*cf.* Problem 4.8)

$$\begin{aligned}\psi_{in} \underset{r\to\infty}{\sim} \left(e^{ikz}+e^{-ikz}\right)&\sum_{I=\text{even}}^{I_{\max}}\sum_{M=-I}^{I}|IM\rangle\langle IM|i_1i_1m_1m_2) \\ &+ \left(e^{ikz}-e^{-ikz}\right)\sum_{I=\text{odd}}^{I_{\max}}\sum_{M=-I}^{I}|IM\rangle\langle IM|i_1i_1m_1m_2).\end{aligned} \tag{4.131}$$

Note that the symmetric spin states, $|IM\rangle$ with $I =$ odd, combine with the anti-symmetric orbital pair wavefunctions; the anti-symmetric spin states, $|IM\rangle$ with $I =$ even, combine with the symmetric orbital pair wavefunctions. Since the total spin of the pair is conserved in the collision this must also hold for the parity of the orbital part. Thus, the symmetric spin states (anti-symmetric spin states) can only give rise to scattering into odd (even) partial waves and along the same lines of reasoning as used in Section 4.4.1 we find for the corresponding scattering amplitudes

$$f_\pm(\theta) = \begin{cases} f(\theta) + f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{even}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I = \text{even}) \\ f(\theta) - f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{odd}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I = \text{odd})\,. \end{cases} \tag{4.132}$$

These expressions represent a generalization of the expressions for the scattering amplitude $f_\pm(\theta)$ obtained in Section 4.4.1 for spin 1/2 fermionic atoms.

4.4.3.1 Differential and total cross section

The pair-wavefunction for the scattered wave is asymptotically given by

$$\psi_{sc} \underset{r\to\infty}{\sim} \sum_{I}^{I_{\max}}\sum_{M=-I}^{I}\langle IM|i_1i_1m_1m_2)[f(\theta)+(-1)^I f(\pi-\theta)]|I,M\rangle e^{ikr}/r, \tag{4.133}$$

The total current density of scattered atoms (irrespective of the spin state) at position $\mathbf{r} = (r,\theta,\phi)$ is found to be

$$\boldsymbol{j}_{out}(\mathbf{r}) = 2\sum_{I}^{I_{\max}}\sum_{M=-I}^{I}|(i_1i_1m_1m_2|IM\rangle|^2\left|f(\theta)+(-1)^I f(\pi-\theta)\right|^2|I,M\rangle\frac{v}{r^2}\hat{\mathbf{r}}, \tag{4.134}$$

with $0 \leq \theta \leq \pi/2$. Here we used the orthogonality of the singlet and triplet wavefunctions. The probability current $dI_{out}(\theta,\phi) = j_{out}(r,\theta,\phi)dS$ that *any* of the colliding atoms scatters through a surface element $d\mathbf{S} = \hat{\mathbf{r}}r^2d\Omega$ in the direction (θ,ϕ) is given by

$$dI_{out}(\theta,\phi) = 2\sum_{I}^{I_{\max}}\sum_{M=-I}^{I}|(i_1i_1m_1m_2|IM\rangle|^2 v\left|f(\theta)+(-1)^I f(\pi-\theta)\right|^2 d\Omega.$$

Note that any atom observed in the direction $\mathbf{\Omega}$ must originate *either* from the incident wave $e^{ikz}|\updownarrow\updownarrow)$ *or* form the incident wave $e^{-ikz}|m_1m_2)$. The partial cross sections for scattering in the direction (θ,ϕ) is given by

$$\begin{aligned} d\sigma_{m_1m_2}(\theta,\phi) &= dI_{out}(\theta,\phi)/j_z \\ &= \sum_{I}^{I_{\max}}\sum_{M=-I}^{I}|(i_1i_1m_1m_2|IM\rangle|^2\left|f(\theta)+(-1)^I f(\pi-\theta)\right|^2 d\Omega, \end{aligned} \tag{4.135}$$

where $j_z = 2v$ is the total incident current density towards the scattering center. The total cross section is given by

$$\sigma_{m_1m_2} = \sum_{I}^{I_{\max}}\sum_{M=-I}^{I}|(i_1i_1m_1m_2|IM\rangle|^2\sigma_I, \text{ where } \sigma_I = \int_0^{\pi/2} 2\pi\sin\theta\left|f(\theta)+(-1)^I f(\pi-\theta)\right|^2 d\theta. \tag{4.136}$$

Evaluating the integral like in Section 4.3.1 we obtain

$$\sigma_I = \begin{cases} \sigma_+ = \dfrac{8\pi}{k^2}\sum\limits_{l=\text{even}}(2l+1)\sin^2\eta_l & (I=\text{even}) \\ \sigma_- = \dfrac{8\pi}{k^2}\sum\limits_{l=\text{odd}}(2l+1)\sin^2\eta_l & (I=\text{odd}). \end{cases} \tag{4.137}$$

Thus the expressions for the cross sections with $I = \text{odd}$ are found to coincide with the expression obtained for σ_- in Section 4.3.1 for two fermionic atoms with the same internal state. Substituting Eq. (4.137) into Eq. (4.136) we establish that the cross section is given by the average of the even (σ_+) and odd (σ_-) parity contributions,

$$\sigma_{m_1m_2} = \sum_{I=\text{even}}^{I_{\max}}\sum_{M=-I}^{I}|(i_1i_1m_1m_2|IM\rangle|^2\sigma_- + \sum_{I=\text{odd}}^{I_{\max}}\sum_{M=-I}^{I}|(i_1i_1m_1m_2|IM\rangle|^2\sigma_+. \tag{4.138}$$

The summations both yield 1/2, therefore Eq. (4.138) reduces to

$$\sigma_{m_1m_2} = \frac{1}{2}(\sigma_- + \sigma_+) = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\eta_l \qquad \text{for } m_1 \neq m_2, \tag{4.139}$$

which coincides with Eq. (4.117) obtained in Section 4.4.1 for the special case $i_1 = i_2 = 1/2$. Hence the elastic cross section of two fermions in different spin eigenstates is given by the same expression as was obtained for distinguishable atoms.

To obtain the effective elastic cross section in an unpolarized gas we have to calculate the statistical average over all $(2i_1+1)^2$ possible initial spin configurations $\{|i_1i_1m_1m_2)\}$. From these possibilities we have $(2i_1+1)$ cases with $m_1 = m_2$ and cross section $\sigma_{m_1m_1} = \sigma_-$. The remaining $(2i_1+1)^2 - (2i_1+1) = (2i_1+1)\,2i_1$ possibilities correspond to $m_1 \neq m_2$ and cross section $\sigma_{m_1m_2} = \frac{1}{2}(\sigma_- + \sigma_+)$. Therefore, the effective elastic cross section is given by

$$\sigma = \frac{1}{(2i_1+1)^2}\sum_{m_1,m_2}\sigma_{m_1m_2} = \frac{1}{(2i_1+1)}\left[i_1\sigma_+ + (i_1+1)\,\sigma_-\right]. \tag{4.140}$$

Problem 4.8. Derive the following relation for fermions:

$$\tfrac{1}{2}\left[|i_1i_1m_1m_2) \pm |i_1i_1m_2m_1)\right] = \sum_{I=\text{odd/even}}^{2i_1}\sum_{M=-I}^{I}|IM\rangle\langle IM|i_1i_1m_1m_2).$$

Solution. Using a Clebsch-Gordan decomposition we have

$$\begin{aligned}\tfrac{1}{2}\left[|i_1 i_1 m_1 m_2) \pm |i_1 i_1 m_2 m_1)\right] &= \frac{1}{2}\sum_{I=0}^{2i_1}\sum_{M=-I}^{I} |IM\rangle \left[\langle IM|i_1 i_1 m_1 m_2) \pm \langle IM|i_1 i_1 m_2 m_1)\right] \\ &= \frac{1}{2}\sum_{I=0}^{2i_1}\sum_{M=-I}^{I} \left[1 \pm (-1)^{I-2i_1}\right] |IM\rangle\langle IM|i_1 i_1 m_1 m_2).\end{aligned}$$

Here we used the property $\langle IM|i_1 i_1 m_2 m_1) = (-1)^{I-2i_1}\langle IM|i_1 i_1 m_1 m_2)$, which becomes

$$\langle IM|i_1 i_1 m_2 m_1) = -(-1)^{I}\langle IM|i_1 i_1 m_1 m_2)$$

for fermions because $2i_1$ is odd. The latter summation can be rewritten as the requested expression.
□

5

Feshbach resonances

5.1 Introduction

In the previous chapters we only considered a single interaction potential to describe the scattering between two cold atoms. Along this potential the atoms enter and leave the scattering region elastically. However, in general the interaction potential depends on the internal states of the atoms and when during the collision the internal states change the atoms may become trapped in a bound molecular state. This is known as scattering into a *closed* channel. Similarly, the term *open* channel is used for scattering into all states in which the atoms leave the scattering region, with or without excess energy.

In this chapter we discuss how the spin dependence of the interatomic interaction gives rise to open and closed channels. The presence of *closed* channels affects the elastic collisions between atoms when their energy is close to resonant with the energy of the atoms in the incoming channel. In such a case we are dealing with a bound-state resonance embedded in the continuum of states of the open channel. Within the *Feshbach theory* one separates the resonance due to the bound state from the background contribution of the continuum. Such resonances are known in nuclear physics as Feshbach resonances [23] and in atomic physics as Fano resonances [21]. In molecular physics they give rise to *predissociation* of molecules in excited states or the inverse process [29]. In the context of ultracold gases they are of special importance as they allow *in situ* modification of the interaction between the atoms, thus effecting the *scattering length.* Whereas the scattering length is typically of the order of the Van der Waals range, $r_0 \approx 50 - 100\, a_0$, near a Feshbach resonance it can reach values exceeding interparticle separation, $a \gg 10\,000\, a_0$.

The theory of the *in situ* modification of the scattering length with the aid of a Feshbach resonance was pioneered by B.J. Verhaar and his group [68]. Although the value of the Feshbach phenomenon for the investigation of quantum gases is currently undisputed the early experiences were discouraging. The resonance enhances the duration of the collision. This also enhances the chance of molecule formation through stabilization by a third atom in a process called *three-body recombination.* In bosonic systems this results in severe atom losses as was observed in early experiments with hydrogen [61] and sodium [33]. A turn to the better came when the Feshbach resonances proved useful for suppressing recombination in gases with severe losses; i.e., in systems with a negative scattering length (e.g., ^{85}Rb [12]) or anomalously large positive scattering length (e.g., ^{133}Cs [71]). This enabled Bose-Einstein condensation of these systems as well as the formation of the first Feshbach molecules [20]. The real breakthrough came when it was found that three-body recombination is strongly suppressed in two component Fermi gases of ^{6}Li [65, 13, 35] and ^{40}K [59]. In such systems always two of the three fermions (required for recombination) have to be in the same state; Pauli exclusion will prevent a close encounter of those atoms whereas they can interact resonantly or even form a long-lived molecule with the third collision partner [56]. For comprehensive reviews see [39, 9].

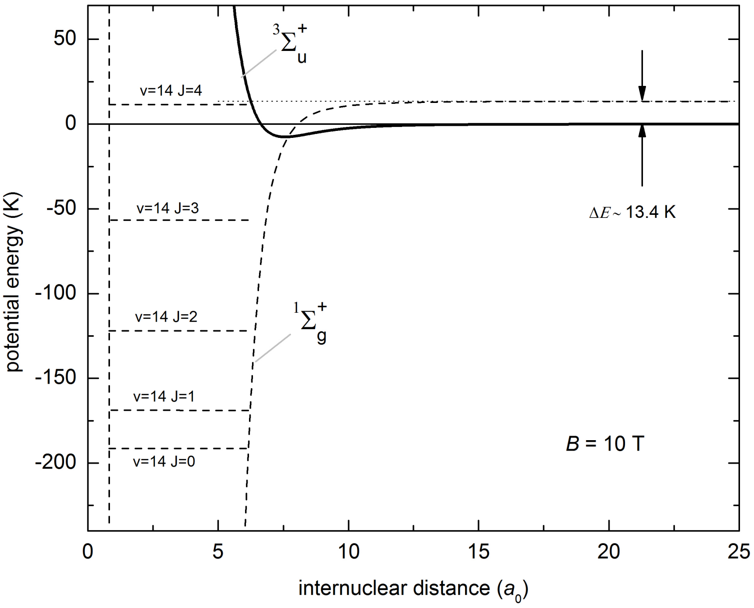

Figure 5.1: Example showing the $M_S = -1$ branch of the triplet potential $^3\Sigma_u^+$ (the anti-bonding potential - solid line) which acts between two spin-polarized hydrogen atoms. Choosing the zero of energy corresponding to two spin-polarized atoms at large separation the singlet potential $^1\Sigma_g^+$ (the bonding potential - dashed line) is shifted upwards with respect to the triplet by 13.4 K in a magnetic field of 10 T. The triplet potential is *open* for s-wave collisions, whereas the singlet is *closed* because its asymptote is energetically inaccessible in low-temperature gases.

5.2 Open and closed channels

5.2.1 Pure singlet and triplet potentials and Zeeman shifts

To introduce the concept of open and closed channels we consider two one-electron atoms in their electronic ground state. At short inter-nuclear distances, $r \lesssim 15\ a_0$, the electrons redistribute themselves in the Coulomb field of the nuclei. As the electronic motion is fast as compared to the nuclear motion, the electronic wavefunction can adapt itself adiabatically to the position of the nuclei. This effectively decouples the electronic motion from the nuclear motion and enables the Born-Oppenheimer approximation, in which the potential energy curves are calculated for a set of fixed nuclear distances (clamped nuclei) and the nuclear motion is treated as a perturbation. The potentials obtained in this way are known as adiabatic potentials.

The lowest adiabatic potentials correspond asymptotically to two atoms in their electronic ground states. These are Σ potentials because in its electronic ground state the molecule has zero orbital angular momentum ($\Lambda = 0$).[1] Depending on the symmetry of the *electronic spin state* the potentials are either of the *singlet* and *bonding* type $X^1\Sigma_g^+$, subsequently denoted by $V_s(r)$, or of the *triplet* and *anti-bonding* type $a^3\Sigma_u^+$, further denoted by $V_t(r)$. To assure anti-symmetry of Σ molecular states under exchange of the electrons, the symmetric spin state (*triplet*) must correspond to an odd (*ungerade*) orbital wavefunction. Similarly, the anti-symmetric spin state (*singlet*) must correspond to an even (*gerade*) orbital wavefunction.[2]

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[1] The molecular orbital wavefunctions are denoted by Σ, Π, Δ, $\cdots$ corresponding to $\Lambda = 0, 1, 2, \cdots$, where Λ is the quantum number of total electronic orbital angular momentum around the symmetry axis.

[2] The superscript + refers to the symmetry of the orbital wavefunction under reflection with respect to a plane containing the symmetry axis.

For our purpose it suffices to represent the interatomic interaction by an expression of the form

$$\mathcal{V}(r) = V_D(r) + J(r)\mathbf{s}_1 \cdot \mathbf{s}_2, \tag{5.1}$$

where $V_D(r) = \frac{1}{4}[V_s(r) + 3V_t(r)]$ and $J(r) = V_t(r) - V_s(r)$ are known as the direct and exchange contributions, respectively. Asymptotically, $V_D(r)$ describes the Van der Waals attractive tail. As this function decays exponentially with internuclear distance, beyond typically 15 a_0 the exchange interaction may be neglected and $V_t(r)$ and $V_s(r)$ coincide. Introducing the total electronic spin of the system, $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, with corresponding eigenstates $|s_1, s_2, S, M_S\rangle$, the spin-dependence can be written in the form $\mathbf{s}_1 \cdot \mathbf{s}_2 = \frac{1}{2}\left(\mathbf{S}^2 - \mathbf{s}_1^2 - \mathbf{s}_2^2\right)$. Because $\mathbf{s}_1^2$ and $\mathbf{s}_2^2$ only have a single eigenvalue (3/4 for spin 1/2) in the $|s_1, s_2, S, M_S\rangle$ representation, the eigenvalues may replace the operators, which results in the simplified expression

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \tfrac{1}{2}\mathbf{S}^2 - \tfrac{3}{4} \tag{5.2}$$

and allows us to write the spin states more compactly as $|S, M_S\rangle$, with $S \in \{0, 1\}$ and $-S \leq M_S \leq S$. One easily verifies that $\mathcal{V}(r)\,|0,0\rangle = V_s(r)\,|0,0\rangle$ and $\mathcal{V}(r)\,|1,M_S\rangle = V_t(r)\,|1,M_S\rangle$, thus properly yielding the singlet and triplet potentials. Equivalently, the potential $\mathcal{V}(r)$ can be replaced by

$$\mathcal{V}_S(r) \equiv V_s(r)|0,0\rangle\langle 0,0| + \sum_{M_S=-1}^{1} V_t(r)|1,M_S\rangle\langle 1,M_S|. \tag{5.3}$$

In the presence of a magnetic field the molecule experiences a spin-Zeeman interaction, which also depends on the total electron spin,

$$\mathcal{H}_Z = \gamma_e \mathbf{s}_1 \cdot \mathbf{B} + \gamma_e \mathbf{s}_2 \cdot \mathbf{B} = \gamma_e \mathbf{S} \cdot \mathbf{B}, \tag{5.4}$$

where $\gamma_e = g_s \mu_B/\hbar$ is the gyromagnetic ratio of the electron, $\gamma_e/2\pi = 2.802495364(70)$ MHz/Gauss, with $g_s \approx 2$ the electronic g-factor and μ_B the Bohr magneton. Therefore, the states with non-zero magnetic quantum number M_s will show a Zeeman effect causing the triplet potential to shift up ($M_S = 1$) or down ($M_S = -1$) with respect to the singlet potential,

$$\Delta E_Z = g_s \mu_B B M_S. \tag{5.5}$$

In Fig. 5.1 this is illustrated for the case of hydrogen in the $M_S = -1$ state and for a field of $B = 10$ T. The triplet potential is *open* for s-wave collisions in the low-energy limit, whereas the singlet is *closed* because its asymptote is energetically inaccessible in low-temperature gases. The highest bound level of the singlet potential corresponds to the $|v = 14, J = 4\rangle$ vibrational-rotational state of the H_2 molecule and has a binding energy of 0.7 ± 0.1 K. Note that the triplet potential is so shallow that it does not support any bound state. This is an anomaly caused by the light mass of the H-atom. In general both the singlet and the triplet potentials support bound states. By adjusting the magnetic field to $B \simeq 1$ T the asymptote of the triplet potential can be made resonant with the $|v = 14, J = 4\rangle$ bound state. The consequences for an electron-spin polarized gas of hydrogen atoms was observed to be enormous because even a weak triplet-singlet coupling gives rise - in the presence of a third body - to rapid recombination to molecular states.[1]

5.2.2 Radial motion in singlet and triplet potentials

To describe the relative motion in the presence of triplet and singlet potentials we ask for eigenstates of the hamiltonian

$$\mathcal{H} = \frac{1}{2\mu}\left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) + \mathcal{V}_S(r). \tag{5.6}$$

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[1] M.W. Reynolds, I. Shinkoda, R.W. Cline and W.N. Hardy, *Physical Review B*, **34** (1986) 4912.

This hamiltonian is diagonal in the representation $\{|R_l^S, l, m_l\rangle\, |s_1, s_2, S, M_S\rangle\}$, where $\langle \mathbf{r}\, |R_l^S, l, m_l\rangle = R_l^S(r) Y_l^m(\theta, \phi)$. Restricting ourselves to specific values of s_1, s_2, S and l the eigenvalues may replace the operators and the hamiltonian (5.6) takes the form of an effective hamiltonian for the radial motion

$$\mathcal{H}_{\rm rel} = \frac{p_r^2}{2\mu} + \frac{l\,(l+1)\,\hbar^2}{2\mu r^2} + V_S(r) \tag{5.7}$$

The corresponding Schrödinger equation is a radial wave equation as introduced in Chapter 2, which for given values of s_1, s_2, S and l is given by

$$R''_{S,l} + \frac{2}{r} R'_{S,l} + [\varepsilon - U_{S,l}(r)]\, R_{S,l} = 0, \tag{5.8}$$

with $U_{S,l}(r) = \left(2\mu/\hbar^2\right) \mathcal{V}_{S,l}(r)$ and

$$\mathcal{V}_{S,l}(r) = \mathcal{V}_S(r) + \frac{l\,(l+1)\,\hbar^2}{2\mu r^2} \tag{5.9}$$

represents the effective potential energy curves for given values of S and l.

For $\varepsilon > 0$ (open channel) the solutions of Eq.(5.8) are radial wavefunctions $R_{l,S}\,(k, r) = \langle r | R_{k,l}^S\rangle$ corresponding to a scattering energy in the continuum,

$$\varepsilon_k = k^2. \tag{5.10}$$

For $\varepsilon < 0$ (closed channel) the solutions of Eq.(5.8) are radial wavefunctions $R_{v,l,S}\,(r) = \langle r | R_{v,l}^S\rangle$ corresponding to the bound states $|\psi_{v,l}^S\rangle$ of energy

$$\varepsilon_{v,l}^S = -\kappa_{v,S}^2 + l\,(l+1)\,\mathcal{R}_{v,l}^S, \tag{5.11}$$

where $\mathcal{R}_{v,l}^S = \langle R_{v,l}^S | r^{-2} | R_{v,l}^S\rangle$ is the *rotational constant.* In Fig. 5.1 the five highest ro-vibrational energy levels are shown for the singlet potential of hydrogen. Note the increasing level separation.

5.2.3 Coupling of singlet and triplet channels

Aside from the electron spin also the nuclear spin $\mathbf{i}$ couples to the magnetic field $\mathbf{B}$, which is known as the nuclear Zeeman interaction,

$$\mathcal{H}_Z = -\gamma_n \mathbf{i} \cdot \mathbf{B}, \tag{5.12}$$

where $\gamma_n = g_n \mu_N/\hbar$ is the gyromagnetic ratio of the nucleus and μ_n the nuclear magneton. Thus, the states with non-zero magnetic quantum number m_i will show a Zeeman effect,

$$\Delta E_Z = g_n \mu_N B m_i. \tag{5.13}$$

A weak coupling between the triplet and singlet channels arises when including the hyperfine interaction of the atoms

$$\mathcal{H}_{\rm hf} = \left(a_{\rm hf1}/\hbar^2\right) \mathbf{i}_1 \cdot \mathbf{s}_1 + \left(a_{\rm hf2}/\hbar^2\right) \mathbf{i}_2 \cdot \mathbf{s}_2, \tag{5.14}$$

where $\mathbf{i}_1$ and $\mathbf{i}_2$ are the nuclear spins of atom 1 and 2, respectively. In general the two hyperfine coefficients differ ($a_{\rm hf1} \neq a_{\rm hf2}$). For instance, in the case of the HD molecule, the two hyperfine coefficients correspond to those of the hydrogen and deuterium atoms. Eq.(5.14) can be rewritten in the form $\mathcal{H}_{\rm hf} = \mathcal{H}_{\rm hf}^+ + \mathcal{H}_{\rm hf}^-$, where

$$\mathcal{H}_{\rm hf}^\pm = \left(a_{\rm hf1}/2\hbar^2\right) (\mathbf{s}_1 \pm \mathbf{s}_2) \cdot \mathbf{i}_1 \pm \left(a_{\rm hf2}/2\hbar^2\right) (\mathbf{s}_1 \pm \mathbf{s}_2) \cdot \mathbf{i}_2. \tag{5.15}$$

For $a_{\rm hf1} = a_{\rm hf2} = a_{\rm hf}$ these equations reduce to

$$\mathcal{H}_{\rm hf}^\pm = \left(a_{\rm hf}/2\hbar^2\right) (\mathbf{s}_1 \pm \mathbf{s}_2) \cdot (\mathbf{i}_1 \pm \mathbf{i}_2)\,. \tag{5.16}$$

Because $\mathcal{H}_{\mathrm{hf}}^{+}$ depends on the total electronic spin $\mathbf{S}=\mathbf{s}_1+\mathbf{s}_2$ it may induce changes in M_S but the total spin $\mathbf{S}$ is conserved; i.e., $\mathcal{H}_{\mathrm{hf}}^{+}$ does *not* couple singlet and triplet channels (see problem 5.1). On the other hand the term $\mathcal{H}_{\mathrm{hf}}^{-}$ does not conserve $\mathbf{S}$ but couples triplet to singlet and *vice versa* (see problem 5.2).

Problem 5.1. Show that $\mathcal{H}_{\mathrm{hf}}^{+}$ as defined in Eq.(5.15) converts between triplet states but does not induce singlet-triplet mixing,

$$\begin{aligned}\mathcal{H}_{\mathrm{hf}}^{+}=\Big(\frac{a_{\mathrm{hf1}}}{\hbar}i_{1z}+\frac{a_{\mathrm{hf2}}}{\hbar}i_{2z}\Big)\,&\frac{|1,1\rangle\langle1,1|-|1,-1\rangle\langle1,-1|}{2}\\&+\Big(\frac{a_{\mathrm{hf1}}}{\hbar}i_{1-}+\frac{a_{\mathrm{hf2}}}{\hbar}i_{2-}\Big)\,\frac{|1,1\rangle\langle1,0|+|1,0\rangle\langle1,-1|}{2\sqrt{2}}\\&\qquad+\Big(\frac{a_{\mathrm{hf1}}}{\hbar}i_{1+}+\frac{a_{\mathrm{hf2}}}{\hbar}i_{2+}\Big)\,\frac{|1,0\rangle\langle1,1|+|1,-1\rangle\langle1,0|}{2\sqrt{2}}.\end{aligned}$$

Solution. Because $\mathcal{H}_{\mathrm{hf}}^{+}$ depends on the total electronic spin $\mathbf{S}=\mathbf{s}_1+\mathbf{s}_2$ we can rewrite the inner products of Eq. (5.15) in the form

$$\mathcal{H}_{\mathrm{hf}}^{+}=\sum_{\gamma=1}^{2}\left(a_{\mathrm{hf}\gamma}/2\hbar^2\right)\left\{S_z i_{\gamma z}+\tfrac{1}{2}\left[S_+ i_{\gamma-}+S_- i_{\gamma+}\right]\right\}, \tag{5.17}$$

where $\gamma\in\{1,2\}$ is the nuclear index. Hence, although $\mathcal{H}_{\mathrm{hf}}^{+}$ may induce changes in M_S the total spin $\mathbf{S}$ is conserved.[1] □

Problem 5.2. Show that $\mathcal{H}_{\mathrm{hf}}^{-}$ as defined in Eq.(5.15) converts singlet states into triplet states and vice versa,

$$\begin{aligned}\mathcal{H}_{\mathrm{hf}}^{-}=\Big(\frac{a_{\mathrm{hf1}}}{\hbar}i_{1z}-\frac{a_{\mathrm{hf2}}}{\hbar}i_{2z}\Big)\,&\frac{|1,0\rangle\langle0,0|+|0,0\rangle\langle0,1|}{2}\\&-\Big(\frac{a_{\mathrm{hf1}}}{\hbar}i_{1-}-\frac{a_{\mathrm{hf2}}}{\hbar}i_{2-}\Big)\,\frac{|1,1\rangle\langle0,0|+|0,0\rangle\langle1,1|}{2\sqrt{2}}\\&\qquad+\Big(\frac{a_{\mathrm{hf1}}}{\hbar}i_{1+}-\frac{a_{\mathrm{hf2}}}{\hbar}i_{2+}\Big)\,\frac{|1,-1\rangle\langle0,0|+|0,0\rangle\langle1,-1|}{2\sqrt{2}}.\end{aligned}$$

Solution. We first write Eq. (5.15) in the form

$$\mathcal{H}_{\mathrm{hf}}^{-}=\sum_{\gamma=1}^{2}(-)^{\gamma-1}\left(a_{\mathrm{hf}\gamma}/2\hbar^2\right)\left\{(s_{1z}-s_{2z})\,i_{\gamma z}+\tfrac{1}{2}\left[(s_{1+}-s_{2+})\,i_{\gamma-}+(s_{1-}-s_{2-})\,i_{\gamma+}\right]\right\}. \tag{5.18}$$

Acting on the singlet state $|S,M_S\rangle=|0,0\rangle=\sqrt{1/2}\,[|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle]$ the components of the difference term $(\mathbf{s}_1-\mathbf{s}_2)$ yield

$$(s_{1z}-s_{2z})\,|0,0\rangle=\hbar\,|1,0\rangle\,;\;(s_{1+}-s_{2+})\,|0,0\rangle=-\sqrt{2}\hbar\,|1,1\rangle\,;\;(s_{1-}-s_{2-})\,|0,0\rangle=\sqrt{2}\hbar\,|1,-1\rangle \tag{5.19}$$

Acting on the triplet states non-zero results are obtained only in the cases

$$(s_{1z}-s_{2z})\,|1,0\rangle=\hbar\,|0,0\rangle\,;\;(s_{1-}-s_{2-})\,|1,1\rangle=-\sqrt{2}\hbar\,|0,0\rangle\,;\;(s_{1+}-s_{2+})\,|1,-1\rangle=\sqrt{2}\hbar\,|0,0\rangle\,. \tag{5.20}$$

Hence, the $\mathcal{H}_{\mathrm{hf}}^{-}$ operator converts triplet into singlet and *vice versa.* □

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[1] Note that $S_{\pm}\,|S,M_S\rangle=\hbar\sqrt{S\,(S+1)-M_S\,(M_S\pm1)}\,|S,M_S\pm1\rangle$.

5.2.4 Radial motion in the presence of singlet-triplet coupling

To describe the radial motion in the presence of singlet-triplet coupling we extend the effective hamiltonian for the radial motion $\mathcal{H}_{\mathrm{rel}}$ with the electronic plus nuclear Zeeman term

$$\mathcal{H}_Z = \gamma_e \mathbf{S} \cdot \mathbf{B} - \gamma_1 \mathbf{i}_1 \cdot \mathbf{B} - \gamma_2 \mathbf{i}_2 \cdot \mathbf{B}, \tag{5.21}$$

with γ_1 and γ_2 the gyromagnetic ratios of the nuclei 1 and 2, and the hyperfine terms given by Eq. (5.14),

$$\mathcal{H} = \mathcal{H}_{\mathrm{rel}} + \mathcal{H}_Z + \mathcal{H}_{\mathrm{hf}}^{+} + \mathcal{H}_{\mathrm{hf}}^{-}. \tag{5.22}$$

The first two terms of this hamiltonian are diagonal in the $\{\left|R_l^S, l, m_l\right\rangle |s_1, s_2, S, M_S\rangle |i_1, i_2, m_1, m_2\rangle\}$ representation, the third term gives rise to hyperfine coupling within the singlet and triplet manifolds separately and the last term is purely off-diagonal and non-zero only when connecting the singlet and triplet manifolds.

To find the eigenvalues of the Schrödinger equation $\mathcal{H}\,|\Psi\rangle = E\,|\Psi\rangle$ we have to solve the following secular equation

$$\det \left| \langle S', M_S', m_1', m_2'| \langle R_l^{S'}| \mathcal{H} - E \left|R_l^S\right\rangle |S, M_S, m_1, m_2\rangle \right| = 0. \tag{5.23}$$

Here we used the property of the hamiltonian (5.22) that it does not mix states of different l and m_l. Because this hamiltonian also conserves the total angular momentum projection $M_F = M_S + m_1 + m_2$ only matrix elements with $M_S' + m_1' + m_2' = M_S + m_1 + m_2$ are non-zero. Importantly, all terms of the hamiltonian (5.22) except the singlet-triplet mixing term $\mathcal{H}_{\mathrm{hf}}^{-}$ conserve S and, hence, are diagonal in the orbital part $\left|R_l^S\right\rangle$.

With regard to the mixing term $\mathcal{H}_{\mathrm{hf}}^{-}$ we first consider singlet-triplet coupling in the closed channel. This involves coupling between the bound states $|R_v^{0,l}\rangle$ (possibly quasibound states) of the singlet potential with those of the triplet potentials, $|R_{v'}^{1,l}\rangle$. Then, we can factor out the radial integral and the secular equation becomes for given l

$$\det \left| [\varepsilon_v^{S,l} + E_\sigma(B) - E]\delta_{\sigma,\sigma'} + \langle \sigma' | \mathcal{H}_{\mathrm{hf}}^{+} | \sigma \rangle \delta_{\nu,\nu'} + \langle \sigma' | \mathcal{H}_{\mathrm{hf}}^{-} | \sigma \rangle \langle R_{v'}^{S',l} | R_v^{S,l} \rangle \right| = 0. \tag{5.24}$$

Here we use the shorthand notation $|\sigma\rangle \equiv |S, M_S, m_1, m_2\rangle$ and $E_\sigma(B) = (\gamma_e M_S - \gamma_1 m_1 - \gamma_2 m_2)\,B$. Note that $\langle \sigma' | \mathcal{H}_{\mathrm{hf}}^{+} | \sigma \rangle = 0$ unless $S = S'$ and $\langle \sigma' | \mathcal{H}_{\mathrm{hf}}^{-} | \sigma \rangle = 0$ unless $S \neq S'$. The overlap integral $\langle R_{v'}^{S',l} | R_v^{S,l} \rangle$ is a so-called *Franck-Condon factor*. For most combinations of vibrational levels these are small, $\langle R_{v'}^{S',l} | R_v^{S,l} \rangle \ll 1$. Small distances (typically $r \lesssim 15a_0$) do not contribute to the overlap because the exchange dominates and the potentials (and hence also the wavefunctions) differ a lot. Further, the location of the outer turning points will generally be quite different causing also the overlap of the outer region to be small.

An important exception can happen in the presence of *asymptotically bound states* in both the singlet and triplet potential. These are states for which the outer classical turning point is found at inter-nuclear distances where the exchange is negligible (typically $r \gtrsim 15a_0$). Whenever the binding energy of an asymptotically bound state in the singlet potential $|R_{v,l}^0\rangle$ is close to resonant with the binding energy of an asymptotically bound state in the triplet potential $|R_{v',l}^1\rangle$ the Franck-Condon factor of these states is close to unity, $\langle R_{v'}^{S',l} | R_v^{S,l} \rangle \simeq 1$. More in general approximating the least-bound states ($\nu = -1$) of the singlet and triplet potentials by the halo states

$$R_{-1}^{0,0}(r) = \frac{e^{-\kappa_0 r}}{r} \quad \text{and} \quad R_{-1}^{1,0}(r) = \frac{e^{-\kappa_1 r}}{r} \tag{5.25}$$

the Franck-Condon overlap is given by

$$\langle R_{v'}^{S',l} | R_v^{S,l} \rangle = 2\frac{\sqrt{\kappa_0 \kappa_1}}{\kappa_0 + \kappa}. \tag{5.26}$$

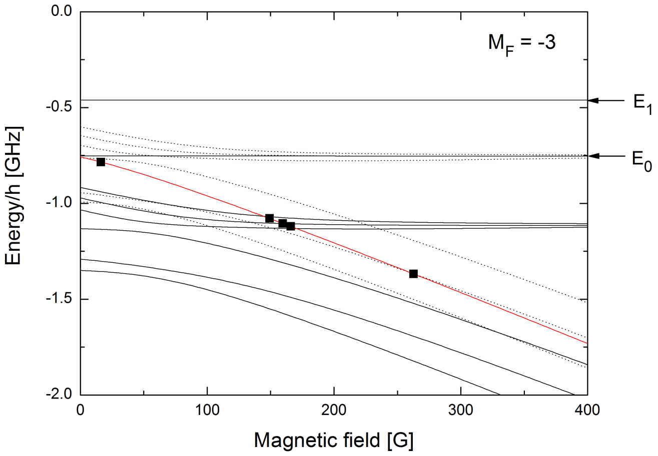

Figure 5.2: Energy levels of ^{6}Li^{40}K for the $l = 0$ (curved drawn lines) and $l = 1$ (curved dotted lines) molecular bound states as a function of magnetic field. The horizontal lines represent the highest bound states in the pure singlet (E_0) and triplet (E_1) potentials. The energy shift of the open channel of atoms in the $|^6\text{Li}; 1/2, 1/2\rangle$ and $|^{40}\text{P}; 9/2, -7/2\rangle$ states carry the experimental data points.

Solving the characteristic equation (5.24) we find that the Franck-Condon term gives rise to molecular states which are no longer pure singlet or triplet states but magnetic-field dependent singlet-triplet mixtures. A good example of nearly complete Franck-Condon overlap is the case of ^{6}Li^{40}K.[1] In Fig. 5.2 we show for this system the level shifts as a function of magnetic field for the case $M_F = M_S + m_1 + m_2 = -3$.

5.3 Coupled channels

5.3.1 Coupling to the continuum

Let us consider a collisional system with hamiltonian $\mathcal{H}_0$. For reasons of compactness of notation we turn to the reduced energy notation of Eqs. (3.6),

$$h_0 = \left(2\mu/\hbar^2\right)\mathcal{H}_0. \tag{5.27}$$

In this notation the continuum states are denoted by $|\mathbf{k}\rangle$ and satisfy the relation

$$h_0|\mathbf{k}\rangle = k^2|\mathbf{k}\rangle. \tag{5.28}$$

The bound states are denoted by $|v\rangle$ and satisfy

$$h_0|v\rangle = \varepsilon_v|v\rangle, \tag{5.29}$$

where ε_v can be positive or negative with respect to the $k = 0$ threshold. This context is sketched is illustrated in Fig. 5.3. Let us focus on the vibrational state $|v\rangle$. In the presence of a weak coupling between the open and the closed channel, $U(r) = 2\mu V(r)/\hbar^2$, where μ is the reduced mass of the colliding pair, the state $|v\rangle$ is slightly perturbed. This perturbed state is denoted by $|\varphi\rangle$,

$$|v\rangle \overset{V}{\to} |\varphi\rangle. \tag{5.30}$$

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[1] E. Wille *et al.*, *Physical Review Letters* **100,** 053201 (2008).

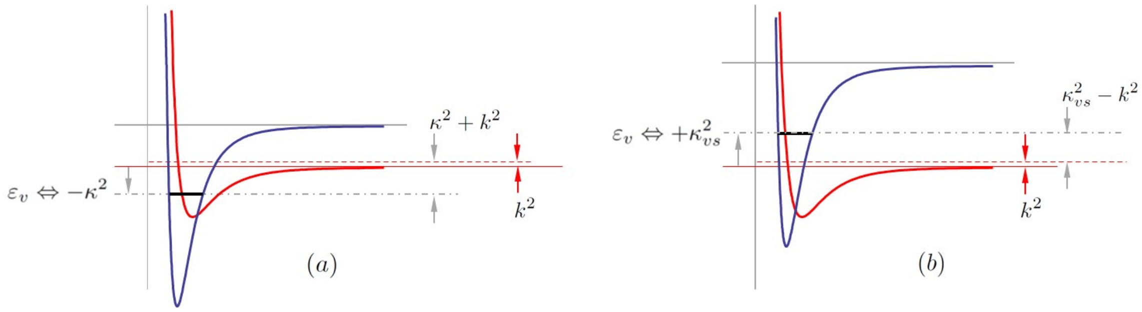

Figure 5.3: Energy levels of an *open* (red curve) and a *closed* (blue curve) channel in the absence of coupling between the channels. The energy of a continuum state in the open channel is indicated by the dashed red line at energy k^2. The energy of a bound state in the closed channel is indicated by the dashed-dotted lines for two cases: a.) bound level below threshold $\varepsilon_v \Leftrightarrow -\kappa^2 < 0$; b.) bound level above threshold $\varepsilon_v \Leftrightarrow \kappa_{vs}^2 > 0$. Note that the threshold is defined as the $k = 0$ asymptote of the open channel.

To analyze the effect of the perturbation we write the hamiltonian in the form

$$h = h_0 + \lambda U(r), \tag{5.31}$$

where the parameter λ is only introduced to keep track of the orders of the perturbation theory. As the perturbation U is supposed to be sufficiently weak we may take the limit $\lambda \to 1$ at any desired moment. The energy of the perturbed state just below the threshold can be written as

$$h|\varphi\rangle = -\kappa^2|\varphi\rangle. \tag{5.32}$$

Our task is to find the relation between ε_v and $-\kappa^2$. For purpose we express the perturbed states as a linear combination of all eigenstates, bound states as well as continuum states,

$$|\varphi\rangle = \sum_{v'} |v'\rangle\langle v'|\varphi\rangle + \int d\mathbf{k}\, |\mathbf{k}\rangle\langle\mathbf{k}|\varphi\rangle. \tag{5.33}$$

On the one hand we have

$$\langle v|h|\varphi\rangle = -\kappa^2\langle v|\varphi\rangle \tag{5.34}$$

and on the other hand

$$\langle v|h|\varphi\rangle = \sum_{v'}\langle v|h_0|v'\rangle\langle v'|\varphi\rangle + \lambda\sum_{v'}\langle v|U|v'\rangle\langle v'|\varphi\rangle \\ + \int d\mathbf{k}\,\langle v|h_0|\mathbf{k}\rangle\langle\mathbf{k}|\varphi\rangle + \lambda\int d\mathbf{k}\,\langle v|U|\mathbf{k}\rangle\langle\mathbf{k}|\varphi\rangle. \tag{5.35}$$

In view of the orthogonality of the eigenstates of h_0 we have $\langle v|h_0|v'\rangle = \varepsilon_{v'}\langle v|v'\rangle = \varepsilon_v\delta_{v,v'}$ and $\langle v|h_0|\mathbf{k}\rangle = k^2\langle v|\mathbf{k}\rangle = 0$. Furthermore, we may approximate $\langle v|U(r)|v'\rangle \simeq \delta\varepsilon_v\delta_{v,v'}$ because the coupling to the open channel only appreciably shifts the resonant level, the other bound states being too far detuned. Eliminating $\langle v|h|\varphi\rangle$ from Eqs. (5.34) and (5.35) we find to *lowest* order in λ after summing over v'

$$-\left(\varepsilon_v + \lambda\delta\varepsilon_v + \kappa^2\right)\langle v|\varphi\rangle = \lambda\int d\mathbf{k}\,\langle v|U|\mathbf{k}\rangle\langle\mathbf{k}|\varphi\rangle. \tag{5.36}$$

To evaluate the integral we search for an expression for $\langle\mathbf{k}|\varphi\rangle$. This expression is obtained by projecting the perturbed vibrational state $|\varphi\rangle$ on a continuum state $|\mathbf{k}\rangle$. We compare again two expressions

$$\langle\mathbf{k}|h|\varphi\rangle = -\kappa^2\langle\mathbf{k}|\varphi\rangle \tag{5.37}$$

and

$$\langle \mathbf{k}|h|\varphi\rangle = \sum_{v'}\langle \mathbf{k}|h_0|v'\rangle\langle v'|\varphi\rangle + \lambda\sum_{v'}\langle \mathbf{k}|U|v'\rangle\langle v'|\varphi\rangle + \int d\mathbf{k}'\langle \mathbf{k}|h_0|\mathbf{k}'\rangle\langle \mathbf{k}'|\varphi\rangle + \lambda\int d\mathbf{k}'\langle \mathbf{k}|U|\mathbf{k}'\rangle\langle \mathbf{k}'|\varphi\rangle. \quad (5.38)$$

In view of the orthogonality of the eigenstates of h_0 we have $\langle \mathbf{k}|h_0|v'\rangle = \varepsilon_{v'}\langle \mathbf{k}|v'\rangle = 0$ and $\langle \mathbf{k}|h_0|\mathbf{k}'\rangle = k'^2\delta(\mathbf{k}-\mathbf{k}')$. Furthermore, we may approximate $\langle \mathbf{k}|U(r)|\mathbf{k}'\rangle \simeq \delta\varepsilon\delta(\mathbf{k}-\mathbf{k}')$ because the coupling to the resonant level shifts all occupied continuum levels ($kr_0 \ll 1$) in a similar way. Eliminating $\langle \mathbf{k}|h|\varphi\rangle$ from Eqs. (5.37) and (5.38) we find to *lowest* order in λ after integration over $\mathbf{k}'$

$$-\left(k^2 + \lambda\delta\varepsilon + \kappa^2\right)\langle \mathbf{k}|\varphi\rangle = \lambda\sum_{v'}\langle \mathbf{k}|U|v'\rangle\langle v'|\varphi\rangle. \quad (5.39)$$

Actually, of the terms in this summation only the term $v' = v$ contributes to lowest order in λ, $\langle v|\varphi\rangle \approx 1$, whereas $|\langle v'|\varphi\rangle| \ll 1$ for $v' \neq v$. Thus, the summation is dominated by a single term,

$$-\left(k^2 + \lambda\delta\varepsilon + \kappa^2\right)\langle \mathbf{k}|\varphi\rangle = \lambda\langle \mathbf{k}|U|v\rangle\langle v|\varphi\rangle. \quad (5.40)$$

Substituting this expression into Eq. (5.36) and retaining only the terms linear in λ we find for $\lambda \to 1$

$$\varepsilon_v + \delta\varepsilon_v + \kappa^2 = \int d\mathbf{k}\frac{|\langle v|U|\mathbf{k}\rangle|^2}{(\kappa^2 + k^2)} + \cdots . \quad (5.41)$$

Since both the vibrational s level and the perturbation are centrally symmetric the integral only depends on $k = |\mathbf{k}|$,

$$u(k) \equiv \langle v|U|\mathbf{k}\rangle = \int d\mathbf{r}\, R_v^*(r)U(r)e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (5.42)$$

Furthermore, as the interaction is short range we know that $U(r)$ vanishes for $r \gg r_0$. This implies that $u(k)$ is constant for $kr_0 \ll 1$,

$$u(k) \simeq \int_0^{r_0} dr\, 4\pi r^2 R_v^*(r)U(r) \equiv u_0.$$

For $kr_0 \gg 1$, $u(k)$ averages to zero. In order not to enter in the particularities of the intermediate region we shall approximate $u(k)$ by a piece-wise constant function: $u(k) = u_0$, up to a cutoff value $k_{\max}$, and $u(k) = 0$ beyond. Within this approximation we can rewrite Eq. (5.41) in the form

$$\varepsilon_v + \delta\varepsilon_v + \kappa^2 \simeq u_0^2\int_0^{k_{\max}}\frac{4\pi k^2}{(\kappa^2 + k^2)}dk = 4\pi u_0^2\left(k_{\max} - \kappa\arctan\frac{k_{\max}}{\kappa}\right). \quad (5.43)$$

Introducing the notation

$$\varepsilon_0 = 4\pi u_0^2 k_{\max} - \delta\varepsilon_v \quad (5.44)$$

we arrive at the following relation between $\varepsilon_v - \varepsilon_0$ and κ,

$$\varepsilon_v - \varepsilon_0 = -\kappa^2 - 4\pi u_0^2\kappa\arctan\frac{k_{\max}}{\kappa}. \quad (5.45)$$

For $\kappa \to 0$ the perturbed binding energy reaches threshold and Eq. (5.45) reduces to $\varepsilon_v = \varepsilon_0$. The quantity ε_0 is called the *resonance shift.* It expresses the shift of the unperturbed energy level as a result of the coupling to the continuum. The quantity

$$\varepsilon_{res} \equiv \varepsilon_v - \varepsilon_0$$

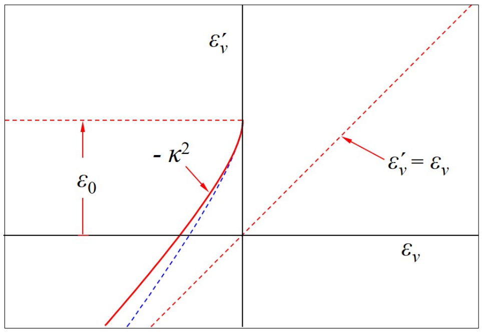

Figure 5.4: Solid curves: energy of an effective level close to threshold (ε_v') as a result of Feshbach coupling of a bound state (ε_v) in the closed channel to the continuum of states in the open channel. The energy shift is maximum (ε_0) when the unperturbed bound level (dashed red line at $\varepsilon_v' = \varepsilon_v$) reaches the threshold ($\varepsilon_v = 0$). The dashed blue curve corresponds to universal expressions which are accurate only close to the center of the resonance. In the limit of narrow resonances (weak coupling) the two curves coincide. In experiments ε_v can be shifted with the aid of a magnetic or optical field.

is called the *position* of the resonance. If the position can be tuned with an external field the position is called the *detuning* from resonance. For $\varepsilon_{res} > 0$ (positive detuning) the resonance is said to be above threshold. Similarly, for $\varepsilon_{res} < 0$ (negative detuning) the resonance position is below threshold. The shift is plotted in Fig. 5.4.

The region $\kappa r_0 \lesssim 1 \ll k_{\max} r_0$ corresponds to conditions *near threshold.* In this region the arctangent becomes insensitive for the value of $k_{\max}$. Approximating $\arctan[k_{\max}/\kappa] \simeq \pi/2$ the expression (5.45) can be written in the form

$$(\varepsilon_v - \varepsilon_0) R^* = -\kappa - R^* \kappa^2. \tag{5.46}$$

Here we introduced the characteristic length R^*, which is a measure for the Feshbach coupling strength (and $1/R^*$ for the *spectral width* of the resonance - see Section 3.5.4) [56]. As R^* has the dimension of length it might be called the *Feshbach resonance range*,

$$2\pi^2 u_0^2 \equiv 1/R^*. \tag{5.47}$$

Note that the value of $k_{\max}$ does not affect the shape of the curve; it only determines the value of the shift ε_0. The threshold region is called *universal* because the relation between ε_v and $-\kappa^2$ is independent of the details of the bound state and the r dependence of the coupling (these become important for $\kappa r_0 \gg 1$, when κ approaches $k_{\max}$). All this being the case, the parameters R^* and ε_0 can be determined by measuring the perturbed binding energy

$$\varepsilon = -\kappa^2 = -\frac{1}{4R^{*2}} \left[\sqrt{1 - 4R^{*2}(\varepsilon_v - \varepsilon_0)} - 1 \right]^2 \tag{5.48}$$

versus the unperturbed energy ε_v at negative detuning. This is, of course, only possible if the latter can be varied by some external parameter, for instance the magnetic field (see Section 5.3.2). Similarly, by measuring $-\kappa^2$, a shift in ε_0 (for instance a differential light shift between open and closed channel) can be determined if R^* and ε_v are known.

Interestingly, for $R^* = \frac{1}{2} r_0$ the r.h.s. of Eq. (5.46) has exactly the same κ dependence as Eq. (3.138). This suggests to use R^* as a generalized range characterizing some spherical potential similar to the spherical well discussed in Section 3.4. Therefore, we interpret the r.h.s. of Eq. (5.46) as the inverse of the resonance contribution of a weakly bound level κ to the scattering length of some *effective potential*:

$$a_{res} = \frac{1}{\kappa + R^* \kappa^2} = -\frac{1}{(\varepsilon_v - \varepsilon_0) R^*}. \tag{5.49}$$

The quantity

$$\varepsilon_{res} \equiv \varepsilon_v - \varepsilon_0 \tag{5.50}$$

is called the *resonance energy.* Note that a_{res} is *positive* for $\varepsilon_v < \varepsilon_0 \Leftrightarrow \varepsilon_{res} < 0$ and *negative* for $\varepsilon_v > \varepsilon_0 \Leftrightarrow \varepsilon_{res} > 0$.

We distinguish two regions for $a_{res} > 0$. For $1/R^* \ll \kappa \ll k_{\max}$ we may neglect the linear term in Eq. (5.46). This is the asymptotic region in which the binding energy scales linearly with the energy of the unperturbed level

$$\varepsilon = -\kappa^2 = \varepsilon_v - \varepsilon_0. \tag{5.51}$$

For $\kappa \ll 1/R^*$ we reach the threshold region. Near the threshold we may neglect the κ^2 term in the denominator of Eq. (5.49) and the expression for the scattering length shows the universal κ dependence, $a_{res} = 1/\kappa$. In this regime the perturbed state approaches the threshold quadratically,

$$\varepsilon = -\kappa^2 = -\left(\varepsilon_v - \varepsilon_0\right)^2 R^{*2}. \tag{5.52}$$

Furthermore, within the above interpretation we can extend the description to include virtual levels ($a_{res} < 0$) by replacing Eq. (5.49) with

$$a_{res} = -\frac{1}{\kappa_{vs} + R^*\kappa_{vs}^2} = -\frac{1}{(\varepsilon_v - \varepsilon_0)R^*}, \tag{5.53}$$

where κ_{vs}^2 corresponds to the energy of a resonance feature in the continuum.

5.3.2 Feshbach resonances induced by magnetic fields

For one-electron atoms the potentials corresponding to the open and the closed channels will show different Zeeman shifts when applying a magnetic field B. This opens the possibility of tuning of the scattering length near Feshbach resonances. Let us suppose that the differential Zeeman shift of the closed channel with respect to the asymptote of the open channel is given by the relation

$$\varepsilon_v(B) - \varepsilon_0 = (2\mu/\hbar^2)\delta\mu_M\,(B - B_0), \tag{5.54}$$

where $\delta\mu_M$ is the difference in differential magnetic moment of the two states near the resonance field B_0. Substituting these expressions into Eq. (3.208) we obtain

$$a = a_{bg} - \frac{\hbar^2}{2\mu R^*\delta\mu_M\,(B - B_0)}. \tag{5.55}$$

This expression can be brought in the well-known form

$$a = a_{bg}\left(1 - \frac{\Delta_B}{B - B_0}\right), \tag{5.56}$$

where Δ_B is called the magnetic width of the resonance, defined by

$$\Delta_B \equiv \frac{\hbar^2}{2\mu a_{bg} R^*\delta\mu_M}. \tag{5.57}$$

The binding energy as a function of magnetic field detuning is

$$\varepsilon = -\kappa^2 = -\frac{1}{r_0^2}\left(\frac{-1 + \sqrt{1 - 4\left(R^*/r_0\right)^2 (2\mu r_0^2/\hbar^2)\delta\mu_M\,(B - B_0)}}{2R^*/r_0}\right)^2$$

Note that for $a_{bg} > r_0$ the scattering length first decreases with increasing field until the resonance is reached; beyond the resonance the scattering length increases until the background value is reached (See Fig. 5.6). For $a_{bg} < 0$ this behavior is inverted.

Zeeman tuning of a Feshbach resonance is an extremely important method in experiments with ultracold gases as it allows *in situ* variation of the scattering properties of the gas. When the energy width of the resonance is large as compared to a typical value for k^2 the term *broad resonance* is used. In this case all atoms experience the same scattering length. When the resonance is narrower than k^2 the scattering length is momentum dependent and one speaks of a *narrow resonance*.

5.3.2.1 Restoring the dimensions

At this point it is appropriate to restore the dimensions. The resonance range is given by

$$R^* = \frac{1}{2\pi u_0^2} = \frac{(\hbar^2/2\mu)^2}{8\pi^2 |\langle v|V|\mathbf{k}\rangle|^2}. \tag{5.58}$$

Expressing the resonant contribution to the scattering length in terms of this quantity we find

$$a_{res} = \frac{\hbar^2}{2\mu R^*(E_v - E_0)}, \tag{5.59}$$

where

$$E_0 = \frac{2\hbar^2 k_{\max}}{\pi\mu R^*} \tag{5.60}$$

is the resonance shift. Writing the resonant contribution to the scattering length in the form

$$k_{res} a_{res} = \frac{\Gamma/2}{E_v - E_0}, \tag{5.61}$$

where $k_{res}^2 = |\varepsilon_{res}|$, the spectral width of the resonance becomes

$$\Gamma = \frac{\hbar^2 k_{res}}{\mu R^*}. \tag{5.62}$$

The magnetic width is

$$\Delta_B = \frac{\hbar^2}{2\mu a_{bg} R^* \delta\mu_M}. \tag{5.63}$$

The resonance shift is

$$E_0 = \frac{4}{\pi} k_{\max} a_{bg} \delta\mu_M \, \Delta_B. \tag{5.64}$$

The relation between Δ_B and R^* is

$$a_{bg}\delta\mu_M \Delta_B = \frac{\hbar^2}{2\mu R^*}.$$

The bound states in the closed channel correspond to singlet states and they can be Zeeman shifted with respect to $\varepsilon = 0$ asymptote of the $M_S = -1$ triplet channel with the aid of a magnetic field. A given singlet bound state at energy $E_c = \left(\hbar^2/m\right)\varepsilon_c$ will shift with respect to the triplet asymptote in accordance with

$$E_c(B) = E_c + \mu_M B,$$

where μ_M is the difference in magnetic moment of the two channels. In this particular case $\mu_M = 2\mu_B$. Replacing ε_c by $\varepsilon_c(B) = \varepsilon_c + \mu_M \left(m/\hbar^2\right) B = \mu_M \left(m/\hbar^2\right)(B - B_{res})$, where $B_{res} = -\left(\hbar^2/m\right)\varepsilon_c/\mu_M$ is the resonance field Eq. (5.94) can be written as

$$\frac{1}{r_0 - a} = \frac{1}{r_0 - a_{bg}} - \frac{B_{\gamma_{res}}}{(r_0 - a_{bg})(B - B_{res})}, \tag{5.65}$$

where we introduced $B_{\gamma_{res}} = \left(\hbar^2/m\right)\gamma_{res}\left(a_{bg} - r_0\right)/\mu_M$, a characteristic field reflecting the strength of the resonance and chosen to be *positive for* $a_{bg} > r_0$. Eq. (5.65) can be rewritten as

$$a = a_{bg}\left[1 + \frac{(r_0 - a_{bg})}{a_{bg}}\left(\frac{B_{\gamma_{res}}}{B - B_{res} + B_{\gamma_{res}}}\right)\right] = a_{bg}\left(1 - \frac{\Delta_B}{B - B_0}\right), \tag{5.66}$$

where $\Delta_B = B_{\gamma_{res}}\left(r_0 - a_{bg}\right)/a_{bg} = \left(\hbar^2/m\right)\gamma_{res}\left(a_{bg} - r_0\right)^2/a_{bg}\mu_M$ is the Feshbach resonance width, again chosen to be *positive for* $a_{bg} > r_0$, and $B_0 = B_{res} - B_{\gamma_{res}}$ the apparent Feshbach resonance field. Not surprisingly, in case of weak Feshbach coupling ($B_{\gamma_{res}} \ll B_{res}$) one has $B_0 \simeq B_{res}$ and Eq. (5.66) reduces to

$$a \simeq a_{bg}\left(1 - \frac{\Delta_B}{B - B_{res}}\right). \tag{5.67}$$

Note that for $a_{bg} > r_0$ the scattering length first decreases with increasing field until the resonance is reached; beyond the resonance the scattering length increases until the background value is reached (See Fig. 5.6). For $a_{bg} < 0$ this behavior is inverted.

Zeeman tuning of a Feshbach resonance is an extremely important method in experiments with ultracold gases as it allows *in situ* variation of the scattering properties of the gas. When the energy width of the resonance is large as compared to a typical value for k^2 the term *broad resonance* is used. In this case all atoms experience the same scattering length. When the resonance is narrower than k^2 the scattering length is momentum dependent and one speaks of a *narrow resonance*.

5.3.3 Relation to the scattering amplitude

Rather than expanding the arctangent we factorize the S matrix,

$$S_0(k) = e^{-2ika_{bg}}e^{-2ika_{res}(k)}. \tag{5.68}$$

The resonance contribution to the phase shift can be written in the form[1]

$$-2ika_{res}(k) = 2i\arctan\left[k\gamma_{res}/(\varepsilon_{res} - k^2)\right] = -\ln\left[\frac{\varepsilon_{res} - k^2 - ik\gamma_{res}}{\varepsilon_{res} - k^2 + ik\gamma_{res}}\right]. \tag{5.69}$$

Hence, we find for the resonant contribution to the S matrix

$$S_{res}(k) = \frac{\varepsilon_{res} - k^2 + ik\gamma_{res}}{\varepsilon_{res} - k^2 - ik\gamma_{res}} = 1 + \frac{2ik\gamma_{res}}{\varepsilon_{res} - k^2 - ik\gamma_{res}}. \tag{5.70}$$

Using (4.47) and (5.49/5.53) we find for the scattering amplitude [56]

$$f_{res} = -\frac{\gamma_{res}}{k^2 - \varepsilon_{res} + ik\gamma_{res}} = -\frac{1}{1/a_{res} + k^2R^* + ik}. \tag{5.71}$$

Restoring the dimensions this becomes

$$f_{res} = -\frac{1}{k_{res}}\frac{\Gamma/2}{E - E_{res} + i(k/k_{res})(\Gamma/2)}. \tag{5.72}$$

---

[1] Here we use the logarithmic representation of the arctangent with a real argument α,

$$\arctan\alpha = \frac{i}{2}\ln\frac{1 - i\alpha}{1 + i\alpha}.$$

5.3.4 Pure singlet and triplet potentials modeled by spherical square wells

Let us model a two channel system with square well potentials like in section 3.4.2, with the triplet potential represented by a square well of range r_0 shown as the solid line in Fig. 5.5, with $V_t(r) = -\kappa_o^2$ for $r \le r_0$ and $V_t(r) = 0$ for $r > r_0$; i.e., *open* for s-wave collisions at energy $\varepsilon = k^2$. Similarly, the singlet potential is represented by a square well of the same range r_0, the dashed gray line in Fig. 5.5, with $V_s(r) = -\kappa_c^2$ for $r \le r_0$, *measured relative to the asymptote of the triplet potential* at $\varepsilon = 0$ and $V_s(r) \gg k^2$ for $r > r_0$; i.e., at the energy $\varepsilon = k^2$ only supporting *bound* states because its asymptotic energy is much higher than the collision energy. In the present example pure triplet and singlet potentials are associated with *open* and *closed* s-wave scattering channels, respectively.

For the triplet potential the radial wave function is given by Eq. (3.69). The full radial wavefunction, including spin part, describing the motion in the open channel is written as

$$|\psi_o\rangle = \frac{\sin(kr+\eta_0)}{kr}\,|1,m_S\rangle \qquad \text{for } r \ge r_0 \tag{5.73a}$$

$$|\psi_o\rangle = \frac{\sin K_+ r}{K_+ r}\,|1,m_S\rangle \qquad \text{for } r < r_0 \tag{5.73b}$$

where $K_+ = \sqrt{\kappa_o^2 + k^2}$ is the wavenumber of the relative motion.

The singlet potential only has bound-state radial wave functions with the full wavefunction describing the motion in the closed channel being written as[1]

$$|\psi_c\rangle = 0 \qquad \text{for } r \ge r_0 \tag{5.74a}$$

$$|\psi_c\rangle = \frac{\sin K_- r}{K_- r}\,|0,0\rangle \qquad \text{for } r < r_0. \tag{5.74b}$$

Bound states occur for $K_- r_0 = n\pi = q_n r_0$; i.e., for energies $\varepsilon_n = q_n^2$ with respect to the potential bottom. We have $K_- = \sqrt{\kappa_c^2 + k^2}$ for the wavenumber of the relative motion at the collision energy $\varepsilon = k^2$. where $V_s(r) = -\kappa_c^2$ for $r < r_0$ corresponds to the depth of the singlet potential (see Fig. 5.5). The energy $\varepsilon_c = \varepsilon_n - \kappa_c^2 - k^2$ defines the energy of the n-th bound state of the closed channel *relative to* $\varepsilon = k^2$ and can be positive or negative.

5.3.5 Coupling between open and closed channels

In this section we consider the case of a weak coupling Ω between the open and the closed channel.[2] In the presence of this coupling the interaction operator of the previous section takes the form

$$U(r) = -\kappa_o^2\,|1,m_S\rangle\langle 1,m_S| - \kappa_c^2\,|0,0\rangle\langle 0,0| + \Omega\,\{|0,0\rangle\langle 1,m_S| + |1,m_S\rangle\langle 0,0|\} \qquad \text{for } r < r_0 \tag{5.75}$$

with $U(r) = 0$ for $r \ge r_0$. Here we used the definition $U(r) \equiv \left(2\mu/\hbar^2\right)\mathcal{V}(r)$. The coupling will mix the eigenstates of the uncoupled hamiltonian into new eigenstates $|\psi_\pm\rangle$ and cause the wavenumbers $K_\pm$ to shift to new values which we shall denote by $q_\pm$.

Turning to distances within the well ($r < r_0$) we note that for arbitrary triplet-singlet mixtures the solutions of the corresponding 1D-Schrödinger equation

$$\left[-\nabla_r^2 + U(r)\right]|\chi\rangle = \varepsilon\,|\chi\rangle \tag{5.76}$$

should be of the form

$$|\chi\rangle = A\sin qr\,\{\cos\theta\,|1,m_S\rangle + \sin\theta\,|0,0\rangle\} \qquad \text{for } r < r_0 \tag{5.77a}$$

$$|\chi\rangle = \sin(kr_0+\eta_0)\,|1,m_S\rangle \qquad \text{for } r \ge r_0. \tag{5.77b}$$

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[1] Here we presume for simplicity $V_t(r) \to \infty$ for $r \ge r_0$.

[2] See Cheng Chin, *cond-mat*/0506313 (2005).

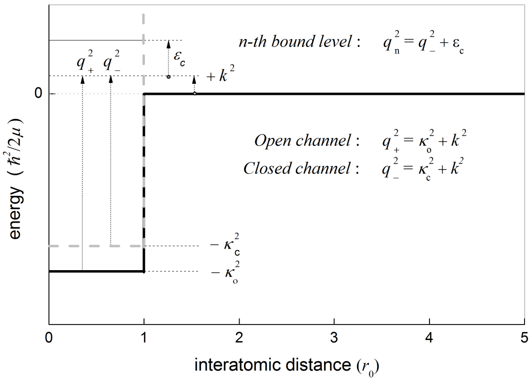

Figure 5.5: Plot of the potentials corresponding to the open (black solid line) and closed (gray dashed line) channel with related notation. The asymptote of the closed channel is presumed to be at a high positive energy and is not shown in this figure.

Here the coupling angle θ defines the spin mixture of the coupled states such that the spin state remains normalized. For $\theta = 0$ the wavenumber q corresponds to the pure triplet value ($q = K_+$) and with increasing θ the wavenumber crosses over to the pure singlet value $q = K_-$ at $\theta = \pi/2$.

Substituting Eq. (5.77a) into the 1D-Schrödinger equation we obtain two coupled equations

$$\langle 1, m_S| \left[-\nabla_r^2 + U(r) - k^2\right] |\chi\rangle = A \sin qr \left\{ \left[q^2 - \kappa_o^2 - k^2\right] \cos\theta + \Omega \sin\theta \right\} = 0 \tag{5.78a}$$

$$\langle 0, 0| \left[-\nabla_r^2 + U(r) - k^2\right] |\chi\rangle = A \sin qr \left\{ \Omega \cos\theta + \left[q^2 - \kappa_c^2 - k^2\right] \sin\theta \right\} = 0. \tag{5.78b}$$

The solutions are obtained by solving the secular equation

$$\begin{vmatrix} \left[q^2 - \kappa_o^2 - k^2\right] & \Omega \\ \Omega & \left[q^2 - \kappa_c^2 - k^2\right] \end{vmatrix} = 0, \tag{5.79}$$

which amounts to solving a quadratic equation in $\left(q^2 - k^2\right)$ and results in

$$q_\pm^2 = k^2 + \frac{1}{2}\left(\kappa_o^2 + \kappa_c^2\right) \pm \frac{1}{2}\sqrt{\left(\kappa_o^2 - \kappa_c^2\right)^2 + 4\Omega^2}. \tag{5.80}$$

For weak coupling (i.e., for $\Omega \ll \kappa_o^2, \kappa_c^2$ and $\left|\kappa_o^2 - \kappa_c^2\right|$) and presuming $\kappa_o^2 - \kappa_c^2 > 0$ as in Fig. 5.5 the two solutions can be expressed in terms of shifts with respect to the unperturbed wavenumbers

$$q_\pm^2 = K_\pm^2 \pm \frac{\Omega^2}{\left(\kappa_o^2 - \kappa_c^2\right)} + \cdots . \tag{5.81}$$

Note that the coupling makes the deepest well deeper and the shallowest well shallower.

The eigenstates corresponding to the new eigenvalues $q_\pm$ can be written as

$$|\chi_\pm\rangle = A_\pm \sin q_\pm r \, |\pm\rangle , \tag{5.82}$$

where we introduced the notation $|\pm\rangle = \cos\theta_\pm |1, m_S\rangle + \sin\theta_\pm |0, 0\rangle$. To establish how $\theta_\pm$ depends on the coupling Ω we return to Eqs.(5.78) and notice that these equations should hold for arbitrary values of $r \le r_0$. Using the upper equation to fix θ_+ and the lower equation to fix θ_- we find for the limit of weak coupling

$$\tan\theta_+ = \cot\theta_- = -\frac{q_\pm^2 - K_\pm^2}{\Omega} \simeq -\frac{\Omega}{\left(\kappa_o^2 - \kappa_c^2\right)}. \tag{5.83}$$

Hence for weak coupling the coupling angles satisfy the relation $\theta_+ = (n+1/2)\,\pi - \theta_- \equiv \theta$ and the spin states are given by

$$|+\rangle = +\cos\theta\,|1,m_S\rangle + \sin\theta\,|0,0\rangle \tag{5.84a}$$

$$|-\rangle = -\sin\theta\,|1,m_S\rangle + \cos\theta\,|0,0\rangle\,. \tag{5.84b}$$

Having established the effect of the coupling Ω on both $q_\pm$ and $\theta_\pm$ we are in a position to write down the general solution of the radial wave equation for $r \le r_0$,

$$|\psi\rangle = A_+\frac{\sin q_+ r}{q_+ r}\,|+\rangle + A_-\frac{\sin q_- r}{q_- r}\,|-\rangle\,. \tag{5.85}$$

To fully pin down the wavefunction and to obtain the phase shift in the presence of the coupling we have to impose onto $|\psi\rangle$ the boundary conditions at $r = r_0$. Because for $r \ge r_0$ the wavefunction is a pure triplet state we rewrite Eq. (5.85) in the form $|\psi(r)\rangle = \psi_t(r)\,|1,m_S\rangle + \psi_s(r)\,|0,0\rangle$, expressing the effect of the coupling on the triplet and singlet amplitudes,

$$\begin{aligned}|\psi(r)\rangle = &\left\{A_+\cos\theta\frac{\sin q_+ r}{q_+ r} - A_-\sin\theta\frac{\sin q_- r}{q_- r}\right\}|1,m_S\rangle + \\ &+\left\{A_+\sin\theta\frac{\sin q_+ r}{q_+ r} + A_-\cos\theta\frac{\sin q_- r}{q_- r}\right\}|0,0\rangle\,.\end{aligned} \tag{5.86}$$

We notice that the amplitudes $\psi_t(r)$ and $\psi_s(r)$ consist of two terms, one term displaying the spatial dynamics of the $|\psi_+(r)\rangle$ eigenstate of the coupled system and another term doing the same for the $|\psi_-(r)\rangle$ state.

At the boundary the singlet amplitude $\psi_s(r)$ should vanish, which implies the condition

$$\frac{A_-}{A_+} = -\frac{q_-\sin q_+ r_0}{q_+\sin q_- r_0}\tan\theta. \tag{5.87}$$

Further, the amplitude $\psi_t(r)$ of the triplet component should be continuous in $r = r_0$, which implies

$$\psi_t(r_0) = \frac{\sin k(r_0-a)}{kr_0} = A_+\left\{\cos\theta\frac{\sin q_+ r_0}{q_+ r_0} - \frac{A_-}{A_+}\sin\theta\frac{\sin q_- r_0}{q_- r_0}\right\}. \tag{5.88}$$

In combination with Eq. (5.87) this equation can be rewritten in a form defining the A_+ or A_- coefficients independently,

$$\frac{\sin(kr_0+\eta_0)}{kr_0} = \frac{\sin q_+ r_0}{q_+ r_0}\frac{A_+}{\cos\theta} = -\frac{\sin q_- r_0}{q_- r_0}\frac{A_-}{\sin\theta}. \tag{5.89}$$

Using this result in imposing continuity on the logarithmic derivative $\psi_t'(r)/\psi_t(r)$ of the triplet amplitude in $r = r_0$ we obtain

$$k\cot(kr_0+\eta_0) = q_+\cot q_+ r_0\cos^2\theta + q_-\cot q_- r_0\sin^2\theta \equiv Q_+ + Q_- = Q, \tag{5.90}$$

which reduces in the limit $k \to 0$ to

$$\frac{1}{r_0-a} = Q_+ + Q_-. \tag{5.91}$$

The first term on the r.h.s. gives the contribution of the triplet channel to the scattering length. As this is the open channel it is only marginally affected by the weak coupling to the closed channel. Comparing with Eq. (3.74) and approximating $\cos^2\theta \simeq 1$ and $q_+ \simeq K_+$ this term is written as

$$Q_+ = \frac{q_+\cos^2\theta}{\tan q_+ r_0} \simeq \frac{1}{r_0 - a_{bg}}, \tag{5.92}$$

where a_{bg} is known as the *background scattering length.* To first approximation a_{bg} simply equals the scattering length in the absence of the coupling.

The second term on the r.h.s. of Eq. (5.91) is the contribution of the closed channel. In general this term will be small because the coupling angle θ is small in the limit of weak coupling. However, an important exception occurs for $q_- r_0 = n\pi$, when this term diverges. This happens when a bound state of the closed channel is resonant with the collision energy $\varepsilon = k^2$ in the open channel. Defining ε_c as the energy of the n-th bound state *relative to* $\varepsilon = k^2$, the resonance condition for this state can be written as $q_n r_0 = n\pi = r_0\sqrt{\kappa_c^2 + k^2 + \varepsilon_c}$. For $|\varepsilon_c| \ll \kappa_c^2 + k^2$ this enables the expansion $q_- = \sqrt{\kappa_c^2 + k^2} \simeq q_n \left(1 - \varepsilon_c/2q_n^2 + \cdots\right)$. In accordance, the denominator of the second term of Eq. (5.91) can be expanded as $\tan q_- r_0 \simeq -\varepsilon_c r_0/2q_n$ and approximating $q_- \simeq q_n \simeq \kappa_c$ we obtain

$$Q_- = \frac{q_- \sin^2\theta}{\tan q_- r_0} \simeq -\frac{2\kappa_c^2\theta^2}{\varepsilon_c r_0}. \tag{5.93}$$

Thus, combining Eqs.(5.92) and (5.93), we arrive at the following important expression for the scattering length:

$$\frac{1}{r_0 - a} = \frac{1}{r_0 - a_{bg}} - \frac{\gamma_{res}}{\varepsilon_c}, \tag{5.94}$$

where $\Gamma = 4\kappa_c^2\theta^2/r_0$ is known as the *Feshbach coupling strength.* Eq. (5.94) shows that the scattering length diverges whenever ε_c is small. Hence, the divergence occurs whenever the coupling connects the open channel to a resonant level in the closed channel. This resonance phenomenon is known as a *Feshbach resonance.*

5.3.6 Feshbach resonances

In this section we characterize Feshbach resonances in a system of one closed and one open channel using the model potentials of the previous section. As a starting point we note that resonances occur whenever

$$k\cot\eta_0 = 0 \Leftrightarrow \eta_0 = (n + \tfrac{1}{2})\pi. \tag{5.95}$$

Indeed, in this case the scattering amplitude diverges in accordance with the unitary limit,

$$f_0 = \frac{1}{k\cot\eta_0 - ik} = -\frac{1}{ik} \tag{5.96}$$

Our first task is to obtain a criterion for the occurrence of Feshbach resonances. Writing the boundary condition (5.90) in the form

$$\eta_0 \simeq -kr_0 + \tan^{-1}\frac{k}{Q_+ + Q_-} \tag{5.97}$$

We can expand $q_-\cot q_- r_0$ around the points of zero crossing. Writing $q_- = [\kappa_c^2 + (k_{\rm res} + \delta k)^2]^{1/2}$, where $\delta k = k - k_{\rm res}$, we have for $|\delta k| k_{\rm res} \ll Q_{\rm res}^2 \equiv \kappa_c^2 + k_{\rm res}^2$

$$q_- \simeq [\kappa_0^2 + k_{\rm res}^2 + 2\delta k\, k_{\rm res}]^{1/2} \simeq Q_{\rm res} + \delta k\, k_{\rm res}/Q_{\rm res}. \tag{5.98}$$

Hence, close to the zero crossings $\left(|\delta k| k_{\rm res} \ll Q_{\rm res}^2\right)$ we may approximate $q_- \simeq Q_{\rm res}$ and obtain

$$\frac{k}{Q_+ + Q_-} \simeq -\frac{1}{Q_+ + \delta k\, r_0\theta^2} \simeq \frac{-\left(k + k_{\rm res}\right)}{Q_+ + (k^2 - k_{\rm res}^2)r_0}. \tag{5.99}$$

Using this expression the resonant phase shift can be written as a function of the collision energy $E = \hbar^2 k^2/2\mu$

$$\tan\eta_{\rm res} = \frac{-\Gamma/2}{\delta E_{\rm res} + E - E_{\rm res}}, \tag{5.100}$$

where $\Gamma(k)=\hbar^2\left(k+k_{\mathrm{res}}\right)/(\mu r_0\sin\theta^2)$ is called the *width* and $E_{\mathrm{res}}-\delta E_{\mathrm{res}}=\hbar^2k_{\mathrm{res}}^2/2\mu-\delta E_{\mathrm{res}}$ the *position*

$$\frac{\hbar^2\left(k+k_{\mathrm{res}}\right)}{2\mu r_0}\frac{r_0}{(r_0-a)}$$

we can apply the angle-addition formula for the tangent. Restricting ourselves to slow collisions ($kr_0\ll 1$) the boundary condition becomes

$$k\cot\eta_0=\frac{1}{r_0}\frac{Qr_0+k^2r_0^2+\cdots}{1+k^2r_0^2-(Qr_0+k^2r_0^2)(1+\frac{1}{3}k^2r_0^2+\cdots)}. \tag{5.101}$$

For simplicity we restrict ourselves in the rest of this section to cases without resonance structure in the open channel; i.e., $Q_+r_0\simeq 1$ for $kr_0\ll 1$. Comparing Eqs. (5.95) and (5.97) the criterion for the occurrence of a Feshbach resonance is found to be

$$Qr_0+k^2r_0^2\simeq 1+Q_-r_0=0. \tag{5.102}$$

Dividing Eq. (5.101) in numerator and denominator by $\left(Q+k^2r_0+\cdots\right)$ the boundary condition takes the form

$$k\cot\eta_0=\frac{1}{r_0}\frac{1}{a_{res}(k)-r_0(1+\frac{1}{3}k^2r_0^2+\cdots)}, \tag{5.103}$$

where $a_{res}(k)$ is the k-dependent resonant contribution to the scattering length

$$a_{res}(k)=\frac{r_0}{1+Q_-r_0}. \tag{5.104}$$

In this notation the scattering amplitude and the cross section are given by

$$f_0=\frac{a_{res}(k)-r_0(1+\frac{1}{3}k^2r_0^2+\cdots)}{1-ik[a_{res}(k)-r_0]} \tag{5.105a}$$

$$\sigma(k)=4\pi\frac{[a_{res}(k)-r_0]^2}{1+k^2[a_{res}(k)-r_0]^2}. \tag{5.105b}$$

Here we used $a_{res}(k)k^2r_0^3\ll[a_{res}(k)-r_0]^2$. Since $a_{res}(k)$ diverges tangent-like (or cotangent-like) around $k=k_{res}$ we find that the cross section has an *asymmetric* lineshape (*provided* $r_0\neq 0$), and is *zero* when $a(k)=r_0$. Note that the cross section changes-over from the value $\sigma=4\pi r_0^2$ for conditions far from resonance ($a_{res}=0$) to $\sigma=4\pi/k^2$ exactly on resonance. Introducing the overall scattering length $-a=a_{res}(k)-r_0$ the expression for the cross section takes the well known general form

$$\sigma(k)=4\pi\frac{a^2}{1+k^2a^2}, \tag{5.106}$$

and a is given by

$$a=r_0\left(1-\frac{1}{1+Q_-r_0}\right). \tag{5.107}$$

What remains to be done is to write the scattering length as a function $a=a(B,E)$ of collision energy E and magnetic field B. For this purpose we expand Q_-r_0 around the value -1. Restricting ourselves for convenience to deep potentials ($\kappa_cr_0\gg 1$) we note that $q_-r_0\gg 1$ and $Q_-r_0=q_-r_0\cot q_-r_0\sin^2\theta=-1$ for $q_-r_0\simeq(n+\frac{1}{2})\pi$. Recalling the boundary condition for the bound states in the closed channel, $q_nr_0=n\pi$ and accounting for the change in well depth (5.81),

$-\left(\kappa_o^2-\kappa_c^2\right)\tan^2\theta$, we obtain $q_-r_0 = r_0\sqrt{\kappa_c^2-(\kappa_o^2-\kappa_c^2)\tan^2\theta+k^2+\varepsilon_n-\varepsilon_n}$, which we write for purposes of the expansion of $\cot q_-r_0$ around $q_nr_0+\frac{1}{2}\pi$ in the form

$$q_-r_0 \simeq \left(q_nr_0+\tfrac{1}{2}\pi\right)-\tfrac{1}{2}\pi-\tfrac{1}{2}\varepsilon_nr_0/q_n-\tfrac{1}{2}\tan^2\theta\,\left(\kappa_o^2-\kappa_c^2\right)r_0^2/q_n.$$

For very weak coupling,

$$\tfrac{1}{2}\left(\kappa_o^2-\kappa_c^2\right)r_0^2\frac{\tan^2\theta}{q_nr_0}\ll\tfrac{1}{2}\pi,$$

we can neglect the change in well depth and obtain

$$\begin{aligned}1+Q_-r_0 &= 1+q_-r_0\cot q_-r_0\sin^2\theta\\ &= 1-\tfrac{1}{2}\pi q_nr_0\sin^2\theta+\tfrac{1}{2}\varepsilon_nr_0^2\sin^2\theta\left(1+\tfrac{1}{2}\varepsilon_nr_0/q_n\right),\end{aligned}$$

where the expansion of the cotangent is only valid as long as $\frac{1}{2}\varepsilon_nr_0/q_n \ll \frac{1}{2}\pi$. Furthermore, for very weak coupling, $\frac{1}{2}\pi q_nr_0\sin^2\theta\ll 1$, we may further approximate,

$$\frac{1}{1+Q_-r_0}=\frac{\gamma_{res}}{\gamma_{res}+\varepsilon_n}.$$

Here $\Gamma=(2/r_0\sin\theta)^2$ is the resonance width. Substituting $\varepsilon_n\equiv k_n^2-k^2$, with k_n^2 representing the resonance energy relative to the asymptote of the open channel at the magnetic field of the measurement, we obtain

$$\frac{1}{1+Q_-r_0}=\frac{\mu_{rel}\Delta_B}{\mu_{rel}\Delta_B+\mu_{rel}\left(B-B_n\right)-\hbar^2k^2/2\mu}.$$

Thus, the resonance is observed at the field where $B_0=B_n-\Delta_B$

$$\Delta_B=\frac{\hbar^2}{2\mu}\frac{2}{r_0^2\sin^2\theta}$$

$$a=r_0\left(1+\frac{\mu_{rel}\Delta_B}{\hbar^2k^2/2\mu-\mu_{rel}\left(B-B_0\right)}\right). \tag{5.108}$$

The phase shift is given by

$$\eta_0=-kr_0-\tan^{-1}\frac{kr_0\mu_{rel}\Delta_B}{\hbar^2k^2/2\mu-\mu_{rel}\left(B-B_0\right)}. \tag{5.109}$$

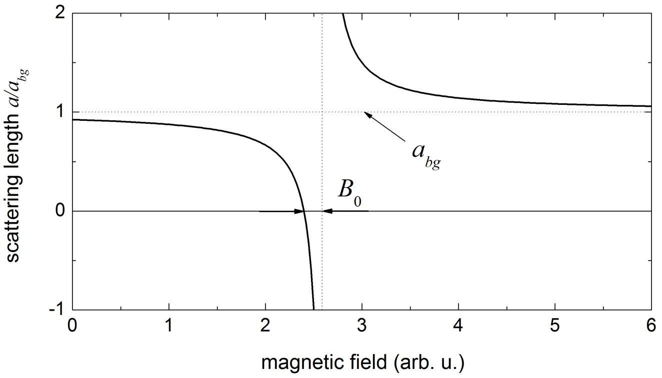

Figure 5.6: Example of the magnetic field dependence of a scattering length in the presence of a Feshbach resonance. Note that far from the resonance the scattering length attains its *background* value a_{bg}.

6

Kinetic phenomena in dilute quasi-classical gases

The statistical theory of Chapter 1 was developed to describe the equilibrium properties of gaseous systems. This does not provide us information about the time scales on which the equilibrium is reached. Thermal equilibrium in dilute atomic gases arises as the result of random collisions between the atoms, which is the domain of kinetic theory. In the present chapter we discuss how binary collisions affect the phase space distribution of a dilute gas of neutral atoms moving quasi-classically under the influence of an external potential. To keep the discussion general we allow for the presence ν components, in principle all experiencing different confinement potentials, $\mathcal{U}_i(\mathbf{r})$ with $i \in \{1, \cdots, \nu\}$.

6.1 Boltzmann equation for a collisionless gas

Let us presume that at a given time t the phase-space distribution of a dilute gas of neutral atoms is given by the dimensionless distribution function $f(\mathbf{r}, \mathbf{p}, t)$, not necessarily the equilibrium function. The quantity $f(\mathbf{r}, \mathbf{p}, t)$ represents the *phase-space occupation* at point $(\mathbf{r}, \mathbf{p})$; i.e., the number of atoms at time t present within an elementary phase space volume $(2\pi\hbar)^3$ near the phase point $(\mathbf{r}, \mathbf{p})$. In quasi-classical gases this occupation is small, $f(\mathbf{r}, \mathbf{p}, t) < 1$. We ask for the evolution of $f(\mathbf{r}, \mathbf{p}, t)$ as a function of time. The number of atoms at time t present within an infinitesimal volume $d\mathbf{r}d\mathbf{p}$ in phase space near the phase point $(\mathbf{r}, \mathbf{p})$ is given by $(2\pi\hbar)^{-3} f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r}d\mathbf{p}$. In the absence of collisions the same number of atoms will be found at a slightly later time $t' = t + dt$ in a slightly displaced and distorted volume $d\mathbf{r}'d\mathbf{p}'$ near the phase point $(\mathbf{r}', \mathbf{p}')$. Hence,

$$f(\mathbf{r}', \mathbf{p}', t') d\mathbf{r}'d\mathbf{p}' = f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r}d\mathbf{p}. \tag{6.1}$$

The points $(\mathbf{r}, \mathbf{p})$ and $(\mathbf{r}', \mathbf{p}')$ are related by a coordinate transformation in phase space, which follows from the Newton equations of motion,

$$\mathbf{r}' = \mathbf{r} + \dot{\mathbf{r}}\, dt = \mathbf{r} + (\mathbf{p}/m)\, dt \tag{6.2a}$$
$$\mathbf{p}' = \mathbf{p} + \dot{\mathbf{p}}\, dt = \mathbf{p} + \mathbf{F}\, dt, \tag{6.2b}$$

where $\dot{\mathbf{p}} = \mathbf{F} = -\operatorname{grad}\mathcal{U}(\mathbf{r})$ is the force imposed on the atoms by the external potential $\mathcal{U}(\mathbf{r})$. Fortunately, the Jacobian of the transformation $d\mathbf{r}'d\mathbf{p}' = |\partial(\mathbf{r}', \mathbf{p}')/\partial(\mathbf{r}, \mathbf{p})|\, d\mathbf{r}d\mathbf{p}$ is unity (see Problem 6.1). Therefore, Eq. (6.1) can be written in the form

$$f(\mathbf{r} + \dot{\mathbf{r}}\, dt, \mathbf{p} + \dot{\mathbf{p}}\, dt, t + dt) - f(\mathbf{r}, \mathbf{p}, t) = 0. \tag{6.3}$$

Physically this means that the phase space density is conserved for an observer moving along with the atoms, which expresses the *Liouville theorem*. By Taylor expansion of $f(\mathbf{r} + \dot{\mathbf{r}}\, dt, \mathbf{p} + \dot{\mathbf{p}}\, dt, t + dt)$

in Cartesian coordinates to first order in dt Eq. (6.3) takes the form $Df(\mathbf{r},\mathbf{p},t)dt = 0$, where D is the differential operator defined by[1]

$$D \equiv \dot{r}_i \frac{\partial}{\partial r_i} + \dot{p}_i \frac{\partial}{\partial p_i} + \frac{\partial}{\partial t} \quad \text{with } i \in \{x, y, z\}. \tag{6.4}$$

Hence, Eq. (6.3) holds when the linear partial differential equation $Df(\mathbf{r},\mathbf{p},t) = 0$ is satisfied. This equation is called the Boltzmann equation for collisionless classical gases. In vector notation it takes the form

$$\left(\dot{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{p}} + \frac{\partial}{\partial t}\right) f(\mathbf{r},\mathbf{p},t) = 0, \tag{6.5}$$

where $\partial/\partial\mathbf{r} \equiv \partial_{\mathbf{r}} \equiv \boldsymbol{\nabla}$ and $\partial/\partial\mathbf{p} \equiv \partial_{\mathbf{p}}$ are the gradient operators in position and momentum space, $\partial/\partial t \equiv \partial_t$ the partial derivative with respect to time, $\dot{\mathbf{r}} = \mathbf{v}$ the atomic velocity and $\dot{\mathbf{p}} = \mathbf{F}$ the force on the atoms. Thus, Eq.(6.5) also can be written in the compact form

$$(\mathbf{v} \cdot \partial_{\mathbf{r}} + \mathbf{F} \cdot \partial_{\mathbf{p}} + \partial_t)\, f(\mathbf{r},\mathbf{p},t) = 0. \tag{6.6}$$

Solving a partial differential equation with 7 variables is in general a non-trivial task. In contrast, it is easy to verify that the equilibrium distribution function $f_0(\mathbf{r},\mathbf{p},t)$ for ideal gases obtained in Chapter 1 is indeed a solution of Eq. (6.6),

$$f_0(\mathbf{r},\mathbf{p},t) = n_0\Lambda^3 \exp[-H_0(\mathbf{r},\mathbf{p})/k_BT]. \tag{6.7}$$

Here $H_0(\mathbf{r},\mathbf{p}) = p^2/2m + \mathcal{U}(\mathbf{r})$ is the classical Hamiltonian for atoms of mass m in the external potential $\mathcal{U}(\mathbf{r})$, $n_0 = N/V_e$ the central density for a cloud of N atoms with $V_e = \int \exp[-\mathcal{U}(\mathbf{r})/k_BT]d\mathbf{r}$ the effective volume and $\Lambda = (2\pi\hbar^2/mk_BT)^{1/2}$ the thermal wavelength, both at temperature T. For the left hand side of Eq. (6.6) we obtain with Eq. (6.7)

$$Df_0 = -v_i \frac{\partial \mathcal{U}}{\partial r_i} f_0 - F_i \frac{p_i}{m} f_0, \tag{6.8}$$

which indeed evaluates to zero since $-(\partial\mathcal{U}/\partial r_i) = F_i = \dot{p}_i$ and $p_i/m = v_i$.

Problem 6.1. Show that the Jacobian for the transformation

$$d\mathbf{r}'d\mathbf{p}' = \left|\frac{\partial(\mathbf{r}',\mathbf{p}')}{\partial(\mathbf{r},\mathbf{p})}\right| d\mathbf{r}d\mathbf{p}, \tag{6.9}$$

describing the infinitesimal distortion of an infinitesimal volume in phase space as a result of free evolution in time is unity.

Solution. The free evolution in the x direction is described by

$$\begin{aligned} x' &= x + \dot{x}\,dt = x + (p_x/m)\,dt \\ p_x' &= p_x + \dot{p}_x\,dt = p_x + F_x\,dt. \end{aligned}$$

Hence, the Jacobian for the transformation in the x direction $dx'dp_x' = |\partial(x', p_x')/\partial(x, p_x)|\, dxdp_x$ is given by

$$\frac{\partial(x', p_x')}{\partial(x, p_x)} = \begin{vmatrix} \partial x'/\partial x & \partial x'/\partial p_x \\ \partial p_x'/\partial x & \partial p_x'/\partial p_x \end{vmatrix} = \begin{vmatrix} 1 & (1/m)\,dt \\ (\partial F_x/\partial x)\,dt & 1 \end{vmatrix} = 1 - \frac{\partial F_x}{m\partial x}(dt)^2.$$

The Jacobian of the transformation 6.9 is given by the modulus of the product of three such terms. Since the deviation from unity vanishes quadratically with dt the Jacobian becomes unity in the infinitesimal limit. □

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[1] Here we use the Einstein summation convention for repeating indices.

6.2 Boltzmann equation in the presence of collisions

The obvious challenge is to include collisions in the Boltzmann equation. Starting again from the phase-space occupation $f(\mathbf{r},\mathbf{p},t)$ of a dilute atomic gas at time t trapped in the external potential $\mathcal{U}(\mathbf{r})$, we note that on a time scale $t \ll \tau$; i.e., short as compared to the average time interval τ between two collisions of the same atom, the time evolution of $f(\mathbf{r},\mathbf{p},t)$ remains governed by the Newton equations of motion (6.2). This holds certainly for the infinitesimal time dt. However, even during the time dt atoms can scatter *into* or *out off* the infinitesimal volume $d\mathbf{r}d\mathbf{p}$ during its motion from point $(\mathbf{r},\mathbf{p})$ to point $(\mathbf{r}+\dot{\mathbf{r}}\,dt,\mathbf{p}+\dot{\mathbf{p}}\,dt)$ in phase space. Denoting the infinitesimal change in the number of atoms over the period dt by $(2\pi\hbar)^{-3}\,\Gamma_{\mathrm{c}}(\mathbf{r},\mathbf{p},t)d\mathbf{r}d\mathbf{p}dt$ Eq. (6.3) has to be replaced by.

$$f(\mathbf{r}+\dot{\mathbf{r}}\,dt,\mathbf{p}+\dot{\mathbf{p}}\,dt,t+dt)d\mathbf{r}'d\mathbf{p}' = f(\mathbf{r},\mathbf{p},t)d\mathbf{r}d\mathbf{p} + \Gamma_{\mathrm{c}}(\mathbf{r},\mathbf{p},t)d\mathbf{r}d\mathbf{p}dt. \tag{6.10}$$

Taylor expansion of $f(\mathbf{r}+\dot{\mathbf{r}}\,\delta t,\mathbf{p}+\dot{\mathbf{p}}\,\delta t,t+d\delta)$ in Cartesian coordinates to first order in δt yields for the total time derivative of the phase space occupation

$$\frac{d}{dt}f(\mathbf{r},\mathbf{p},t) = \lim_{\delta t\to 0}\frac{f(\mathbf{r}+\dot{\mathbf{r}}\,\delta t,\mathbf{p}+\dot{\mathbf{p}}\,\delta t,t+d\delta) - f(\mathbf{r},\mathbf{p},t)}{\delta t} = \dot{\mathbf{r}}\cdot\frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{p}}\cdot\frac{\partial f}{\partial \mathbf{p}} + \frac{\partial f}{\partial t} \tag{6.11}$$

Combining Eqs. (6.10) and (6.11) we obtain after substitution of $\dot{\mathbf{r}} = \mathbf{v}$ and $\dot{\mathbf{p}} = \mathbf{F}$

$$(\mathbf{v}\cdot\partial_{\mathbf{r}} + \mathbf{F}\cdot\partial_{\mathbf{p}} + \partial_t)\,f(\mathbf{r},\mathbf{p},t) = \Gamma_{\mathrm{c}}(\mathbf{r},\mathbf{p},t). \tag{6.12}$$

In shorthand notation this equation becomes

$$\frac{df}{dt} = Df = \Gamma_{\mathrm{c}}, \tag{6.13}$$

where $f \equiv f(\mathbf{r},\mathbf{p},t)$, $\Gamma_{\mathrm{c}} \equiv \Gamma_{\mathrm{c}}(\mathbf{r},\mathbf{p},t)$ and D is given by Eq. (6.4). Equation (6.12) is called the *Boltzmann equation* and

$$\Gamma_{\mathrm{c}}(\mathbf{r},\mathbf{p},t) \equiv \Gamma_{\mathrm{c}}^{(+)}(\mathbf{r},\mathbf{p},t) + \Gamma_{\mathrm{c}}^{(-)}(\mathbf{r},\mathbf{p},t) \tag{6.14}$$

is the *collision term,* the net rate at which the phase-space occupation $f(\mathbf{r},\mathbf{p},t)$ increases (+) or decreases (−) at point $(\mathbf{r},\mathbf{p})$ and time t.

To obtain an expression for the collision term we analyze in the coming sections the elementary collision processes. We restrict ourselves to elastic collisions. Before the collision the motion of the atoms is presumed to be uncorrelated. This is called the *assumption of molecular chaos.* In dilute gases this fundamental approximation is well satisfied because the collisions occur as well-separated binary events. Further, as the collisional behavior depends on the properties of the colliding atoms, the collision rate depends on the composition of the gas. Therefore, to keep the discussion general in this respect we presume the gas to consist of ν components.

6.2.1 Loss contribution to the collision term

For a dilute gas of ν components the rate of loss of phase-space occupation of atoms of type $i \in \{1,2,\cdots,\nu\}$ at point $(\mathbf{r},\mathbf{p}_i)$ and time t as the result of collisions with atoms of type $j \in \{1,2,\cdots,\nu\}$ is given by

$$\Gamma_{\mathrm{c}}^{(-)}(\mathbf{r},\mathbf{p}_i,t) = -\sum_{j=1}^{\nu} f_i(\mathbf{r},\mathbf{p}_i,t)\frac{1}{(2\pi\hbar)^3}\int d\mathbf{p}_j\, f_j(\mathbf{r},\mathbf{p}_j,t)v_{ij}\sigma_{ij}(v_{ij}). \tag{6.15}$$

where

$$R_{ij} = v_{ij}\sigma_{ij}(v_{ij}) = v_{ij}\int d\Omega'\sigma_{ij}(v_{ij},\Omega') \tag{6.16}$$

is the scattering rate per unit density for one pair of atoms (of types i and j) in a given initial state of relative momentum $\mathbf{p}_{ij} = \mu_{ij}(\mathbf{p}_i/m_i - \mathbf{p}_j/m_j)$ and with *total cross section* $\sigma_{ij}(v_{ij})$ (cf. Appendix

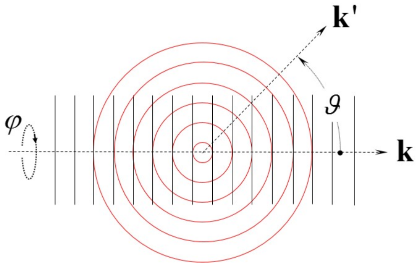

Figure 6.1: Elastic scattering of a matter wave from a centrally symmetric scattering potential in the center-of-mass-fixed coordinate system. Indicated are the scattering angle (polar angle) ϑ and the azimuthal angle φ, which defines the scattering plane.

A.7 for a discussion of center-of mass and relative coordinates). To keep the notation compact and self-explanatory we use the relative speed $v_{ij} = p_{ij}/\mu_{ij} = |\mathbf{p}_i/m_i - \mathbf{p}_j/m_j|$ rather than the relative momentum and write

$$\Omega' = \hat{\mathbf{p}}'_{ij} = (\vartheta', \varphi') \tag{6.17}$$

for the direction of motion of the reduced mass μ_{ij} after scattering. This direction is defined relative to the initial direction $\hat{\mathbf{p}}_{ij}$. The angles are illustrated in Fig. 6.1. The polar angle ϑ' is given by $\cos\vartheta' = \hat{\mathbf{p}}_{ij} \cdot \hat{\mathbf{p}}'_{ij}$ and is called the scattering angle. The azimuthal angle φ' defines the plane of scattering in the center of mass frame. In elastic collisions the relative speed v_{ij} is a conserved quantity.

The total cross section is given by the angular integral over $\sigma_{ij}(v_{ij}, \Omega')$, the *differential cross section* for scattering with relative speed v_{ij} in the direction Ω',

$$\sigma_{ij}(v_{ij}, \Omega') = \begin{cases} |f(v_{ij}, \Omega')|^2 & (i \neq j) \\ \\ |f(v_{ij}, \Omega') \pm f(v_{ij}, -\Omega')|^2 & (i = j)\,. \end{cases} \tag{6.18}$$

The quantity $f(v_{ij}, \Omega')$, with dimension length, is the *scattering amplitude*. As discussed in Chapter 4) the relation between the partial cross section and the scattering amplitude depends on the identity of the particles involved: for $i = j$ we distinguish between identical bosons and identical fermions by symmetrization (+) and antisymmetrization (−) of the scattering amplitudes, respectively.

6.2.2 Relation between T matrix and scattering amplitude

To reveal the underlying symmetries of the collision term in the Boltzmann equation we use Fermi's golden rule of time-dependent perturbation theory to write an expression for the loss contribution (6.15),

$$\Gamma_{\mathrm{c}}^{(-)}(\mathbf{p}_i, t) = -\sum_{j=1}^{\nu} n_{\mathbf{p}_i}(t) \sum_{\mathbf{p}_j} n_{\mathbf{p}_j}(t) \sum_{\mathbf{p}'_i, \mathbf{p}'_j} \frac{2\pi}{\hbar} |\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle|^2 \delta(E - E'). \tag{6.19}$$

Here $n_{\mathbf{p}_i}(t)$ is the occupation of state $|\mathbf{p}_i\rangle$ at time t with $i \in \{1, \cdots, \nu\}$. The double summation in Eq. (6.19) represents the overall transition rate R_{ij} from the initial state $|\mathbf{p}_i, \mathbf{p}_j\rangle$ into any state in the quasi-continuum of final states $|\mathbf{p}'_i, \mathbf{p}'_j\rangle$ under conservation of energy and momentum (Fermi's golden rule). The matrix elements $\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle$ represent the transition amplitude between the (unit normalized and properly symmetrized) eigenstates $|\mathbf{p}_i, \mathbf{p}_j\rangle$ and $|\mathbf{p}'_i, \mathbf{p}'_j\rangle$ before and, respectively, after the collision. These matrix elements define the so-called transition matrix (short: T matrix) and have the dimension of energy. The operator T is called the transition operator and depends in cold atomic gases only the electromagnetic interaction, which is invariant under *time reversal* ($t \to -t$) and *space inversion* ($\mathbf{r} \to -\mathbf{r}$),

$$\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle = \langle -\mathbf{p}_i, -\mathbf{p}_j | T | -\mathbf{p}'_i, -\mathbf{p}'_j \rangle \qquad \text{(time reversal)} \tag{6.20}$$

$$\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle = \langle -\mathbf{p}'_i, -\mathbf{p}'_j | T | -\mathbf{p}_i, -\mathbf{p}_j \rangle \qquad \text{(space inversion)}. \tag{6.21}$$

Hence, the T matrix is also invariant under the combination of these two operations, which is the *state inversion* of initial and final states,[1]

$$\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle = \langle \mathbf{p}_i, \mathbf{p}_j | T | \mathbf{p}'_i, \mathbf{p}'_j \rangle \qquad \text{(state inversion)}. \tag{6.22}$$

To determine the relation between the T matrix and the scattering amplitude $f(v_{ij}, \Omega')$ we make the continuum transition (1.15) from the quantum mechanical expression (6.19) to its quasi-classical analogue,

$$\Gamma_{\mathrm{c}}^{(-)}(\mathbf{r}, \mathbf{p}_i, t) = -\sum_{j=1}^{\nu} f_i(\mathbf{r}, \mathbf{p}_i, t) \frac{1}{(2\pi\hbar)^3} \int d\mathbf{r}_j d\mathbf{p}_j f_j(\mathbf{r}, \mathbf{p}_j, t) \times R_{ij}, \tag{6.23}$$

where the overall transition rate R_{ij} takes the form

$$R_{ij} = \frac{1}{(2\pi\hbar)^6} \int d\mathbf{r}'_i d\mathbf{r}'_j d\mathbf{p}'_i d\mathbf{p}'_j \frac{2\pi}{\hbar} |\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle|^2 \delta(E - E'). \tag{6.24}$$

In making this transition we presumed implicitly that it is possible to define at position $\mathbf{r}$ a quantization volume L^3 over which the system can be treated as a locally homogeneous quasi-classical gas. The quasi-classical approximation is valid if L can be chosen large as compared to the range r_0 of the interaction potential, $r_0 \ll L$; the gas is homogeneous over the volume L^3 if L is much smaller than the characteristic size L_e of the gas cloud, $L \ll L_e$. Combining these two conditions we find that the quasi-classical expression for the collision term is valid if

$$r_0 \ll L \ll L_e. \tag{6.25}$$

This is only possible if the confinement by the external potential $\mathcal{U}(\mathbf{r})$ is not too tight. Integrating over the quantization volume we obtain for the transition rate per unit density

$$R_{ij} = \frac{(2\pi\hbar)^{-3} L^9}{4\pi^2\hbar^4} \int d\mathbf{p}'_i d\mathbf{p}'_j \langle \mathbf{p}_i, \mathbf{p}_j | T^\dagger | \mathbf{p}'_i, \mathbf{p}'_j \rangle \langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle \delta(E - E'). \tag{6.26}$$

Next we transform to the center of mass and relative momentum. As the interaction does not affect the center of mass motion it can be factored out and we obtain

$$R_{ij} = \frac{(2\pi\hbar)^{-3} L^9}{4\pi^2\hbar^4} \int d\mathbf{p}' d\mathbf{P}' \langle \mathbf{P} | \mathbf{P}' \rangle \langle \mathbf{P}' | \mathbf{P} \rangle \delta(E - E') \times \begin{cases} |\langle \mathbf{p}' | T | \mathbf{p} \rangle|^2 & (i \neq j) \\ \\ |\langle \mathbf{p}' | T | \mathbf{p} \rangle \pm \langle \mathbf{p}' | T | -\mathbf{p} \rangle|^2 & (i = j)\,. \end{cases} \tag{6.27}$$

To avoid the redundant proliferation of indices we suppressed the common subscript ij in all quantities associated with the center of mass and relative motion; i.e., $\mu_{ij} \to \mu$, $\mathbf{P}_{ij} \to \mathbf{P}$, $\mathbf{p}'_{ij} \to \mathbf{p}'$, *etc.*. After integration over $\mathbf{P}'$ the expression for the scattering rate becomes[2]

$$R_{ij} = \frac{L^6}{4\pi^2\hbar^4} \int d\mathbf{p}' \delta(p^2/2\mu - p'^2/2\mu) \times \begin{cases} |\langle \mathbf{p}' | T | \mathbf{p} \rangle|^2 & (i \neq j) \\ \\ |\langle \mathbf{p}' | T | \mathbf{p} \rangle \pm \langle \mathbf{p}' | T | -\mathbf{p} \rangle|^2 & (i = j)\,. \end{cases} \tag{6.28}$$

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[1] The invariance under state inversion remains valid also in the presence of spin.

[2] Recalling Eq. (1.15) we substitute $\int d\mathbf{P}' \langle \mathbf{P} | \mathbf{P}' \rangle \langle \mathbf{P}' | \mathbf{P} \rangle = (2\pi\hbar/L)^3 \int d\mathbf{P}' \langle \mathbf{P} | \mathbf{P}' \rangle \delta(\mathbf{P} - \mathbf{P}')$.

Here we used the normalization $\langle \mathbf{P}|\mathbf{P}\rangle = 1$. Transforming to spherical coordinates for the relative motion $d\mathbf{p}' = d\Omega' dp' p'^2$ and using the delta function property $\delta(p^2/2\mu - p'^2/2\mu) = (\mu/p')\,\delta(p-p')$ we obtain after integration over p'

$$R_{ij} = v_{ij} \int d\Omega' \sigma_{ij}(v_{ij}, \Omega'), \tag{6.29}$$

where we restored the indices and

$$\sigma_{ij}(v_{ij}, \Omega') = \frac{\mu^2 L^6}{4\pi^2\hbar^4} \times \begin{cases} |\langle \mathbf{p}'|T|\mathbf{p}\rangle|^2 & (i \neq j) \\ \\ |\langle \mathbf{p}'|T|\mathbf{p}\rangle \pm \langle \mathbf{p}'|T|-\mathbf{p}\rangle|^2 & (i = j)\,. \end{cases} \tag{6.30}$$

is the differential cross section (with $|\mathbf{p}'| = |\mathbf{p}|$). Comparing Eq. (6.18) with (6.30) we arrive at the following relation between the scattering amplitude and the transition matrix element,

$$f(v_{ij}, \Omega') = \frac{\mu L^3}{2\pi\hbar^2} \langle \mathbf{p}'_{ij}|T|\mathbf{p}_{ij}\rangle. \tag{6.31}$$

6.2.3 Gain contribution to the collision term

We are now half-way in deriving an expression for the full collision term $\Gamma_{\mathrm{c}}(\mathbf{r}, \mathbf{p}_i, t)$ in the Boltzmann equation and turn to the gain contribution $\Gamma_{\mathrm{c}}^{(+)}(\mathbf{r}, \mathbf{p}_i, t)$, which represents the overall transition rate from any initial state $|\mathbf{p}'_i, \mathbf{p}'_j\rangle$ to any of the final states $|\mathbf{p}_i, \mathbf{p}_j\rangle$ in which the atom of type i emerges under conservation of energy and momentum moving with momentum $\mathbf{p}_i$ at position $\mathbf{r}$.[1] Implementing right from the start the invariance of the T matrix under state inversion of the initial and final states, this contribution can be written as

$$\Gamma_{\mathrm{c}}^{(+)}(\mathbf{p}_i, t) = \sum_{j=1}^{\nu} \sum_{\mathbf{p}'_i, \mathbf{p}'_j} n_{\mathbf{p}'_i}(t) n_{\mathbf{p}'_j}(t) \sum_{\mathbf{p}_i} \frac{2\pi}{\hbar} |\langle \mathbf{p}'_i, \mathbf{p}'_j|T|\mathbf{p}_i, \mathbf{p}_j\rangle|^2 \delta(E - E'). \tag{6.32}$$

Like in the case of the loss contribution we make the continuum transition (1.15) and transform to the center of mass and relative momentum. To keep the discussion compact we demonstrate this only for unlike atoms,

$$\Gamma_{\mathrm{c}}^{(+)}(\mathbf{r}, \mathbf{p}_i, t) = \sum_{j=1}^{\nu} \frac{1}{(2\pi\hbar)^3} \int d\mathbf{p}_j d\mathbf{P}' d\mathbf{p}' f_i(\mathbf{r}, (m_i/M)\,\mathbf{P}' + \mathbf{p}', t)\, f_j(\mathbf{r}, (m_j/M)\,\mathbf{P}' - \mathbf{p}', t) \times$$
$$\frac{L^6}{4\pi^2\hbar^4} \langle \mathbf{P}|\mathbf{P}'\rangle \delta(\mathbf{P} - \mathbf{P}') |\langle \mathbf{p}'|T|\mathbf{p}\rangle|^2 \delta(E - E'). \tag{6.33}$$

After integration over $\mathbf{P}'$ the becomes

$$\Gamma_{\mathrm{c}}^{(+)}(\mathbf{r}, \mathbf{p}_i, t) = \sum_{j=1}^{\nu} \frac{1}{(2\pi\hbar)^3} \int d\mathbf{p}_j d\mathbf{p}' f_i(\mathbf{r}, (m_i/M)\,\mathbf{P} + \mathbf{p}', t)\, f_j(\mathbf{r}, (m_j/M)\,\mathbf{P} - \mathbf{p}', t) \times$$
$$\frac{L^6}{4\pi^2\hbar^4} |\langle \mathbf{p}'|T|\mathbf{p}\rangle|^2 \delta(p^2/2\mu - p'^2/2\mu). \tag{6.34}$$

This integration takes care of the momentum conservation. Transforming to spherical coordinates for the relative motion $d\mathbf{p}' = d\Omega' dp' p'^2$ and integrating over p' we also account for the energy conservation

$$\Gamma_{\mathrm{c}}^{(+)}(\mathbf{r}, \mathbf{p}_i, t) = \sum_{j=1}^{\nu} \frac{1}{(2\pi\hbar)^3} \int d\mathbf{p}_j \int d\Omega'\, f_i(\mathbf{r}, \mathbf{p}'_i, t) f_j(\mathbf{r}, \mathbf{p}'_j, t) v_{ij} \sigma_{ij}(v_{ij}, \Omega'). \tag{6.35}$$

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[1] Note that for the loss/gain contribution the primed quantities refer to the initial/final states.

Here $\mathbf{p}_i' = (m_i/M)\,\mathbf{P} + \mathbf{p}'$, $\mathbf{p}_j' = (m_j/M)\,\mathbf{P} - \mathbf{p}'$ and $\sigma_{ij}(v_{ij},\Omega')$ is the differential cross section. It is straightforward to show that Eq.(6.35) also holds in the general case; i.e., for like as well as atoms. Importantly, Eq.(6.35) cannot be further reduced to the form (6.15) because $\mathbf{p}_i'$ and $\mathbf{p}_j'$ depend on Ω'.

6.2.4 Boltzmann equation

Combining the gain and loss terms we obtain the Boltzmann equation for component i of a ν component mixture

$$(\mathbf{v}\cdot\partial_{\mathbf{r}} + \mathbf{F}_i\cdot\partial_{\mathbf{p}_i} + \partial_t)\,f_i = \sum_{j=1}^{\nu}\frac{1}{(2\pi\hbar)^3}\int d\mathbf{p}_j d\Omega' v_{ij}\sigma_{ij}(v_{ij},\Omega')(f_i'f_j' - f_i f_j). \tag{6.36}$$

Here we use the shorthand notation $f_i' \equiv f_i(\mathbf{r},\mathbf{p}_i',t)$, $f_j' \equiv f_j(\mathbf{r},\mathbf{p}_j',t)$ and $f_i \equiv f_i(\mathbf{r},\mathbf{p}_i,t)$, $f_j \equiv f_j(\mathbf{r},\mathbf{p}_j,t)$, where the primed momentum states are given by

$$\mathbf{p}_i' = (m_i/M_{ij})\,(\mathbf{p}_i + \mathbf{p}_j) + \mu_{ij}\,|\mathbf{p}_i/m_i - \mathbf{p}_j/m_j|\,\hat{\mathbf{p}}_{ij}' \tag{6.37a}$$

$$\mathbf{p}_j' = (m_j/M_{ij})\,(\mathbf{p}_i + \mathbf{p}_j) - \mu_{ij}\,|\mathbf{p}_i/m_i - \mathbf{p}_j/m_j|\,\hat{\mathbf{p}}_{ij}'. \tag{6.37b}$$

To finish this section we verify that the equilibrium distribution function for ideal gases obtained in Chapter 1 indeed provides a solution of Eq. (6.36). Using the Boltzmann distribution the product $f_i'f_j'$ is given by

$$f_i(\mathbf{r},\mathbf{p}_i',t)f_j(\mathbf{r},\mathbf{p}_j',t) = n_i\Lambda_i^3 n_j\Lambda_j^3\exp[-H_{ij}(\mathbf{r},\mathbf{p}_i',\mathbf{p}_j')/k_BT], \tag{6.38}$$

with n_i and Λ_i the central density and thermal wavelength of component i. Since $H_{ij}(\mathbf{r},\mathbf{p}_i',\mathbf{p}_j') = p_i'^2/2m_i + \mathcal{U}_i(\mathbf{r}) + p_j'^2/2m_j + \mathcal{U}_j(\mathbf{r}) = P^2/2M + p^2/2\mu + \mathcal{U}_i(\mathbf{r}) + \mathcal{U}_j(\mathbf{r}) = H_{ij}(\mathbf{r},\mathbf{p}_i,\mathbf{p}_j)$, the difference $f_i'f_j' - f_if_j$ vanishes,

$$f_i(\mathbf{r},\mathbf{p}_i',t)f_j(\mathbf{r},\mathbf{p}_j',t) - f_i(\mathbf{r},\mathbf{p}_i,t)f_j(\mathbf{r},\mathbf{p}_j,t) = 0. \tag{6.39}$$

This implies that also the collision integral vanishes, as it should because in thermal equilibrium all occupations are stationary.

6.3 Collision rates in equilibrium gases

As an exercise we calculate the collision rate in a dilute gaseous mixture of ν components at temperature T and confined by the external potentials $\mathcal{U}_i(\mathbf{r})$ with $i \in \{1,\cdots,\nu\}$. The collision rate of atoms of type i is given by

$$\dot{N} = \sum_{j=1}^{\nu}\frac{1}{(2\pi\hbar)^3}\int d\mathbf{r}d\mathbf{p}_i\Gamma_{\mathrm{coll}}^{(-)}(\mathbf{r},\mathbf{p}_i,t). \tag{6.40}$$

Substituting Eq. (6.15) the expression for $\dot{N}$ becomes

$$\dot{N}_i = -\sum_{j=1}^{\nu}\frac{1}{(2\pi\hbar)^6}\int d\mathbf{r}d\mathbf{p}_i d\mathbf{p}_j f_i(\mathbf{r},\mathbf{p}_i,t)f_j(\mathbf{r},\mathbf{p}_j,t)v_{ij}\sigma_{ij}(v_{ij}). \tag{6.41}$$

Next we substitute the equilibrium distributions

$$f_i(\mathbf{r},\mathbf{p}_i) = n_i\Lambda_i^3 e^{-H_i(\mathbf{r},\mathbf{p}_i)/k_BT}, \tag{6.42}$$

where $H_i(\mathbf{r},\mathbf{p}_i) = p_i^2/2m_i + \mathcal{U}_i(\mathbf{r})$ is the classical hamiltonian for atoms of type i in the external potential $\mathcal{U}_i(\mathbf{r})$, $n_i = N_i/V_e^{(i)}$ the central density for a cloud of N_i atoms with $V_e^{(i)} = \int\exp[-\mathcal{U}_i(\mathbf{r})/k_BT]d\mathbf{r}$

the effective volume and $\Lambda_i = (2\pi\hbar^2/m_i k_B T)^{1/2}$ the thermal wavelength, both at temperature T. Turning to center of mass and relative coordinates, $\int d\mathbf{p}_i d\mathbf{p}_j = \int d\mathbf{P}d\mathbf{p}$, and suppressing again the double subscripts ($\mathbf{P}_{ij} \to \mathbf{P}$ and $\mathbf{p}_{ij} \to \mathbf{p}$) the rate of collisions between atoms of type i and $j \neq i$ takes the form

$$\dot{N}_i = \frac{n_i\Lambda_i^3 n_j\Lambda_j^3}{(2\pi\hbar)^6}\int d\mathbf{r}d\mathbf{P}d\mathbf{p}\ (p/\mu)\ \sigma_{ij}(p)\exp\left[-\frac{P^2}{2Mk_BT}-\frac{p^2}{2\mu k_BT}-\frac{\mathcal{U}_i(\mathbf{r})+\mathcal{U}_j(\mathbf{r})}{k_BT}\right]. \tag{6.43}$$

For $i = j$ we should include a factor 1/2 to avoid double counting. Evaluating the integrals and specializing for convenience to the case of the same external potential for all components, $\mathcal{U}_i(\mathbf{r}) = \mathcal{U}(\mathbf{r})$ for $i \in \{1, \cdots, \nu\}$, we obtain for the collision rate

$$\tau_c^{-1} = \frac{\dot{N}_i}{N_i} = \frac{1}{2}n_i\langle v\,\sigma_{ii}\rangle\frac{V_{2e}}{V_e} + \sum_{j\neq i} n_j\langle v\,\sigma_{ij}\rangle\frac{V_{2e}}{V_e}, \tag{6.44}$$

where

$$\langle v\,\sigma\rangle = \left(\frac{\Lambda_\mu}{2\pi\hbar}\right)^3\int d\mathbf{p}\ (p/\mu)\ \sigma(p)e^{-p^2/2\mu k_BT} \tag{6.45}$$

is the thermally averaged collision rate per unit density and $V_{2e} = \int \exp[-2\mathcal{U}(\mathbf{r})/k_BT]d\mathbf{r}$ the effective volume corresponding to the distribution of pairs. In particular, for a *homogeneous* one-component gas of density n_0 with a velocity-independent cross section we have $\langle v\,\sigma\rangle = \bar{v}_{rel}\,\sigma$ and find for the collision rate the well-known expression

$$\tau_c^{-1} = \frac{1}{\sqrt{2}}n_0\bar{v}\,\sigma, \tag{6.46}$$

where $\bar{v} = \sqrt{8k_BT/\pi m}$ is the average speed of the atoms.

6.4 Thermalization

As a first example of the use of the Boltzmann equation we analyze the process of *thermalization* by elastic collisions (*thermal relaxation*). Thermalization is the generic name for all kinds of processes giving rise to relaxation towards *thermal equilibrium* starting from a non-equilibrium situation. The characteristic time for thermalization by elastic collisions is called the *thermal relaxation time* τ.[1] Obviously, there are many different ways to be out of equilibrium. Here we will simply select the most convenient one from the computational point of view.

We consider a two-component gas consisting of N_1 of atoms of type 1 mixed with N_2 atoms of type 2. Choosing $N_2 \ll N_1$ the abundant component plays the role of a *heat reservoir.* In the most general case the two components will be of different atomic species. For simplicity we presume both components to be confined by the same trapping potential $\mathcal{U}(\mathbf{r})$. Further, we presume *isotropic scattering* between the atoms of the two components as well as an energy-independent *differential cross section* $\sigma(v,\Omega') \equiv d\sigma/d\Omega' = \sigma/4\pi$. As we shall see the latter assumption represents a substantial simplification because the corresponding *total cross section* σ will appear in front of the collision integral. To define the initial condition we presume the inter-component cross section σ_{12} to be initially zero.[2] In this way we can prepare a mixture in which both components $i \in \{1, 2\}$ are thermally distributed in the same trapping potential $\mathcal{U}(\mathbf{r})$ but with distributions of slightly different temperatures T_i,

$$f_i(\mathbf{r},\mathbf{p}_i,t) = n_i\Lambda_i^3 e^{-H_i(\mathbf{r},\mathbf{p}_i)/k_BT_i}. \tag{6.47}$$

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[1] Spin relaxation is an example of relaxation by inelastic collisions.

[2] In ultracold atomic gases this can be realized experimentally near an inter-species Feshbach resonance where the inter-species cross section can be made to vanish (cf. Chapter 5).

Here $n_i\Lambda_i^3 = N_i/Z_1^{(i)}$ is the degeneracy parameter in the trap center, with $Z_1^{(i)}$ is the single-particle partition function and $H_i(\mathbf{r},\mathbf{p}_i) = p_i^2/2m_i + \mathcal{U}(\mathbf{r})$ the quasi-classical hamiltonian of component i. Since $N_2 \ll N_1$ and the deviation from equilibrium is small the temperature T_1 of the majority component remains approximately constant, $T_1 \simeq T$, and $T_2 = T + \delta T$, with $\delta T/T \ll 1$. Hence, we can write

$$f_2(\mathbf{r},\mathbf{p}_2,t) = \frac{N_2}{Z_1^{(2)}} e^{-H_2(\mathbf{r},\mathbf{p}_2)/k_BT}\left[1 + H_2(\mathbf{r},\mathbf{p}_2)\frac{\delta T/T}{k_BT} + \cdots\right]\left[1 - (\gamma + 3/2)\frac{\delta T/T}{k_BT} + \cdots\right], \quad (6.48)$$

where the first factor in brackets results from the expansion of the exponent and the second from the expansion of $Z_1^{(2)}$ using Eq. (1.85). Because the collisions conserve the energy of the pair we obtain to first order in the deviation

$$f_1'f_2' - f_1f_2 = f_1^{(0)}f_2^{(0)}\frac{p_2'^2 - p_2^2}{2m_2}\frac{k_B}{(k_BT)^2}\delta T(t), \quad (6.49)$$

where

$$f_i^{(0)} = n_i\Lambda_i^3 e^{-H_i(\mathbf{r},\mathbf{p}_i)/k_BT} \quad (6.50)$$

is the *equilibrium distribution* of component i at temperature T. The quantity $(p_2'^2 - p_2^2)/2m_2$ is the energy transfer in the collision (cf. Appendix A.7.3). It can be written in the form

$$\frac{p_2'^2 - p_2^2}{2m_2} = -\frac{\mathbf{P}\cdot\mathbf{q}}{M} = \frac{Pp}{M}(u - u'), \quad (6.51)$$

where $\mathbf{q} = \mathbf{p}' - \mathbf{p}$ is the momentum transfer in the collision and $u = \cos\theta$ $(u' = \cos\theta')$, with $0 \le \theta, \theta' \le \pi$ the angles between the directions of $\mathbf{p}$, $\mathbf{p}'$ and $\mathbf{P}$.

At time $t = 0$ we switch the inter-component cross section to a non-zero value $\sigma_{12} \neq 0$ and ask for the rate of change of the heat content of the minority component 2

$$\dot{E}_2 = \frac{d}{dt}\langle H_2(\mathbf{r},\mathbf{p}_2)\rangle = \frac{1}{(2\pi\hbar)^3}\int d\mathbf{r}\, d\mathbf{p}_2 H_2(\mathbf{r},\mathbf{p}_2)\frac{d}{dt}f_2(\mathbf{r},\mathbf{p}_2,t). \quad (6.52)$$

Here, the quantity in the brackets represents the sum of the average kinetic and potential energy per atom. For power-law traps this quantity follows with Eq. (1.87)

$$E_2 = \langle H_2(\mathbf{r},\mathbf{p}_2)\rangle = (\gamma + 3/2)\, N_2k_BT_2(t). \quad (6.53)$$

The *thermal relaxation time* is defined as

$$\frac{1}{\tau} = -\frac{\delta\dot{T}}{\delta T} = -\frac{\dot{E}_2}{E_2}. \quad (6.54)$$

The connection with the Boltzmann using $df_2(\mathbf{r},\mathbf{p}_2,t)/dt = Df_2(\mathbf{r},\mathbf{p}_2,t)$. We find by substitution of Eq. (6.36) into Eq. (6.52)

$$\dot{E}_2 = \frac{\sigma_{12}}{(2\pi\hbar)^6 4\pi}\int d\mathbf{r}\, d\mathbf{p}_1 d\mathbf{p}_2 d\Omega' H_2(\mathbf{r},\mathbf{p}_2)v_{12}(f_1'f_2' - f_1f_2). \quad (6.55)$$

This expression holds for the case of inter-component scattering in a binary mixture. Note that the total cross section appears conveniently in front of the collision integral. Turning to center of mass and relative coordinates and using the linearization (6.49) Eq. (6.52) becomes

$$\dot{E}_2 = -\frac{\sigma_{12}}{(2\pi\hbar)^6 4\pi}\int d\mathbf{r} d\mathbf{P} d\mathbf{p} d\hat{\mathbf{p}}' f_1^{(0)}f_2^{(0)}H_2(\mathbf{r},\mathbf{p}_2)\frac{p}{\mu M}(\mathbf{P}\cdot\mathbf{q})\frac{k_B\delta T(t)}{(k_BT)^2}. \quad (6.56)$$

Integrating over the azimuthal angles of $\hat{\mathbf{p}}'$ and $\hat{\mathbf{p}}$ around the direction of $\mathbf{P}$ this expression takes the form

$$\dot{E}_2 = \frac{\pi\,\sigma_{12}\,k_B}{(2\pi\hbar)^6}\int d\mathbf{r}d\mathbf{P}p^2dp\,f_1^{(0)}f_2^{(0)}\int_{-1}^{+1}dudu'H_2(\mathbf{r},\mathbf{p}_2)\frac{Pp^2}{\mu M}\left(u-u'\right)\frac{k_B\delta T\left(t\right)}{(k_BT)^2}. \tag{6.57}$$

Note that all terms of odd power in u or u' vanish. To search for even powers of u we note that

$$\frac{p_2^2}{2m_2} = \frac{\left(m_2\mathbf{P}/M-\mathbf{p}\right)^2}{2m_2} = \frac{m_2}{M}\frac{P^2}{2M}+\frac{m_1}{M}\frac{p^2}{2\mu}-\frac{Pp}{M}u. \tag{6.58}$$

Thus, writing only the u-dependent term we have

$$H_2(\mathbf{r},\mathbf{p}_2) = p_2^2/2m_2+\mathcal{U}(\mathbf{r}) = -\frac{Pp}{M}u+\cdots. \tag{6.59}$$

Substituting this expression into Eq. (6.57) we find, with the aid of Eq. (6.54), after integration over $\mathbf{r}$ and all directions of $\mathbf{P}$ to first order in the deviation δT for the thermal relaxation rate

$$\frac{1}{\tau} = -\frac{4\pi^2\,\sigma_{12}V_{2e}n_1\Lambda_1^3n_2\Lambda_2^3}{(2\pi\hbar)^6\left(\gamma+3/2\right)N_2\left(k_BT\right)^2}\int_0^\infty dPdp\,e^{-(P/\alpha)^2-(p/\beta)^2}\int_{-1}^{+1}du\frac{P^4p^5}{\mu M^2}u^2. \tag{6.60}$$

where $\alpha=\sqrt{2Mk_BT}$and $\beta=\sqrt{2\mu k_BT}$ and $\Lambda_i=\sqrt{2\pi\hbar^2/m_ik_BT}$. Evaluating the integrals we arrive at

$$\tau_{th}^{-1} = \xi\frac{n_1\bar{v}_{rel}\sigma_{12}}{2\left(\gamma+3/2\right)}\frac{V_{2e}}{V_e}, \tag{6.61}$$

where $\bar{v}_{rel}=\sqrt{8k_BT/\pi\mu}$ is the average relative speed between the atoms of the two components. In terms of the inter-component collision time this expression takes the form

$$\tau_{th}^{-1} = \frac{\xi}{2\left(\gamma+3/2\right)}\tau_c^{-1}, \tag{6.62}$$

where $\xi=4\mu/M$ a the mass-mismatch factor (cf. Appendix A.7.3). Note that for $m_2 \ll m_1$ we have $\xi \simeq 4m_1/m_2$ and the thermalization rate decreases accordingly. For a homogeneous gas ($\gamma=0$) of two-component with atoms of the same mass ($\xi=1$) this expression reduces to

$$\tau_{th}^{-1} = \frac{1}{3}\tau_c^{-1}, \tag{6.63}$$

showing that it takes in this case about three collisions to approach thermal equilibrium to the $1/e$ level. To conclude this section we note that the results were obtained starting from a specific deviation from equilibrium. Therefore, care is required in making statements of the type ‘it takes three collisions to thermalize a dilute gas’.

7

Quantum mechanics of many-body systems

7.1 Introduction

In this chapter we introduce the basic theory for describing interacting many-body quantum systems. We start (Section 7.2) by quantizing a homogeneous gas of noninteracting atoms using the familiar basis of single atom wavefunctions with periodic boundary conditions and normalization to a quantization volume of appropriate size. Already when inspecting a gas of two *identical* atoms (i.e., atoms atoms with the same internal structure) we meet an essential quantum mechanical phenomenon: exchange degeneracy. If two identical atoms are in *different* states, there is no way by which we can determine which atom is in which state because all expectation values are invariant under exchange of the atoms of the pair. In particular this holds for the energy of the pair. When the two atoms are in the *same* state there is nothing to be distinguished and the exchange issue is manifestly absent.

Although exchange degeneracy may seem innocent at first sight, it has far reaching consequences for many-body quantum systems. It turns out that only the two *eigenstates* of the exchange operator are observed for pairs of identical particles in physical systems. For this reason one distinguishes two species of identical particles: bosons and fermions (see Section 7.3). If the many-body eigenstates of a system of identical particles are *symmetric* under exchange of any two of these particles, the particles are called *bosons*. If these eigenstates are *antisymmetric* under such exchange we speak of *fermions*. As will be shown in Section 7.3.1, the norm of antisymmetric many-body wavefunctions is identically zero whenever any of the single-particle states is more than singly occupied. This means that double occupation is absent in fermionic systems, which expresses the well known *Pauli exclusion principle*. Consequently, doubly (or multiply) occupied states can only be observed in bosonic systems (which is consistent with the absence of degeneracy under exchange of particles in the same state).

As is manifest for a set of fermions but equally relevant for bosons, the occupation of a given single-particle state by one particle affects the probability of occupation of that state by other particles of the set. In other words, the statistical distribution over the energy levels depends on the occupation of those levels, even in the absence of electromagnetic interaction between the particles. This collisionless statistics is known as *quantum statistics*. As the hamiltonian is by definition invariant under exchange of any two identical particles, the statistical nature of the particles is conserved in time. The origin of this statistical nature is deeply rooted in relativistic quantum field theory, which provides the underpinning for the *spin-statistics theorem* [53]: bosons always have *integral* spin and fermions *half-integral* spin. This theorem has been subject of fierce debate for decades but its derivation falls outside the scope of the present lectures [46].

The presence of quantum statistics has far reaching consequences for the description of interacting quantum gases because the strategy developed for treating interactions in classical gases completely fails in the quantum case. It is no longer allowed to restrict ourselves to a test particle surrounded by a cluster of interacting neighbors because we have to include *all* atoms of the gas to enforce the proper statistics. We are dealing with a many-body problem even without interactions. Moreover, since interactions between the atoms couple the single-atom states we need a formalism that rigorously enforces the exchange symmetry of the many-body wavefunction. This formalism is known as the *second quantization* method, although a less confusing name would be *occupation number representation* or construction operator formalism. This formalism is introduced in Section 7.5. In particular we introduce construction operators by which we can create or annihilate particles in properly symmetrized many-body states and show that the proper quantum statistics is enforced by an algebra defined through the commutation relations between the construction operators. A special form of construction operators, introduced for the description of non-uniform properties, are field operators. These are discussed in Section 7.6.

All this being said it is often not so obvious what is actually meant by “particle”. It certainly depends on the presence or absence of interactions. For instance, whereas isolated protons and neutrons behave as particles with well-defined properties (mass, charge, spin, $\cdots$), in the presence of nuclear forces they can transform into one another and are better regarded as two states of a new particle, the nucleon. From this point of view the nucleon is a particle composed as a linear combination of a proton and a neutron. Its internal structure is determined by a new degree of freedom, the isospin of the nucleon. Importantly, the presence of isospin does not affect the properties of the constituent particles, it is an additional property representing a symmetry in the isospin subspace of the nucleon. Since both the proton and the neutron are fermions also the nucleon is a fermion. The proton and neutron themselves can be regarded as composite particles constructed from quarks. In turn, the nucleons are the building blocks of the atomic nuclei. As the nucleons are fermionic, the even mass nuclei are bosons, and those with odd mass fermions. For neutral atoms, the number of electrons equals the number of protons in the nucleus, which implies that the number of neutrons determines the quantum statistics of the entire atom. These examples show that the conditions determine how we define our particles. With regard to quantum gases, we consider the constituent atoms as “particles” as long a they have a well defined internal structure. If they have the same internal structure they are called identical. When their structure brakes down, for instance by molecule formation, new quantum numbers appear (related to the symmetries of the new structure) but the statistical nature under exchange of complete atoms (i.e., all components of the atom) is conserved (see Section 7.3.1).

7.2 Quantization of the gaseous state

7.2.1 Single-atom states

To start the discussion we consider the Schrödinger equation for the spatial motion of a single atom, considering it as a point-like particle of mass m but without further internal structure,

$$-\frac{\hbar^2}{2m}\nabla^2\varphi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_k\varphi_{\mathbf{k}}(\mathbf{r}). \tag{7.1}$$

Introducing periodic boundary conditions, $\varphi(x+L, y+L, z+L) = \varphi(x, y, z)$, we find for the eigenfunctions and eigenvalues

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}} \text{ and } \varepsilon_k = \frac{\hbar^2k^2}{2m}. \tag{7.2}$$

The wavefunctions $\varphi_{\mathbf{k}}(\mathbf{r})$ represent *plane wave solutions* normalized to the quantization volume $V = L^3$, $\mathbf{k}$ is the wave *vector* of the atom, where $k = |\mathbf{k}| = 2\pi/\lambda$ is the wave *number*, with λ the *De Broglie wavelength.* The periodic boundary conditions imply a discrete spectrum of wavenumbers, $k_\alpha = (2\pi/L)\,n_\alpha$, with $n_\alpha \in \{0, \pm1, \pm2, \cdots\}$ and $\alpha \in \{x, y, z\}$.

7.2.2 Pair wavefunctions and exchange degeneracy

As the simplest example of a gas we consider the case of two atoms per quantization volume V. The hamiltonian for the motion of these atoms is given by

$$\mathcal{H} = \sum_{i=1,2} \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 + \mathcal{U}(\mathbf{r}_i) \right) + \mathcal{V}(\mathbf{r}_{12}), \tag{7.3}$$

where m_1 and m_2 are the masses of the atoms and $\mathcal{V}(\mathbf{r}_{12})$ a potential describing the interatomic interaction. The solutions of the corresponding Schrödinger equation are pair wavefunctions. Single-atom states are no longer defined as these have become non stationary through coupling by the interaction. However, they regain significance in the *collisionless limit* (see Section 1.1) which can be realized (for short-range interactions) by making the density sufficiently low. In the collisionless limit the Schrödinger equation can be approximated by

$$\left(-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 \right) \psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = E_{k_1,k_2} \psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) \,. \tag{7.4}$$

As in this expression the variables separate, the pair solution can be written as a product of two single-atom wavefunctions of the type (7.2),

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{V} e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2}. \tag{7.5}$$

Note that this wavefunction is unit normalized (one pair). The energy and momentum are given by

$$E_{k_1,k_2} = \frac{\hbar^2 k_1^2}{2m_1} + \frac{\hbar^2 k_2^2}{2m_2} \quad \text{and} \quad \mathbf{P} = \hbar\mathbf{k}_1 + \hbar\mathbf{k}_2. \tag{7.6}$$

Thus we found that the momentum of the pair is not affected by exchanging the two particles (of different mass) *but the energy is*,

$$E_{k_1,k_2} \neq E_{k_2,k_1} \quad \text{for } k_1 \neq k_2. \tag{7.7}$$

This shows that for a pair of *unlike* atoms (i.e., atoms with different internal structure as expressed by the difference in mass) product wavefunctions of the type (7.5) represent uniquely defined quantum mechanical eigenstates for the eigenvalues E_{k_1,k_2} and E_{k_2,k_1} (two states, two energies). It means that the states of the atoms (of mass m_1 and m_2) can be determined by measuring the energy of the pair. In other words, the particles are distinguishable by their internal structure.

For *identical* atoms (i.e., atoms with the same internal structure) the situation is fundamentally different. Since $m_1 = m_2$ we find that for identical atoms in *different* states ($k_1 \neq k_2$) the product wavefunctions (7.5) are degenerate with pair wavefunctions in which the atoms are exchanged,

$$E_{k_1,k_2} = E_{k_2,k_1} \quad \text{for } k_1 \neq k_2. \tag{7.8}$$

This is called *exchange degeneracy* (two states, one energy). This phenomenon shows that we cannot determine which atom is in which state by measuring the energy of the pair. Actually, it is fundamentally impossible to distinguish the atoms by any measurement because (by definition of being identical) the expectation values of all observables of the pair are invariant under exchange of the atoms. For identical atoms in the *same* state ($\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$) the exchange degeneracy is *manifestly absent* because there is *nothing to be distinguished.*

The exchange degeneracy implies that any linear combination of the type

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{V} \frac{1}{\sqrt{|c_1|^2 + |c_2|^2}} (c_1 e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2} + c_2 e^{i\mathbf{k}_2\cdot\mathbf{r}_1} e^{i\mathbf{k}_1\cdot\mathbf{r}_2}) \tag{7.9}$$

represents itself a properly normalized eigenstate of the pair provided $\mathbf{k}_1 \neq \mathbf{k}_2$. In this two-dimensional subspace we can construct two orthonormal basis states for the pair,

$$\psi^{\pm}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V}\sqrt{1/2}(e^{i\mathbf{k}_1\cdot\mathbf{r}_1}e^{i\mathbf{k}_2\cdot\mathbf{r}_2} \pm e^{i\mathbf{k}_2\cdot\mathbf{r}_1}e^{i\mathbf{k}_1\cdot\mathbf{r}_2}). \tag{7.10}$$

These are called the *symmetric* and *antisymmetric* eigenstates of the pair.

In the absence of exchange degeneracy (i.e., for $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$) Eq. (7.5) represents the proper solution,

$$\psi_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V}e^{i\mathbf{k}\cdot\mathbf{r}_1}e^{i\mathbf{k}\cdot\mathbf{r}_2}. \tag{7.11}$$

This state is symmetric and unit normalized to start with, so there is no need for explicit symmetrization. However, giving preference to a fixed procedure, we can always use the generic form 7.10 provided we correct for double counting of probabilities (see Problem 7.1),[1]

$$\psi_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) = \sqrt{\tfrac{1}{2}}\psi^{+}_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2). \tag{7.12}$$

Problem 7.1. Show that $\psi^{+}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)$ has norm $\mathcal{N} = 1$ for $\mathbf{k}_1 \neq \mathbf{k}_2$ but $\mathcal{N} = 2$ for $\mathbf{k}_1 = \mathbf{k}_2$.

Solution. We first turn to Dirac notation. The symmetrized state is given by

$$\psi^{+}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) \equiv (\mathbf{r}_1,\mathbf{r}_2|\mathbf{k}_1,\mathbf{k}_2\rangle = \sqrt{1/2}\left\{(\mathbf{r}_1,\mathbf{r}_2|\mathbf{k}_1,\mathbf{k}_2) + (\mathbf{r}_1,\mathbf{r}_2|\mathbf{k}_2,\mathbf{k}_1)\right\},$$

where $|\mathbf{k}_a,\mathbf{k}_b)$ (with the curved bracket) stands for the ordered product state, $|\mathbf{k}_a,\mathbf{k}_b) \equiv |\mathbf{k}_a\rangle_1\,|\mathbf{k}_b\rangle_2$, with $\psi_{\mathbf{k}}(\mathbf{r}_1) \equiv \langle\mathbf{r}_1|\mathbf{k}\rangle \equiv \langle\mathbf{r}|\mathbf{k}\rangle_1$ representing the state of particle 1. Calculating the norm we find

$$\begin{aligned}\mathcal{N} = \langle\mathbf{k}_1,\mathbf{k}_2|\mathbf{k}_2,\mathbf{k}_1\rangle &= \sqrt{1/2}\left\{(\mathbf{k}_1,\mathbf{k}_2| + (\mathbf{k}_2,\mathbf{k}_1|\right\}\sqrt{1/2}\left\{|\mathbf{k}_1,\mathbf{k}_2) + |\mathbf{k}_2,\mathbf{k}_1)\right\}\\ &= \tfrac{1}{2}\left\{(\mathbf{k}_1,\mathbf{k}_2|\mathbf{k}_1,\mathbf{k}_2) + (\mathbf{k}_1,\mathbf{k}_2|\mathbf{k}_2,\mathbf{k}_1) + (\mathbf{k}_2,\mathbf{k}_1\mathbf{k}_1,\mathbf{k}_2) + (\mathbf{k}_2,\mathbf{k}_1|\mathbf{k}_2,\mathbf{k}_1)\right\}\\ &= 1 + \delta_{\mathbf{k}_1,\mathbf{k}_2}.\end{aligned}$$

Here we used $(\mathbf{k}_1,\mathbf{k}_2|\mathbf{k}_2,\mathbf{k}_1) = (\mathbf{k}_2,\mathbf{k}_1|\mathbf{k}_1,\mathbf{k}_2) = \delta_{\mathbf{k}_1,\mathbf{k}_2}$ and $(\mathbf{k}_1,\mathbf{k}_2|\mathbf{k}_2,\mathbf{k}_1) = (\mathbf{k}_2,\mathbf{k}_1|\mathbf{k}_2,\mathbf{k}_1) = 1$. □

7.3 Identical particles and the exchange operator

At this point a fascinating twist happens in the discussion because (as pointed out in the introduction) arbitrary linear combinations of the type (7.9) were never observed for pairs of identical particles in physical systems. In accordance with the *spin-statistics theorem* one either observes *symmetric* pair states (for particles of *integral* spin - *bosons*) or *antisymmetric* pair states (for particles of *half-integral* spin - *fermions*). Apparently it is not allowed to neglect the internal degrees of freedom when studying ensembles of identical particles.

So, we start allover and formalize the discussion by including the spin states from the beginning. As before, two particles are called identical if there is no physical way to establish whether or not they particles have been exchanged. This condition is satisfied for particles with identical internal structure because, in quantum mechanics, it is fundamentally impossible to label a particle by tracking its motion along an orbit. The latter is only possible in classical mechanics as it requires

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[1] Beware that in some text books this is done, in others not. By always using the generic form, the atoms can be exchanged as if they are distinguishable (like the atoms in a classical gas). This offers some convenience because we are familiar with the classical world around us. The price we pay is that we have to correct our findings for double counting of doubly (multiply) occupied single-particle states. In the other approach we have to keep track of which exchange give rise to degeneracy and which not. It is a matter of taste. In the present lectures we use the generic form and correct for double counting.

the simultaneous determination of position and momentum. Including the spin, the state of the identical pair is given by the pair wavefunction

$$\psi\left(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2\right), \tag{7.13}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the *position coordinates* and σ_1 and σ_2 the *spin coordinates*, respectively (see Appendix B.1.4). The squared modulus of the wavefunction,

$$|\psi\left(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2\right)|^2, \tag{7.14}$$

corresponds to the probability of observing one particle (say particle 1) at position $\mathbf{r}_1$ in spin state σ_1 with the other particle (say particle 2) at position $\mathbf{r}_2$ in spin state σ_2. With this procedure we labeled the particles by the position of observation. It does *not* mean that we observe a labeled particle. The latter is only possible for particles with a difference in internal structure (the "label") which is absent for identical particles. Next we interchange the particles before doing the measurement. This can be done, also when the particles are identical. Formally this is realized by introducing the *exchange operator* $\mathcal{P}$,

$$\mathcal{P}\psi\left(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2\right) \equiv \psi\left(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1\right). \tag{7.15}$$

As "tracking" is impossible in quantum mechanics, we have no physical means to determine whether or not two identical particles have been exchanged. This means that the probability to observe particle 2 at position $\mathbf{r}_1$ in spin state σ_1 with particle 1 at position $\mathbf{r}_2$ in spin state σ_2 has to be equal to that of observing particle 1 at position $\mathbf{r}_1$ in spin state σ_1 with particle 2 at position $\mathbf{r}_2$ in spin state σ_2 :

$$|\psi\left(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2\right)|^2 = |\psi\left(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1\right)|^2. \tag{7.16}$$

This shows that $\mathcal{P}$ has to be *norm-conserving*,

$$\langle\psi|\mathcal{P}^{\dagger}\mathcal{P}|\psi\rangle = \langle\psi|\psi\rangle = 1, \tag{7.17}$$

but also that the actual labels 1 and 2 have no physical significance.

Let us have a closer look at the exchange operator. Because $\mathcal{P}$ is norm-conserving, we have

$$\mathcal{P}^{\dagger}\mathcal{P} = 1 \tag{7.18}$$

and

$$\mathcal{P}|\psi\rangle = e^{-i\theta}|\psi\rangle. \tag{7.19}$$

Furthermore, exchanging the particles twice must leave the pair state unchanged. Rewriting the phase angle in the form $\theta = n\,\pi + \varphi$ (which can be done without loss of generality) we find from Eq. (7.19)

$$\mathcal{P}^2|\psi\rangle = e^{-i2\varphi}|\psi\rangle. \tag{7.20}$$

So the question arises for what value of φ the pair state is invariant under all possible ways to exchange the particles twice. For 3D systems (and in the absence of topological excitations)[1] this is the case only for $\varphi = 0$; i.e., for

$$\mathcal{P}^2 = 1. \tag{7.21}$$

Writing $\mathcal{P}^{\dagger} = \mathcal{P}^{\dagger}\mathcal{P}^2 = \mathcal{P}$ we see that $\mathcal{P}$ is *hermitian*; i.e., the eigenvalues of $\mathcal{P}$ are real an take the values ±1. In view of the definition (7.15) these eigenvalues correspond to pair wavefunctions which are either *symmetric* (+1) or *antisymmetric* (−1) under exchange of the particles. Taking into

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[1] The general case was analyzed by Jon Leinaas and Jan Myrheim in 1977 [41]. In 2D (or 3D in the presence of vorticity), the phase angle θ corresponds to a rotation angle, with $\theta_1 = n\,\pi + \varphi$ being equivalent to $\theta_2 = -(n\,\pi - \varphi)$. This implies that exchange with $\theta_1 + \theta_2 = 2\varphi \neq 0$ is a physical option. It gives rise to quantum statistics with its own type of identical particle called anyon (with fractional spin defined by $\theta = 2\pi s$) [72].

account the relation between spin and statistics the action of the exchange operator is summarized by the expression

$$\mathcal{P}\psi\left(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2\right)=e^{-i2\pi s}\psi\left(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2\right), \tag{7.22}$$

where s is the (integral or half-integral) spin of the particle.

Since, by definition, the pair hamiltonian $\mathcal{H}$ is invariant under exchange of identical particles, $\mathcal{P}$ commutes with $\mathcal{H}$, which implies that $\mathcal{P}$ and $\mathcal{H}$ share a complete set of eigenstates. Therefore, the eigenstates of $\mathcal{P}$ span the full Hilbert space of the pair and $\mathcal{P}$ is not only hermitian but also an *observable*. Apparently, for *identical* particles the pair wavefunction has to be an *eigenfunction* of the exchange operator; i.e., the exchange symmetry of the wavefunction is conserved in time.

7.3.1 Internal symmetry versus external symmetry and Pauli principle

Let us have a closer look at the spin states. For two identical particles of spin s, the total spin S and its magnetic quantum number M_S are good quantum numbers. The total spin state $|S,M_S\rangle$ can be decomposed with respect to the quantum numbers of the individual spins using a Clebsch-Gordan decomposition,

$$|S,M_S\rangle=\sum_{m_1,m_2}|s,m_1;s,m_2)(s,m_1;s,m_2|S,M_S\rangle, \tag{7.23}$$

where $|s,m_1;s,m_2)\equiv|sm_1\rangle_1\,|sm_2\rangle_2$ is an ordered product state (curved bracket). As is well known, the Clebsch-Gordan coefficient of a stretched state ($S\equiv S_{max}=s_1+s_2$, $M_S=S_{max}$) is always unity and manifestly symmetric,

$$(s_1,s_1;s_2,s_2|S_{max},S_{max}\rangle=(s_2,s_2;s_1,s_1|S_{max},S_{max}\rangle=1.$$

Actually, in general, the exchange symmetry is *symmetric* for $S=S_{max}$, $S_{max}-2$, $S_{max}-4,\cdots$ and *antisymmetric* for $S=S_{max}-1$, $S_{max}-3,\cdots$ and always independent of the value of M_S. For *bosons* $S_{max}=2s$ is always *even*, whereas for *fermions* it is always *odd*. Therefore, for *bosons* the *even* (*odd*) total spin states are *symmetric* (*antisymmetric*) whereas for *fermions* this is the case for *odd* (*even*) total spin.

As an example we have a look at the well-known case of two $s=1/2$ fermions (e.g., electrons),

$$\left.\begin{array}{ll}|1,+1\rangle & =|\uparrow\uparrow)\\ |1,0\rangle & =\sqrt{1/2}\,\{|\uparrow\downarrow)+|\downarrow\uparrow)\}\\ |1,-1\rangle & =|\downarrow\downarrow)\end{array}\right\}\quad(S=1)$$
$$|0,0\rangle\;=\sqrt{1/2}\,\{|\uparrow\downarrow)-|\downarrow\uparrow)\}\qquad(S=0)\,. \tag{7.24}$$

Note that the odd total spin state ($S=1$) is symmetric as was asserted above for fermions.

As for a pair of *fermions* in a state of *odd* total spin, the total spin state $|S,M_S\rangle$ is always *symmetric* under exchange of the particles, the orbital wavefunction must be *antisymmetric*,[1]

$$\psi^{-}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)|S,M_S\rangle=\frac{1}{V}\sqrt{1/2}\left(e^{i\mathbf{k}_1\cdot\mathbf{r}_1}e^{i\mathbf{k}_2\cdot\mathbf{r}_2}-e^{i\mathbf{k}_2\cdot\mathbf{r}_1}e^{i\mathbf{k}_1\cdot\mathbf{r}_2}\right)|S,M_S\rangle\quad\text{for } S=odd. \tag{7.25}$$

This expression shows that $\psi^{-}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)$ is identically zero for $\mathbf{k}_1=\mathbf{k}_2=\mathbf{k}$,

$$\psi^{-}_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)|S,M_S\rangle\equiv0. \tag{7.26}$$

Hence, the formalism shows that the two fermions (in *symmetric* spin states) have zero probability to be in the same momentum state, in accordance with the *Pauli exclusion principle.*

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[1] Here we conveniently write the state $|S,M_S\rangle$ rather than the spinor $\chi_{S,M_S}(\sigma_1,\sigma_2)\equiv(\sigma_1,\sigma_2|S,M_S\rangle$ because the probability to be in the state $|S,M_S\rangle$ is not of interest in the present context.

Furthermore, $\psi^{-}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)$ also vanishes for $\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}$ (whatever the value of $\mathbf{k}_1$ and $\mathbf{k}_2$),

$$\psi^{-}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r},\mathbf{r})\,|S,M_S\rangle = 0, \tag{7.27}$$

Hence, two fermions (in *symmetric* spin states) have zero probability to be at the same position, which means that they avoid each other by quantum interference. In this sense the quantum correlations represent *kinematic correlations* between the particles.

Interestingly, *also* for a pair *bosons* in states of *odd* total spin, the orbital wavefunction has to be *antisymmetric* because, for bosons, the total spin state $|S,M_S\rangle$ is always *antisymmetric* under exchange of the particles; i.e., Eq. (7.25) also applies in this case. In accordance $\psi^{-}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)$ is identically zero for $\mathbf{k}_1=\mathbf{k}_2=\mathbf{k}$ and also zero for $\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}$ (whatever the value of $\mathbf{k}_1$ and $\mathbf{k}_2$). In other words, we expect the same kinematic correlations as discussed for the fermionic case. This is dramatically demonstrated in molecular physics by comparing hydrogen and deuterium molecules.

Both for hydrogen (nuclear spin $I=\frac{1}{2}$) and deuterium (nuclear spin $I=1$) the molecular states with total spin total spin $I_{tot}=1$ are only observed in combination with *antisymmetric* rotational states (the *odd* rotational quantum numbers). This remarkable consequence of the relation between spin and statistics is summarized in Table 7.1. The exclusion of rotational levels was conjectured by David Dennison in 1927 to explain the specific heat of molecular hydrogen [16]. As the ground states of the hydrogen and deuterium molecules have an even rotational quantum number ($J=0$) and transitions between even and odd rotational levels requires a nuclear spin flip, the mentioned isomers behave at low temperature as metastable species known under the names *ortho-hydrogen* and *para-deuterium.*

Similarly, for a pair of *bosons or fermions* in a state of *even* total spin, the total spin state $|S,M_S\rangle$ always combines with a *symmetric* orbital state,

$$\psi^{+}_{\mathbf{k}_1,\mathbf{k}_1}(\mathbf{r}_1,\mathbf{r}_2)\,|S,M_S\rangle = \frac{1}{V}\sqrt{1/2}\left(e^{i\mathbf{k}_1\cdot\mathbf{r}_1}e^{i\mathbf{k}_2\cdot\mathbf{r}_2}+e^{i\mathbf{k}_2\cdot\mathbf{r}_1}e^{i\mathbf{k}_1\cdot\mathbf{r}_2}\right)|S,M_S\rangle \quad \text{for } S=even. \tag{7.28}$$

In molecular physics this leads to the isomers *para-hydrogen* and *ortho-deuterium* (also included in Table 7.1). By comparing hydrogen and deuterium, the relation between spin and statistics was used to conjecture the value of the *deuteron* spin (hence, indirectly, also the spin of the *neutron*) by Gilbert Lewis and Muriel Ashley in 1933 [44].

The physics of the hydrogen isomers provides a good example of how interactions affect the particles in a many-body system. At sufficiently low density we can study a gas of hydrogen atoms. These are composite bosons, consisting of an electron bound to a proton. The interactions between the hydrogen atoms gives rise to molecule formation, which is an inelastic process in which the individual atoms loose their integrity. The molecules represent new particles (a bound state of 2 electrons and two protons rather than a bound state of two atoms). They are characterized by additional quantum numbers such as the total nuclear spin (which gives rise to the ortho-para rotational structure of the hydrogen molecule). Although the integrity of the atoms is lost the symmetry under simultaneous exchange of one proton and one electron is conserved.

As long as the constituent particles of a many-body system do not loose their integrity they can be used as particles in a microscopic many-body theory. This applies, for instance, for the electrons in atoms or solids. In the case of the atomic quantum gases we are dealing with composite particles and microscopic many-body theories can be developed as long as the interactions remain sufficiently weak. Systems of weakly-interacting particles can be transformed into systems of non-interacting systems quasiparticles. In the presence of strong interactions (e.g., in liquid helium or near Feshbach resonances) analytic theories brake down and one has to rely on phenomenological or numerical approaches.

7.3.2 Spinorbitals, symmetric and antisymmetric product states

As the internal and external degrees of freedom are related through the spin-statistics theorem it is important to treat them on equal footing by writing the wavefunction in the form of a multi-valued function called *spinorbital*. For an atom at position $|\mathbf{r}\rangle$ and in spin state $|\sigma\rangle$ the spinorbitals are $(2s+1)$-valued functions of the form

$$\varphi_{\mathbf{k},sm_s}(\mathbf{r},\sigma) = \frac{1}{V^{1/2}} e^{i\mathbf{k}\cdot\mathbf{r}} \chi_{sm_s}(\sigma) . \tag{7.29}$$

Fermions

Let us start with the familiar case of $s = 1/2$ fermions. In this case the *spin-up* spinorbital is a double-valued function,

$$\varphi_{\mathbf{k}\uparrow}(q) = \frac{1}{V^{1/2}} e^{i\mathbf{k}\cdot\mathbf{r}} \chi_{\uparrow}(\sigma) . \tag{7.30}$$

Here we introduced a shorthand notation for the position and spin coordinates: $q \equiv \{\mathbf{r}, \sigma\}$. Note that Eq. (7.25) can be written in the form of a determinant,

$$\psi^{-}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)\,(\sigma_2,\sigma_2\,|1,1\rangle = \sqrt{\tfrac{1}{2}} \begin{vmatrix} \varphi_{\mathbf{k}_1\uparrow}(q_1) & \varphi_{\mathbf{k}_2\uparrow}(q_1) \\ \varphi_{\mathbf{k}_1\uparrow}(q_2) & \varphi_{\mathbf{k}_2\uparrow}(q_2) \end{vmatrix} , \tag{7.31}$$

where we substituted $|S, M_S\rangle \to |1,1\rangle$. In the representation free notation of Dirac it takes the form

$$|\mathbf{k}_1,\mathbf{k}_2\rangle^A\,|1,1\rangle = \sqrt{\tfrac{1}{2}} \begin{vmatrix} |\mathbf{k}_1\!\uparrow\rangle_1 & |\mathbf{k}_2\!\uparrow\rangle_1 \\ |\mathbf{k}_1\!\uparrow\rangle_2 & |\mathbf{k}_2\!\uparrow\rangle_2 \end{vmatrix} . \tag{7.32}$$

Similarly, the symmetric spin state $|1,0\rangle$ in combination with the antisymmetric orbital state $\psi^{-}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2,)$ (again a properly symmetrized fermionic state) can be written as the sum of two determinants|

$$|\mathbf{k}_1,\mathbf{k}_2\rangle^A\,|1,0\rangle = \frac{1}{2} \begin{vmatrix} |\mathbf{k}_1\!\uparrow\rangle_1 & |\mathbf{k}_2\!\downarrow\rangle_1 \\ |\mathbf{k}_1\!\uparrow\rangle_2 & |\mathbf{k}_2\!\downarrow\rangle_2 \end{vmatrix} + \frac{1}{2} \begin{vmatrix} |\mathbf{k}_1\!\downarrow\rangle_1 & |\mathbf{k}_2\!\uparrow\rangle_1 \\ |\mathbf{k}_1\!\downarrow\rangle_2 & |\mathbf{k}_2\!\uparrow\rangle_2 \end{vmatrix} . \tag{7.33}$$

The two-body state (7.28) consisting of an anti-symmetric spin state with both atoms in the symmetric orbital state ($\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$) represents again a determinant,

$$|\mathbf{k},\mathbf{k}\rangle^S\,|0,0\rangle = \sqrt{\tfrac{1}{2}} \begin{vmatrix} |\mathbf{k}\!\downarrow\rangle_1 & |\mathbf{k}\!\uparrow\rangle_1 \\ |\mathbf{k}\!\downarrow\rangle_2 & |\mathbf{k}\!\uparrow\rangle_2 \end{vmatrix} . \tag{7.34}$$

Table 7.1: In the ortho and para isomers of the hydrogen ($I = 1/2$) and deuterium ($I = 1$) molecules the distribution over the rotational levels is different as a result of quantum statistics (only even or odd rotational levels are observed). Furthermore, being bound by two electrons in an antisymmetric state ($S = 0$), the molecules are symmetric under exchange of complete hydrogen atoms (proton + electron) and antisymmetric in the case of deuterium (deuteron + electron) as required by the spin-statistics theorem.

			symmetry				
isomer	I_{tot}	J	ψ_{nucl}	ψ_{rot}	ψ_{vib}	$^1\Sigma_g^+$	ψ_{tot}
ortho-H_2	1	$1,3,5,\cdots$	S	A	S	A	S
para-D_2	1	$1,3,5,\cdots$	A	A	S	A	A
para-H_2	0	$0,2,4,\cdots$	A	S	S	A	S
ortho-D_2	$0,2$	$0,2,4,\cdots$	S	S	S	A	A

In the final combination we combine the symmetric orbital state $\psi^{+}_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)$ with the antisymmetric spin state $|S,M_S\rangle = |0,0\rangle$,

$$|\mathbf{k}_1,\mathbf{k}_2\rangle^S\,|0,0\rangle = \frac{1}{2}\begin{vmatrix} |\mathbf{k}_1\!\uparrow\rangle_1 & |\mathbf{k}_2\!\downarrow\rangle_1 \\ |\mathbf{k}_1\!\uparrow\rangle_2 & |\mathbf{k}_2\!\downarrow\rangle_2 \end{vmatrix} - \frac{1}{2}\begin{vmatrix} |\mathbf{k}_1\!\downarrow\rangle_1 & |\mathbf{k}_2\!\uparrow\rangle_1 \\ |\mathbf{k}_1\!\downarrow\rangle_2 & |\mathbf{k}_2\!\uparrow\rangle_2 \end{vmatrix}. \tag{7.35}$$

Thus, we found that any two-body fermion state in a prescribed total spin state $|S,M_S\rangle$ can be expressed as a determinant of spinorbitals or a linear combination of such determinants. Note that in all cases considered, the states are unit normalized. The determinantal form is particularly attractive to represent identical fermions because of the property of determinants to vanish when two columns or two rows are equal. This assures that the wavefunction vanishes when two fermions are in the same state or share the same (position and spin) coordinates. Furthermore, exchanging two rows or two columns yields a minus sign as required for anti-symmetric wavefunctions.

Reversely, if we know the states of the individual atoms we can use a determinant to construct a properly symmetrized fermionic state. In this application the determinant is called a *Slater determinant.* The difference with the pair states discussed above is that the Slater determinant, in general, does not correspond to a pure spin state $|S,M_S\rangle$ but to a linear combination of such total spin states. For instance, the normalized Slater determinant for a pair of particles in the spinorbitals $|\mathbf{k}_1\!\uparrow\rangle$ and $|\mathbf{k}_2\!\downarrow\rangle$ is given by

$$|\mathbf{k}_1\!\uparrow,\mathbf{k}_2\!\downarrow\rangle^A \equiv \sqrt{\tfrac{1}{2}}\begin{vmatrix} |\mathbf{k}_1\!\uparrow\rangle_1 & |\mathbf{k}_2\!\downarrow\rangle_1 \\ |\mathbf{k}_1\!\uparrow\rangle_2 & |\mathbf{k}_2\!\downarrow\rangle_2 \end{vmatrix} = \sqrt{\tfrac{1}{2}}\left\{|\mathbf{k}_1,\mathbf{k}_2\rangle^S\,|0,0\rangle + |\mathbf{k}_1,\mathbf{k}_2\rangle^A\,|1,0\rangle\right\}. \tag{7.36}$$

This follows directly by adding Eqs. (7.33) and (7.35). On the other hand, in view of Eq. (7.32), the Slater determinant for the spinorbital pair $|\mathbf{k}_1\!\uparrow\rangle$ and $|\mathbf{k}_2\!\uparrow\rangle$ correspond to a pure total state,

$$|\mathbf{k}_1\!\uparrow,\mathbf{k}_2\!\uparrow\rangle^A \equiv \sqrt{\tfrac{1}{2}}\begin{vmatrix} |\mathbf{k}_1\!\uparrow\rangle_1 & |\mathbf{k}_2\!\uparrow\rangle_1 \\ |\mathbf{k}_1\!\uparrow\rangle_2 & |\mathbf{k}_2\!\uparrow\rangle_2 \end{vmatrix} = |\mathbf{k}_1,\mathbf{k}_2\rangle^A\,|1,1\rangle. \tag{7.37}$$

Bosons

Let us now turn to bosons. We immediately step to the approach of symmetrizing the spinorbitals and check if it provides us with the proper combinations of total spin and orbital pair states. For two identical bosons in the internal states $|sm_1\rangle$ and $|sm_2\rangle$ the symmetric spinorbital state is given by

$$|\mathbf{k}_1m_1,\mathbf{k}_2m_2\rangle^S = \sqrt{\tfrac{1}{2}}\sum_P P|\mathbf{k}_1m_1,\mathbf{k}_2m_2). \tag{7.38}$$

Here P is the permutation operator; i.e., we sum over all possible permutations of the particles (in this case only 2: $P=1$ and $P=\mathcal{P}$). Note that we omitted the s value because it only blurs the notation. Since $|\mathbf{k}_1m_1,\mathbf{k}_2m_2)$ is a product state we can separate the spin states from the orbital states and use a Clebsch-Gordan decomposition for the spin state,

$$|\mathbf{k}_1m_1,\mathbf{k}_2m_2) = |\mathbf{k}_1\mathbf{k}_2)\,|m_1m_2) = |\mathbf{k}_1\mathbf{k}_2)\sum_{S=0}^{2s}|SM_S\rangle\langle SM_S|sm_1;sm_2) \tag{7.39a}$$

$$P|\mathbf{k}_1m_1,\mathbf{k}_2m_2) = |\mathbf{k}_2\mathbf{k}_1)\,|m_2m_1) = |\mathbf{k}_2\mathbf{k}_1)\sum_{S=0}^{2s}|SM_S\rangle\langle SM_S|sm_2;sm_1). \tag{7.39b}$$

Since, for *bosons*, the symmetry of Clebsch-Gordan coefficients is even for even S and odd for odd S we find by adding the Eqs. (7.39),

$$|\mathbf{k}_1m_1,\mathbf{k}_2m_2\rangle^S = \sqrt{\tfrac{1}{2}}\left[|\mathbf{k}_1\mathbf{k}_2) + (-1)^S|\mathbf{k}_2\mathbf{k}_1)\right]\sum_{S=0}^{2s}|SM_S\rangle\langle SM_S|sm_1;sm_2). \tag{7.40}$$

This shows that the decomposition combines *symmetric* spin states with *symmetric* orbital states and *antisymmetric* spin states with *antisymmetric* orbital states, just as it should be for bosons (and not unexpected because the pair state was symmetric to begin with). Moreover, the states are unit normalized. However, there is a catch. For $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$ the norm of the state adds up to 2 (recall Problem 7.1). In hindsight, this is no surprise because by explicit symmetrization we incorrectly doubly counted the product state of two identical particles in the same internal state although this state remains itself under exchange. This is easily repaired by dividing the norm of the state by the number of permutations of particles in the same internal state (in our case 2!).

In conclusion: for a given pair of spinorbitals (i.e., knowing the *occupation* of the spinorbital states) can write the properly symmetrized and unit normalized bosonic pair state in the form

$$|\mathbf{k}_1 m_1, \mathbf{k}_2 m_2\rangle^S = \sqrt{\frac{1}{2n!}} \sum_P P|\mathbf{k}_1 m_1, \mathbf{k}_2 m_2), \tag{7.41}$$

where n is the number of particles occupying the same state; i.e., $n = 1$ for $\mathbf{k}_1 \neq \mathbf{k}_2$ and $n = 2$ for $\mathbf{k}_1 = \mathbf{k}_2$. From the above it is straightforward to verify that for two *fermions* the proper expression is

$$|\mathbf{k}_1 m_1, \mathbf{k}_2 m_2\rangle^A = \sqrt{\tfrac{1}{2}} \sum_P (-1)^p P|\mathbf{k}_1 m_1, \mathbf{k}_2 m_2), \tag{7.42}$$

where p is the parity of the permutation ($p = 0, 1$ for even/odd permutations). Note that the $n!$ is lacking because two identical fermions cannot be in the same state.

7.4 Quantum mechanics in the N-body Hilbert space

7.4.1 Introduction - generalization of the symmetrization procedure

The analysis of pair states in the previous sections has prepared us for a generalization of the discussion of identical particles for the many-body case. First we have a look at *fermions*. The Slater determinants are readily extended to describe a system of N fermions in the states $\alpha_1, \cdots, \alpha_N$ (where α_i stands for all internal and external quantum numbers of particle i),

$$|\alpha_1, \cdots, \alpha_N\rangle^A \equiv \sqrt{\frac{1}{N!}} \begin{vmatrix} |\alpha_1\rangle_1 & \cdots & |\alpha_N\rangle_1 \\ \vdots & \cdots & \vdots \\ |\alpha_1\rangle_N & \cdots & |\alpha_N\rangle_N \end{vmatrix}. \tag{7.43}$$

This $N \times N$ determinant represents a straightforward generalization of a product wavefunction with the proper symmetry under interchange of any two fermions and also unit normalized. It is evidently consistent the Pauli principle. It represents a true milestone in many-body physics. Recalling the Leibniz expansion of the determinant (see Appendix D) the many-body state of N fermions occupying the single-particles states $\alpha_1, \cdots, \alpha_N$ is given by

$$|\alpha_1, \cdots, \alpha_N\rangle^A \equiv \sqrt{\frac{1}{N!}} \sum_P (-1)^p P|\alpha_1, \cdots \alpha_N), \tag{7.44}$$

where

$$|\alpha_1, \cdots \alpha_N) \equiv |\alpha_1\rangle_1 \, |\alpha_2\rangle_2 \cdots |\alpha_N\rangle_N \tag{7.45}$$

is the N-body ordered product of the single-particle states $|\alpha_\kappa\rangle_i$, $\kappa \in \{1, \cdots, N\}$ being the *state index* and $i \in \{1, \cdots, N\}$ the *particle index*. Note that the wavefunction in the representation $\{|q_1, \cdots q_N)\}$ is given by

$$\psi_\alpha (q_1, \cdots q_N) \equiv (q_1, \cdots q_N | \alpha_1, \cdots, \alpha_N\rangle. \tag{7.46}$$

The summation in Eq. (7.44) runs over all permutations P of the particles, p being the *parity* of the permutation; i.e., the number of *transpositions* (binary interchanges) required to realize the permutation starting from an initial ordering fixed by convention. As the sum runs over all permutations, it makes no difference whether we permute all particles or permute all states of the particles. We choose the convention in which the permutation operator P *acts on the state index* (κ) and *not on the particle index* (i). With this choice, the interchange of the states of particles 1 and 2 is written as

$$P|\alpha_1,\alpha_2,\cdots\alpha_N)=|\alpha_2,\alpha_1,\cdots\alpha_N)=|\alpha_2\rangle_1\;|\alpha_1\rangle_2\cdots|\alpha_N\rangle_N\,. \tag{7.47}$$

To assure a uniquely defined sign of the Slater determinants we have to adopt a *standard ordering convention* of atomic configurations.

For *bosons* it is straightforward to generalize Eq. (7.41) for a system of N identical particles occupying the single-particle states $\alpha_1,\cdots,\alpha_N$,

$$|\alpha_1,\cdots,\alpha_N\rangle^S\equiv\sqrt{\frac{1}{N!n_1n_2\cdots n_N}}\sum_P P|\alpha_1,\cdots\alpha_N). \tag{7.48}$$

As evidenced by Eqs. (7.44) and (7.48), the quantum mechanical *indistinguishability* of *identical* particles affects the distribution of particles over the single-particle states. For fermions (antisymmetric under exchange) this is made explicit by the Pauli principle, which excludes double occupation of the same state. For bosons (symmetric under exchange) exchange of two particles in the same is must be excluded as being unphysical (the pair state is nondegenerate). In both cases the distribution in configuration space is affected; kinematic correlations happen between the particles in the complete absence of interatomic forces: it is a purely *quantum statistical phenomenon.*

7.4.2 Formal structures in the N-body Hilbert space

For each particle i we can define a Hilbert space $\mathbf{H}_i$ spanned by a basis consisting of a complete orthonormal set of states $\{|\mathbf{k}_s\rangle_i\}$,

$${}_i\langle\mathbf{k}_{s'}|\mathbf{k}_s\rangle_i=\delta_{\mathbf{k}_s,\mathbf{k}_{s'}}\quad\text{and}\quad\sum_{\mathbf{k}_s}|\mathbf{k}_s\rangle_i\,{}_i\langle\mathbf{k}_s|=\underline{1}, \tag{7.49}$$

where $s\in\{1,\cdots,N\}$ is the *state index* and $i\in\{1,\cdots,N\}$ the *particle index.* The ket $|\mathbf{k}_s\rangle_i$ stands for the *full* description of the eigenstates of the particle i, including the internal state (for instance the hyperfine state in the case of atoms). The boldface $\mathbf{k}$ is used to indicate that, in general, we are dealing with some vector of quantum numbers (i.e., it can be a discrete wave vector but in general it is not). The wavefunctions of the Schrödinger picture are obtained as the probability amplitude to find the particle at coordinates q_i,

$$\psi_{\mathbf{k}_s}(q_i)=\langle q_i|\mathbf{k}_s\rangle\equiv\langle q|\mathbf{k}_s\rangle_i. \tag{7.50}$$

For spinless free particles, these wavefunctions can be conveniently chosen to be the plane waves given by Eq. (7.2); for harmonic trapping potentials they will be harmonic oscillator eigenstates; for electrons in the Coulomb field of the nucleus they are the atomic spinorbitals, *etc.*. In the presence of interactions similar single-particle wavefunctions remain a good basis but the interpretation as the eigenstates of a free massive particle is lost.

For the N-body system we can define a Hilbert space as the *tensor product* space

$$\mathbf{H}^N=\mathbf{H}_1\otimes\mathbf{H}_2\otimes\cdots\mathbf{H}_N \tag{7.51}$$

of the N single-particle Hilbert spaces $\mathbf{H}_i$ and represented by the orthonormal basis $\{|\mathbf{k}_1,\cdots,\mathbf{k}_N)\}$, where

$$|\mathbf{k}_1,\mathbf{k}_2,\cdots,\mathbf{k}_N)\equiv|\mathbf{k}_1\rangle_1\;|\mathbf{k}_2\rangle_2\cdots|\mathbf{k}_N\rangle_N \tag{7.52}$$

is the N-body *ordered product* of the single-particle states $|\mathbf{k}_s\rangle_i$ with normalization condition

$$(\mathbf{k}_1', \cdots, \mathbf{k}_N' | \mathbf{k}_1, \cdots, \mathbf{k}_N) = \delta_{\mathbf{k}_1, \mathbf{k}_1'} \cdots \delta_{\mathbf{k}_N, \mathbf{k}_N'} \tag{7.53}$$

and closure

$$\sum_{\mathbf{k}_1, \cdots, \mathbf{k}_N} |\mathbf{k}_1, \cdots, \mathbf{k}_N)\,(\mathbf{k}_1, \cdots, \mathbf{k}_N| = \prod_{i=1}^{N} \left(\sum_{\mathbf{k}_s} |\mathbf{k}_s\rangle_{i\,i}\langle \mathbf{k}_s| \right) = \underline{1}. \tag{7.54}$$

The notation of curved brackets $|\mathbf{k}_1, \cdots, \mathbf{k}_N)$ is reserved for unsymmetrized many-body states; i.e., product states are written with the convention of referring always in the same order from left to right to the states of particle 1 through N. Sometimes we shall use an *implicit definition* of the N-body state $|N_\gamma)$ by specifying the index γ as an array of state indices,

$$|N_\gamma) = |\mathbf{k}_1, \cdots, \mathbf{k}_N) \quad \text{for } \gamma = \{1, \cdots, N\}.$$

The product states represent an ordered set of particles distinguished by their particle index. This makes no sense for identical particles. Identical particles are by definition indistinguishable, which renders any type of ordering impossible. To deal with the indistinguishability we argue that all dynamical properties must remain unchanged under an arbitrary permutation P of the particles. This means that all operators representing a dynamical variable of the system must be invariant under these permutations. This holds in particular for the Hamilton operator and implies that P commutes with the hamiltonian, just as we found for the exchange operator in the two-body case. This is of course not surprising because any permutation can be realized by a sequence of binary interchanges of particles. A many-body state $|\psi^{(S)}\rangle$ is called symmetric (bosonic) if it is invariant under all permutations P,

$$P|\psi^{(S)}\rangle = |\psi^{(S)}\rangle \tag{7.55}$$

Similarly, a many-body state $|\psi^{(A)}\rangle$ is called antisymmetric (fermionic) if it satisfies the property

$$P|\psi^{(A)}\rangle = (-)^p |\psi^{(A)}\rangle, \tag{7.56}$$

where $(-)^p = 1$ for all even permutations and $(-)^p = -1$ for all odd permutations, p being the number of transpositions (binary interchanges) generating the permutation. We thus can identify two orthogonal subspaces within the product space $\mathbf{H}^N$: the symmetric subspace $\mathbf{H}^{(S)}$ (for bosons) and the antisymmetric subspace $\mathbf{H}^{(A)}$ (for fermions),

$$\mathbf{H}^{(S)} \oplus \mathbf{H}^{(A)} \subseteq \mathbf{H}^N. \tag{7.57}$$

7.4.2.1 Fermions

For identical *fermions* in states $\mathbf{k}_1, \cdots, \mathbf{k}_N$ the N-body state has to be *antisymmetric*. To assure the absence of ordering, the state is written as the sum of all permutations of the product state. It is made antisymmetric by using a plus sign for all even permutations and a minus sign for all odd permutations,

$$|\mathbf{k}_1, \cdots, \mathbf{k}_N\rangle \equiv \sqrt{\frac{1}{N!}} \sum_P (-1)^p P |\mathbf{k}_1, \cdots \mathbf{k}_N). \tag{7.58}$$

Note that this expression represents a unit normalized *Slater* determinant and satisfies the condition (7.56). The permutation operator P is chosen *to act on the state index* as this allows us to conserve a particular *ordering convention of the particle index* in the product states. With this choice, the interchange of the states of particles 1 and 2 is written as

$$\mathcal{P}_{12}|\mathbf{k}_1, \mathbf{k}_2, \cdots \mathbf{k}_N) = -|\mathbf{k}_2, \mathbf{k}_1, \cdots \mathbf{k}_N) = -\,|\mathbf{k}_2\rangle_1\, |\mathbf{k}_1\rangle_2 \cdots |\mathbf{k}_N\rangle_N\,. \tag{7.59}$$

To assure a uniquely defined sign of the Slater determinants we adopt an *ordering convention* for the *non-permuted* product state.

7.4.2.2 Bosons

For identical *bosons* the N-body state has to be *symmetric*. This is assured by summing over all permutations while correcting for the degeneracy of occupation (as we did in the two-body case) in order to maintain unit normalization. For a N-body system with n_1 particles in state $\mathbf{k}_1$, n_2 particles in state $\mathbf{k}_2$, $\cdots$ and n_l particles in state $\mathbf{k}_l$ we obtain[1]

$$|\mathbf{k}_1,\mathbf{k}_1,\cdots,\mathbf{k}_l\rangle \equiv \sqrt{\frac{1}{N!n_1!\cdots n_l!}}\sum_P P|\underbrace{\mathbf{k}_1,\mathbf{k}_1,\cdots,}_{n_1}\underbrace{\mathbf{k}_2,\cdots}_{n_2}\cdots\underbrace{\cdots,\mathbf{k}_l}_{n_l}), \tag{7.60}$$

where $N = n_1+n_2+\cdots n_l$. In view of the symmetric form, in the bosonic case there is no significance in the order in which the states are written.

As an example we consider the special case of N bosons in the same state, $|\mathbf{k}_s,\cdots,\mathbf{k}_s)$. Here all $N!$ permutations leave the unsymmetrized wavefunction unchanged and we obtain $N!$ identical terms with normalization coefficient $1/N!$, reflecting the feature that the wavefunction was symmetrized to begin with; i.e., $|\mathbf{k}_s,\cdots,\mathbf{k}_s\rangle = |\mathbf{k}_s,\cdots,\mathbf{k}_s)$.

Symmetrization operators

In the literature one defines symmetrization and antisymmetrization operators. The *symmetrization operator* is (usually) defined as

$$\mathcal{S} \equiv \frac{1}{N!}\sum_P P. \tag{7.61}$$

It projects an arbitrary product state $|\mathbf{k}_1,\cdots\mathbf{k}_N)$ onto the symmetric N-body subspace $\mathbf{H}^{(S)}$. Similarly, the quantity

$$\mathcal{A} \equiv \frac{1}{N!}\sum_P (-1)^p P \tag{7.62}$$

is called the *antisymmetrization operator* . It projects an arbitrary product state $|\mathbf{k}_1,\cdots\mathbf{k}_N)$ onto the antisymmetric subspace $\mathbf{H}^{(A)}$. Note that (for discrete spectra as discussed above) these operators *do not conserve* the normalization of the product state.

Problem 7.2. Show that any pair wavefunction can be written as the sum of a part symmetric under exchange and a part antisymmetric under exchange of the pair.

Solution. For any pair state we have $|\psi\rangle = \frac{1}{2}(1+\mathcal{P})|\psi\rangle + \frac{1}{2}(1-\mathcal{P})|\psi\rangle$, where $\mathcal{P}$ is the exchange operator, $\mathcal{P}^2 = 1$. The first term is symmetric, $\mathcal{P}(1+\mathcal{P})|\psi\rangle = (\mathcal{P}+\mathcal{P}^2)|\psi\rangle = (1+\mathcal{P})|\psi\rangle$, and the second term is antisymmetric, $\mathcal{P}(1-\mathcal{P})|\psi\rangle = (\mathcal{P}-\mathcal{P}^2)|\psi\rangle = -(1-\mathcal{P})|\psi\rangle$. □

Problem 7.3. Show that for $N > 2$

$$\mathcal{S} + \mathcal{A} \neq \underline{1}.$$

7.4.3 Example: Anderson's orthogonality theorem

The generalization from two-body to many-body systems is *not* "just more of the same". This is exactly what makes many-body physics into a fascinating field. As a first illustration we consider the ground state of an ideal Fermi gas of N particles; i.e., the state in which all single-particle levels are occupied up to the Fermi level. Let us denote the single-particle states by $|\mathbf{k}_i\rangle$, with $i \in \{1,\cdots,N\}$. Next we introduce an impurity in the system. This changes both the energies and the wavefunctions of all the fermions. The distorted wavefunctions are denoted by $|\mathbf{q}_i\rangle$. In 1967 Philip

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[1] We use the convention in which all classically defined permutations are included in the summation - see the footnote to Eq. (7.12).

Anderson pointed out that, in the thermodynamic limit, the many-body states $|\alpha\rangle = |\mathbf{k}_1, \cdots, \mathbf{k}_N\rangle$ and $|\beta\rangle = |\mathbf{q}_1, \cdots, \mathbf{q}_N\rangle$ are orthogonal (i.e., $\langle\alpha|\beta\rangle \ll 1$) *no matter how weak the interaction with the impurity* [2]. This feature is fundamental because it offers an example in which perturbation theory works at the two-body level but fails at the many-body level.

To demonstrate the idea behind this theorem, we start by expressing the properly symmetrized states in terms of the unsymmetrized states,

$$\langle\alpha|\beta\rangle = \frac{1}{N!}\sum_{P_k}(-1)^{p_k}P_k\sum_{P_q}(-1)^{p_q}P_q(\mathbf{k}_1, \cdots, \mathbf{k}_N|\mathbf{q}_1, \cdots, \mathbf{q}_N), \tag{7.63}$$

where P_k and P_q are the permutation operators acting on the bra and ket states, respectively. To proceed we factorize each term of the double summation,

$$(\mathbf{k}_1, \cdots, \mathbf{k}_N|\mathbf{q}_1, \cdots, \mathbf{q}_N) = \langle\mathbf{k}_1|\mathbf{q}_1\rangle_1 \cdots \langle\mathbf{k}_N|\mathbf{q}_N\rangle_N = \langle\mathbf{k}_1|\mathbf{q}_1\rangle \cdots \langle\mathbf{k}_N|\mathbf{q}_N\rangle. \tag{7.64}$$

This is possible because, for identical particles, the inner products $\langle\mathbf{k}_i|\mathbf{q}_j\rangle$ are independent of the particle considered. Thus, the projection $\langle\alpha|\beta\rangle$ can be expressed in the form

$$\langle\alpha|\beta\rangle = \frac{1}{N!}\sum_{P_k}(-1)^{p_k}P_k\sum_{P_q}(-1)^{p_q}P_q\langle\mathbf{k}_1|\mathbf{q}_1\rangle \cdots \langle\mathbf{k}_N|\mathbf{q}_N\rangle. \tag{7.65}$$

The first summation gives rise to $N!$ terms, each corresponding to the sequence $\langle\mathbf{k}_1|, \cdots, \langle\mathbf{k}_N|$ combined with one of the permutations of the sequence $|\mathbf{q}_1\rangle, \cdots, |\mathbf{q}_N\rangle$. For each of these terms the second summation will generate the same set of terms because the value of the terms is independent of the order in which the factors $\langle\mathbf{k}_i|\mathbf{q}_j\rangle$ appear. Thus each term appears $N!$ times and the expression for $\langle\alpha|\beta\rangle$ simplifies to

$$\langle\alpha|\beta\rangle = \sum_{P_q}(-1)^{p_q}P_q\langle\mathbf{k}_1|\mathbf{q}_1\rangle \cdots \langle\mathbf{k}_N|\mathbf{q}_N\rangle, \tag{7.66}$$

which can be written as the determinant of the single-particle overlap matrix,

$$\langle\alpha|\beta\rangle = \begin{vmatrix} \langle\mathbf{k}_1|\mathbf{q}_1\rangle & \cdots & \langle\mathbf{k}_1|\mathbf{q}_N\rangle \\ \vdots & \ddots & \vdots \\ \langle\mathbf{k}_N|\mathbf{q}_1\rangle & \cdots & \langle\mathbf{k}_N|\mathbf{q}_N\rangle \end{vmatrix}. \tag{7.67}$$

Specializing to the case $|\mathbf{q}_i\rangle = |\mathbf{k}_i\rangle$ and using the orthonormality of the basis $\{|\mathbf{k}_i\rangle\}$ we readily verify the normalization of the many-body state $|\alpha\rangle$,

$$\langle\alpha|\alpha\rangle = \begin{vmatrix} 1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & 1 \end{vmatrix} = 1. \tag{7.68}$$

On the other hand, if the two states are only approximately equal, $|\mathbf{q}_i\rangle \simeq |\mathbf{k}_i\rangle$, we have $\langle\mathbf{k}_i|\mathbf{q}_i\rangle = 1-\varepsilon$, with $\varepsilon \ll 1$, and $\langle\mathbf{k}_i|\mathbf{q}_j\rangle \ll 1$. Recalling from perturbation theory that off-diagonal elements contribute to higher than the diagonal ones we are led to expect that the off-diagonal ones may be neglected if ε is sufficiently small. This withstands mathematical scrutiny and leaves us with a diagonal determinant; i.e., a product of the diagonal terms which are all slightly smaller than 1. In this case $\langle\alpha|\beta\rangle \to 0$ for $N \to \infty$.

7.5 Occupation number representation

7.5.1 Introduction

The notation of the previous section calls for simplification. This is realized by introducing *construction operators* which satisfy an algebra that enforces the quantum statistics. The first construction operators were introduced by Paul Dirac in 1927 [18]. Starting from Maxwell's equations, Dirac quantized the electromagnetic field by treating the eigenmodes of the field as independent harmonic oscillators. The excitation level of the oscillator represents the mode occupation of the field. The raising (lowering) operators of the oscillator serve to construct the field by creation (annihilation) of photons, the quanta occupying the modes of the radiation field. The commutation relations between the operators define the algebra that enforces the Bose statistics of the field. This work marks the start of quantum field theory. In the same year Pascual Jordan and Oskar Klein showed that the quantization method could be extended to describe quantum many-body systems of bosons satisfying the Schrödinger equation [36]. Adapting the algebra, Jordan and Wigner further extended the method to describe quantum many-body systems of fermionic particles [37]. The above sequence of seminal papers is not complete without the name of Vladimir Fock, who emphasized in 1932 the use of field operators (construction operators for position space) [24]. This approach leads to an operator identity resembling the Schrödinger equation, which explains the unfortunate name *second quantization* for the *construction operator formalism.* In following sections we give a concise introduction in the construction operator formalism for quantum many-body systems. For a systematic introduction (including the discussion of continuous spectra) the lecture notes of Jan de Boer are recommended [15].

7.5.2 Number states in the N-body Hilbert space $\mathbf{H}^N$

The notation of the properly symmetrized states can be compacted by listing only the occupations of the states,

$$|\tilde{n}_\gamma\rangle = |n_1, n_2, \cdots, n_l\rangle \equiv |\underbrace{\mathbf{k}_1, \mathbf{k}_1, \cdots}_{n_1}, \underbrace{\mathbf{k}_2, \mathbf{k}_2, \cdots}_{n_2} \cdots \underbrace{\cdots, \mathbf{k}_l}_{n_l}\rangle, \tag{7.69}$$

where $\gamma = \{1, 1, \cdots 2, 2, \cdots, l\}$, with $l \lesssim N$. In this way the states take the shape of *number states*, which are the basis states of the *occupation number representation* (see next section). For the case of N bosons in the same state $|\mathbf{k}_s\rangle$ the number state is given by $|n_s\rangle \equiv |\mathbf{k}_s, \cdots, \mathbf{k}_s\rangle$; for a single particle in state $|\mathbf{k}_s\rangle$ we have $|1_s\rangle \equiv |\mathbf{k}_s\rangle$. Note that the Bose symmetrization procedure puts no restriction on the value or order of the occupations $n_1, \cdots, n_l$ as long as they add up to the total number of particles, $n_1 + n_2 + \cdots + n_l = N$. For fermions the notation is the same but because the wavefunction changes sign under permutation the order in which the occupations are listed becomes subject to convention (for instance in order of growing energy of the states). Up to this point and in view of Eqs. (7.60) and (7.58) the number states (7.69) have normalization

$$\langle n_1', n_2', \cdots | n_1, n_1, \cdots \rangle = \delta_{n_1, n_1'} \delta_{n_2, n_2'} \cdots \tag{7.70}$$

and closure

$$\sum_{n_1, n_2 \cdots}{}' |n_1, n_2, \cdots\rangle \langle n_1, n_2, \cdots | = \underline{1}, \tag{7.71}$$

where the prime indicates that the sum over all occupations equals the total number of particles, $n_1 + n_2 + \cdots = N$. This is called closure within $\mathbf{H}^N$.

7.5.3 Number states in Grand Hilbert space - construction operators

An important generalization of number states is obtained by interpreting the occupations $n_s, n_t, \cdots$ as the eigenvalues of *number operators* $\hat{n}_s, \hat{n}_t, \cdots$ defined by

$$\hat{n}_s \left| n_s, n_t, \cdots, n_l \right\rangle = n_s \left| n_s, n_t, \cdots, n_l \right\rangle . \tag{7.72}$$

With this definition the expectation value of $\hat{n}_s$ is *exclusively* determined by the occupation of state $|s\rangle$; i.e., *not* by the occupation of all other states. Therefore, the number operators may be interpreted as acting in a *Grand Hilbert space*, also known as *Fock space*, which is the direct sum of the Hilbert spaces of all possible atom number states of a gas cloud, including the vacuum,

$$\mathbf{H}^{Gr} = \mathbf{H}^0 \oplus \mathbf{H}^1 \oplus \cdots \oplus \mathbf{H}^N \oplus \cdots .$$

By adding an atom we shift from $\mathbf{H}^N$ to $\mathbf{H}^{N+1}$, analogously we shift from $\mathbf{H}^N$ to $\mathbf{H}^{N-1}$ by removing an atom. As long as the change in particle number does not affect the occupation of the single-particle state $|s\rangle$ the operator $\hat{n}_s$ yields the same result. Hence, the *number states* $|n_s, n_t, \cdots, n_l\rangle$ from $\mathbf{H}^N$ may be reinterpreted as number states $|n_s, n_t, \cdots, n_l, 0_a, 0_b, \cdots 0_z\rangle$ within $\mathbf{H}^{Gr}$ by specifying - in principle - the occupations of *all* single-particle states. Usually only the occupied states are indicated. Thus the definition (7.69) remains valid but the notation may include empty states. For instance, the number states $|2_q, 1_t, \cdots, 1_l\rangle$ and $|0_s, 2_q, 1_t, \cdots, 1_l\rangle$ represent the same many-body state $|\mathbf{k}_q, \mathbf{k}_q, \mathbf{k}_t, \cdots, \mathbf{k}_l\rangle$.

The basic operators in Grand Hilbert space are the *construction operators* defined as

$$\hat{a}_s^\dagger \left| n_s, n_t, \cdots, n_l \right\rangle \equiv \sqrt{n_s + 1} \left| n_s + 1, n_t, \cdots, n_l \right\rangle \tag{7.73a}$$

$$\hat{a}_s \left| n_s, n_t, \cdots, n_l \right\rangle \equiv \sqrt{n_s} \left| n_s - 1, n_t, \cdots, n_l \right\rangle , \tag{7.73b}$$

where the $\hat{a}_s^\dagger$ and $\hat{a}_s$ are known as *creation* and *annihilation* operators, respectively. The creation operators transform a properly symmetrized N-body eigenstate in $\mathbf{H}^N$ into a $(N+1)$-body eigenstate (of the same symmetry) in $\mathbf{H}^{N+1}$. Analogously, the annihilation operators transform a properly symmetrized N-body eigenstate in $\mathbf{H}^N$ into a $(N-1)$-body eigenstate (of the same symmetry) in $\mathbf{H}^{N-1}$. Note that the annihilation operators yield zero when acting on non-occupied states. This reflects the logic that an already absent particle cannot be annihilated. Note further that $\hat{a}_s^\dagger$ and $\hat{a}_s$ are hermitian conjugates,

$$\langle n_s + 1 | \hat{a}_s^\dagger \left| n_s \right\rangle = \langle n_s | \hat{a}_s \left| n_s + 1 \right\rangle^* = \sqrt{n_s + 1}. \tag{7.74}$$

Hence, *when acting on the bra side* $\hat{a}_s^\dagger$ and $\hat{a}_s$ change their role, $\hat{a}_s^\dagger$ becomes the annihilation operator and $\hat{a}_s$ the creation operator.

For fermions we have to add some additional rules to assure that the construction operators create or annihilate proper fermions. First, a creation operator acting on an already occupied fermion state has to yield zero,

$$\hat{a}_s^\dagger \left| n_q, \cdots, 1_s, \cdots, n_l \right\rangle = 0. \tag{7.75}$$

Secondly, to assure anti-symmetry a creation (annihilation) operator acting on an empty (filled) fermion state must yield $+1$ or -1 depending on whether it takes an even or an odd permutation P between *occupied* states to bring the occupation number to the most left position in the fermion state vector,

$$\hat{a}_s^\dagger \left| 1_q, \cdots, 0_s, \cdots \right\rangle = (-1)^p \left| 1_q, \cdots, 1_s, \cdots \right\rangle \tag{7.76a}$$

$$\hat{a}_s \left| 1_q, \cdots, 1_s, \cdots \right\rangle = (-1)^p \left| 1_q, \cdots, 0_s, \cdots \right\rangle . \tag{7.76b}$$

Let us have a look at a few examples: $\hat{a}_s^\dagger \left| 0_q, 0_s, \cdots \right\rangle = + \left| 0_q, 1_s, \cdots \right\rangle$, $\hat{a}_s^\dagger \left| 1_q, 0_s, \cdots \right\rangle = - \left| 1_q, 1_s, \cdots \right\rangle$ and further $\hat{a}_s \left| 0_q, 1_s, \cdots \right\rangle = \left| 0_q, 0_s, \cdots \right\rangle$ and $\hat{a}_s \left| 1_q, 1_s, \cdots \right\rangle = - \left| 1_q, 0_s, \cdots \right\rangle$.

With the above set of rules *any* occupation of *any* given one-body state $|s\rangle$ can be obtained by repetitive use of the creation operator $\hat{a}_s^\dagger$,

$$\left(\hat{a}_s^\dagger\right)^{n_s} |0_s, n_t, \cdots\rangle = \sqrt{n_s!}\, |n_s, n_t, \cdots\rangle\,. \tag{7.77}$$

The notation can even be further compacted by using implicit definition of the many-body state vectors $|\psi_\gamma\rangle$ and number states $|\tilde{n}_\gamma\rangle$. For instance, the example state $|\psi_\gamma\rangle = |\mathbf{k}_q, \mathbf{k}_q, \mathbf{k}_t, \cdots, \mathbf{k}_l\rangle$, with $\gamma = \{q, q, t, \cdots, l\}$, corresponds to the number state $|n_\gamma\rangle = |2_q, 1_t, \cdots, 1_l\rangle$ in $\mathbf{H}^N$ which is extended to $|\tilde{n}_\gamma\rangle = |2_q, 1_t, \cdots, 1_l, \cdots\rangle$ in $\mathbf{H}^{Gr}$. By straightforward generalization of Eq. (7.77) *any* number state $|\tilde{n}_\gamma\rangle$ can be created by repetitive use of a set of creation operators

$$|\tilde{n}_\gamma\rangle = \prod_{s\in\gamma} \frac{\left(\hat{a}_s^\dagger\right)^{n_s}}{\sqrt{n_s!}}\, |0\rangle\,. \tag{7.78}$$

This expression holds for *both bosons and fermions.* The index $s \in \gamma$ points to the set of one-body states to be populated and $|0\rangle \equiv |0_q, 0_t, \cdots, 0_l\rangle$ is the *vacuum state*. We note that for the special case of a single particle in state $|s\rangle$

$$|s\rangle \equiv |1_s\rangle \equiv |\tilde{1}_s\rangle = \hat{a}_s^\dagger\, |0\rangle\,. \tag{7.79}$$

Thus we have obtained the *occupation number representation.* By extending $\mathbf{H}^N$ to $\mathbf{H}^{Gr}$ the definition of the number states and their normalization $\langle \tilde{n}_{\gamma'} | \tilde{n}_\gamma \rangle = \delta_{\gamma'\gamma}$ has remained unchanged. Note that also the newly introduced vacuum state is normalized,

$$\langle 0|0\rangle = \left\langle 1_s | \hat{a}_s^\dagger \hat{a}_s | 1_s \right\rangle = \langle s|s\rangle = 1,$$

as follows irrespective of the particular choice of single particle state $|s\rangle$. Importantly, by turning to $\mathbf{H}^{Gr}$ the condition on particle conservation is lost. This has the very convenient consequence that in the closure relation (7.71) the restricted sum may be replaced by an *unrestricted* sum, thus allowing for all possible values of N,

$$\sum_\gamma |\tilde{n}_\gamma\rangle \langle \tilde{n}_\gamma| = \sum_{n_1, n_2 \cdots} |n_1, n_2, \cdots\rangle \langle n_1, n_2, \cdots| = \underline{1}. \tag{7.80}$$

This is called closure within $\mathbf{H}^{Gr}$.

Having defined the construction operators the number operator can be expressed as $\hat{n}_s = \hat{a}_s^\dagger \hat{a}_s$ (cf. Problem 7.5). Further we can derive the following commutation relations for bosons $(-)$ and anticommutation relations for fermions $(+)$:[1]

$$\left[\hat{a}_q, \hat{a}_s^\dagger\right]_\pm = \delta_{qs}\ ; \qquad \left[\hat{a}_q, \hat{a}_s\right]_\pm = \left[\hat{a}_q^\dagger, \hat{a}_s^\dagger\right]_\pm = 0, \tag{7.81}$$

For *both bosons and fermions* we have

$$\left[\hat{n}_q, \hat{a}_s^\dagger\right] = +\hat{a}_s^\dagger \delta_{qs}\ ; \quad \left[\hat{n}_q, \hat{a}_s\right] = -\hat{a}_s \delta_{qs}\,. \tag{7.82}$$

Problem 7.4. Show that for bosons the following commutation relation holds

$$\left[\hat{a}_q, \hat{a}_s^\dagger\right] = \delta_{qs}.$$

Solution. By definition $\left[\hat{a}_q, \hat{a}_s^\dagger\right] = \hat{a}_q \hat{a}_s^\dagger - \hat{a}_s^\dagger \hat{a}_q$.
(a) For $q \neq s$ we obtain by applying the definition of the creation operators

$$\begin{aligned}\left[\hat{a}_q, \hat{a}_s^\dagger\right] |n_q, n_s, \cdots\rangle &= \hat{a}_q \sqrt{n_s+1}\, |n_q, n_s+1, \cdots\rangle - \hat{a}_s^\dagger \sqrt{n_q}\, |n_q-1, n_s, \cdots\rangle \\ &= \sqrt{n_q}\sqrt{n_s+1}\, |n_q-1, n_s+1, \cdots\rangle - \sqrt{n_s+1}\sqrt{n_q}\, |n_q-1, n_s+1, \cdots\rangle = 0\end{aligned}$$

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[1] Note that we use the convention $[a,b] \equiv [a,b]_- = ab - ba$ for the commutator and $[a,b]_+ = ab + ba$ for the anti-commutator.

(b) For $q = s$ we obtain we obtain

$$\begin{aligned}\left[\hat{a}_s, \hat{a}_s^\dagger\right] |n_s, \cdots\rangle &= \hat{a}_s\sqrt{n_s+1}\, |n_s+1, \cdots\rangle - \hat{a}_s^\dagger\sqrt{n_s}\, |n_s-1, \cdots\rangle \\ &= (n_s+1)\, |n_s, \cdots\rangle - n_s\, |n_s, \cdots\rangle \\ &= |n_s, \cdots\rangle\,. \end{aligned}$$ □

Problem 7.5. Show that the occupation number operator can be expressed as

$$\hat{n}_s = \hat{a}_s^\dagger \hat{a}_s. \tag{7.83}$$

Solution. The result follows by subsequent operation of $\hat{a}_s$ and $\hat{a}_s^\dagger$ on a number state

$$\begin{aligned}\hat{n}_s\, |n_s, n_t, \cdots, n_l\rangle &= \hat{a}_s^\dagger \hat{a}_s\, |n_s, n_t, \cdots, n_l\rangle \\ &= \sqrt{n_s}\hat{a}_s^\dagger\, |n_s-1, n_t, \cdots, n_l\rangle = n_s\, |n_s, n_t, \cdots, n_l\rangle\,.\end{aligned}$$

Note that this holds for both bosons and fermions. □

Problem 7.6. Show that for both bosons and fermions the following commutation relation holds

$$\left[\hat{n}_q, \hat{a}_s^\dagger\right] = +\hat{a}_s^\dagger \delta_{qs}.$$

7.5.4 Operators in the occupation number representation

Thus far we introduced $\hat{a}_s$, $\hat{a}_s^\dagger$ and $\hat{n}_s$ as operators in Grand Hilbert space. It may be shown that for *any* operator G acting in a N-body Hilbert space $\mathbf{H}^N$ we can define an *extension* $\hat{G}$ into Grand Hilbert space with the aid of the construction operators defined above. In particular we are interested in operators G that may be written as a sum of N one-body operators $g^{(i)}$, $N(N-1)/2!$ two-body operators $g^{(ij)}$, $N(N-1)(N-2)/3!$ three-body operators $g^{(ijk)}$, etc.; i.e., operators of the type

$$\begin{aligned} G &= G^{(1)} + G^{(2)} + G^{(3)} + \cdots \qquad (7.84)\\ &= \sum_i g^{(i)} + \frac{1}{2!}\sum_{i,j}{}' g^{(i,j)} + \frac{1}{3!}\sum_{i,j,k}{}' g^{(i,j,k)} + \cdots\,, \qquad (7.85)\end{aligned}$$

where the primed summations indicate that coinciding particle indices, like $i = j$, are excluded. The best known example of such an operator is the hamiltonian for a gas with binary interactions.

In preparation for the extension of G we first have a look at a cleverly selected one-body operator, the *correlation operator*

$$A_{s's} \equiv \sum_i |s'\rangle_{i\,i}\langle s|\,. \tag{7.86}$$

Acting on the number state $|n_q, \cdots, n_{s'}, \cdots, n_s, \cdots, n_l\rangle$ of $\mathbf{H}^N$, this operator sums over all possible ways in which one of the n_s particles in eigenstate $|s\rangle$ can be replaced by a particle in eigenstate $|s'\rangle$. The extension of $A_{s's}$ from $\mathbf{H}^N$ into $\mathbf{H}^{Gr}$ is given by

$$A_{s's} \equiv \sum_i |s'\rangle_{i\,i}\langle s| \quad \Rightarrow \quad \hat{A}_{s's} = \hat{a}_{s'}^\dagger \hat{a}_s. \tag{7.87}$$

Although this extension has an intuitive appeal its simple form can be misleading. In this respect the proof in Problem 7.7 may speak for itself. The full complexity of the (anti)symmetrization condition is contained in an algebra in which we only create or annihilate particles. The role of the (anti)symmetrization procedure is absorbed in the properties of the construction operators, in particular their commutation relations. The extension of the two-body correlation operator is given by

$$A_{s't'ts} \equiv \sum_{i,j}{}' \, |s'\rangle_j \, |t'\rangle_i \, {}_i\langle t| \, {}_j\langle s| \quad \Rightarrow \quad \hat{A}_{s't'ts} = \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}\hat{a}_t\hat{a}_s, \tag{7.88}$$

where the primed summation symbol implies $i \neq j$. The extensions $\hat{A}_{s't'ts} = \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}\hat{a}_t\hat{a}_s$ for the two-body operator, $\hat{A}_{t's'u'uts} = \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}\hat{a}^\dagger_{u'}\hat{a}_u\hat{a}_t\hat{a}_s$ for the three-body operator as well as similar extensions for more-body operators can be demonstrated in a way closely analogous to the one-body case, be it that the proofs become increasingly tedious and are not given here. In these expressions attention should be paid to the order of the construction operators.

Let us now return to the operator G. First we look at the one-body contribution $G^{(1)} \equiv \sum_i g^{(i)}$. Using twice the single particle closure relation (7.49) this expression can be rewritten as

$$G^{(1)} = \sum_{i=1}^{N} \left(\sum_{s'} |s'\rangle_i \, {}_i\langle s'| \right) g^{(i)} \left(\sum_{s} |s\rangle_i \, {}_i\langle s| \right). \tag{7.89}$$

As all particles are identical, the matrix elements ${}_i\langle s'| \, g^{(i)} \, |s\rangle_i$ all evaluate to the same value $\langle s'| \, g^{(1)} \, |s\rangle$, irrespective of the particle label i. Thus, Eq. (7.89) reduces to

$$G^{(1)} = \sum_{s's} \sum_{i=1}^{N} |s'\rangle_i \, \langle s'| \, g^{(1)} \, |s\rangle \, {}_i\langle s| \, . \tag{7.90}$$

Recognizing the correlation operator $A_{s's} \equiv \sum_i |s'\rangle_i \, {}_i\langle s|$ in Eq. (7.90) we have established that the extension of the operator G_1 is given by

$$\hat{G}^{(1)} = \sum_{s's} \hat{a}^\dagger_{s'} \, \langle s'| \, g^{(1)} \, |s\rangle \, \hat{a}_s. \tag{7.91}$$

Using the same approach for the pair terms $G^{(2)}$ and the three-body terms $G^{(3)}$ we obtain for the extension of the full operator G into the Grand Hilbert space,

$$\hat{G} = \hat{G}^{(1)} + \hat{G}^{(2)} + \hat{G}^{(3)} + \cdots , \tag{7.92}$$

where

$$\hat{G}^{(1)} = \sum_{s's} \hat{a}^\dagger_{s'} \, \langle s'| \, g^{(1)} \, |s\rangle \, \hat{a}_s \tag{7.93}$$

$$\hat{G}^{(2)} = \frac{1}{2!} \sum_{t't} \sum_{s's} \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'} (s', t'|g^{(1,2)}|s, t) \hat{a}_t\hat{a}_s \tag{7.94}$$

$$\hat{G}^{(3)} = \frac{1}{3!} \sum_{u'u} \sum_{t't} \sum_{s's} \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}\hat{a}^\dagger_{u'} (s', t', u'|g^{(1,2,3)}|s, t, u) \hat{a}_u\hat{a}_t\hat{a}_s. \tag{7.95}$$

This expression represents the generic operator to calculate expectation values in many-body systems, *including the effects of interactions between the particles.* Importantly, the particle index (i) does not appear in the notation, as it should for an ensemble of atoms that cannot be ordered because they are identical. The superscripts (1), (1, 2), (1, 2, 3), etc. refer to an arbitrary single atom, an arbitrary single pair of atoms, etc.; hence not to any specific choice of particle(s).

It is important to note the order in which the construction operators appear. Because the matrix element is *not* symmetrized, the indices s and s' are attached to particle 1 (better: the first particle of a product state), t and t' to particle 2, u and u' to particle 3, etc.. For bosons this is of no consequence because $\hat{a}_u, \hat{a}_t, \hat{a}_s, \cdots$ as well as $\hat{a}^\dagger_{s'}, \hat{a}^\dagger_{t'}, \hat{a}^\dagger_{u'}$ commute. For fermions this is not the case and mistakes in the order of the operators gives rise to sign errors.

Problem 7.7. Show that the extension of the correlation operator $A_{s's}$ in $\mathbf{H}^N$ to $\hat{A}_{s's}$ in $\mathbf{H}^{Gr}$ is given by

$$A_{s's} \equiv \sum_{i=1}^{N} |s'\rangle_{i\,i}\langle s| \quad \Rightarrow \quad \hat{A}_{s's} = \hat{a}_{s'}^{\dagger}\hat{a}_s,$$

where $|s\rangle$ and $|s'\rangle$ are eigenstates of the same operator A on which the occupation number representation of $\hat{a}_{s'}^{\dagger}$ and $\hat{a}_s$ is based.

Solution. The proof is given in the notation of Section 7.5.2. We set $|s\rangle = |\mathbf{k}_1\rangle$ and $|s'\rangle = |\mathbf{k}_2\rangle$, both eigenstates of the operator A,

$$A\,|\mathbf{k}_s\rangle = \alpha_s\,|\mathbf{k}_s\rangle\,,$$

with $s \in \{1, 2, \cdots l\}$, where $l \leq N$. In this notation the correlation operator is written as $A_{21} = \sum_i |\mathbf{k}_2\rangle_{ii}\langle\mathbf{k}_1|$ acting on the number state $|n_1, n_2, \cdots, n_l\rangle$.

Bosons: For bosons the number states are defined through (7.69) by the N-body state given in Eq. (7.60), replacing all particles in state $|\mathbf{k}_1\rangle$ by particles in state $|\mathbf{k}_2\rangle$,

$$A_{21}\,|n_1, n_2, \cdots, n_l\rangle = n_1\sqrt{\frac{1}{N!n_1!\cdots n_l!}}\sum_P P|\underbrace{\mathbf{k}_1, \mathbf{k}_1, \cdots,}_{n_1}\underbrace{\mathbf{k}_2, \cdots}_{n_2}\cdots\underbrace{\cdots\mathbf{k}_l}_{n_l}) \tag{7.96a}$$

$$= \sqrt{n_2+1}\sqrt{n_1}\,|n_1-1, n_2+1, \cdots, n_l\rangle\,. \tag{7.96b}$$

Note that term i of the correlation operator only yields a non-zero result if the state $|\mathbf{k}_1\rangle$ is found at position i in the product state. This follows directly from the orthonormality relations (7.49), $|\mathbf{k}_2\rangle_{i\,i}\langle\mathbf{k}_1|\mathbf{k}_s\rangle_i = |\mathbf{k}_2\rangle_i\,\delta_{s,1}$. Because we have initially n_1 particles in state $|\mathbf{k}_1\rangle$ there are n_1 equivalent ways to replace one particle in state $|\mathbf{k}_1\rangle$ by a particle in state $|\mathbf{k}_2\rangle$. The prefactor n_1 in Eq. (7.96a) is the same for all permutations P but results from a different subset of n_1 terms in the correlation operator. Note that if the state $|\mathbf{k}_1\rangle$ is not occupied the operator A_{21} is orthogonal to the number state and the procedure yields zero. Hence, in view of the definitions (7.73) we infer from Eq. (7.96b) that the extension of the operator A_{21} to the Grand Hilbert space is given by $\hat{A}_{21} = \hat{a}_2^{\dagger}\hat{a}_1$,

$$\hat{A}_{21}\,|n_1, \cdots, n_l\rangle = \hat{a}_2^{\dagger}\hat{a}_1\,|n_1, \cdots, n_l\rangle\,.$$

This extension is readily generalized to correlation operators $A_{s's}$ acting on the occupations of arbitrary eigenstates $|s\rangle = |\mathbf{k}_s\rangle$ and $|s'\rangle = |\mathbf{k}'_s\rangle$, thus completing the proof for bosons.

Fermions: For fermions we use a number state defined by the antisymmetric state (7.58):

$$A_{s's}\,|1_1, \cdots, 1_s, \cdots, 1_N\rangle = \sqrt{\frac{1}{N!}}\sum_P(-1)^p P|\mathbf{k}_1, \cdots, \mathbf{k}_{s'}, \cdots, \mathbf{k}_N) = |1_1, \cdots, 1_{s'}, \cdots, 1_N\rangle\,.$$

The operator $A_{s's}$ has replaced in the Slater determinant the column containing all particles in state $|\mathbf{k}_s\rangle$ by a column with all particles in state $|\mathbf{k}'_s\rangle$. This is exactly the result obtained by the action of the operator $\hat{A}_{s's} = \hat{a}_s^{\dagger}\hat{a}_s$,

$$\begin{aligned}\hat{A}_{s's}\,|1_1, \cdots, 1_s, \cdots, 1_N\rangle &= (-1)^p\hat{a}_{s'}^{\dagger}\hat{a}_s\,|1_s, 1_1, \cdots, 1_N\rangle\\ &= (-1)^p\,|1_{s'}, \cdots, 1_N\rangle = |1_1, \cdots, 1_{s'}, \cdots, 1_N\rangle\,,\end{aligned}$$

where p is the number of binary interchanges that brings the column containing all particles in state $|\mathbf{k}_s\rangle$ to the first position in the bracket. □

Example 7.1. An almost trivial but very instructive example of the extension procedure of an operator into Grand Hilbert space is the extension of the *total-number operator*, which is the unit operator $\underline{1}$ summed over all particles of a system,

$$N = \sum_{i=1}^{N}\underline{1}. \tag{7.97}$$

In the notation of the previous section the one-body operator in this example is $g^{(1)} = \underline{1}$ and the more-body operators are all zero. By substitution into Eq. (7.5.4) we obtain

$$\hat{N} = \sum_{s's} \hat{a}^{\dagger}_{s'} \langle s'| \, \underline{1} \, |s\rangle \, \hat{a}_s = \sum_{s's} \hat{a}^{\dagger}_{s'} \hat{a}_s \delta_{s's} \tag{7.98}$$

and substituting $\hat{n}_s = \hat{a}^{\dagger}_s \hat{a}_s$ we arrive at

$$\hat{N} = \sum_s \hat{n}_s. \tag{7.99}$$

7.5.5 Example: Hamiltonian in the occupation number representation

As an important application of the many-body formalism we consider the hamiltonian

$$\mathcal{H} = \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \cdots = \sum_i \left(-\frac{\hbar^2}{2m} \boldsymbol{\nabla}_i^2 + \mathcal{U}(\underline{\mathbf{r}}_i) \right) + \tfrac{1}{2} \sum_{i,j}{}' \mathcal{V}(\underline{\mathbf{r}}_i - \underline{\mathbf{r}}_j) + \cdots , \tag{7.100}$$

representing a gas of N atoms trapped in an external potential $\mathcal{U}(\mathbf{r})$ and interacting pairwise through the (not necessarily central) potential $\mathcal{V}(\underline{\mathbf{r}}_i - \underline{\mathbf{r}}_j)$. In the language of the previous section the one-body contribution to the Hamilton operator is

$$g^{(i)} = -\frac{\hbar^2}{2m} \boldsymbol{\nabla}_i^2 + \mathcal{U}(\underline{\mathbf{r}}_i) \equiv \mathcal{H}_0(\underline{\mathbf{p}}_i, \underline{\mathbf{r}}_i). \tag{7.101}$$

The two-body contribution is

$$g^{(i,j)} = \mathcal{V}(\underline{\mathbf{r}}_i - \underline{\mathbf{r}}_j), \tag{7.102}$$

and because we only consider binary interaction all more-body contributions are zero. Thus, according to Eq. (7.5.4), the extension of the hamiltonian to the occupation number representation is given by the expression

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} + \cdots = \sum_{s,s'} \hat{a}^{\dagger}_{s'} \langle s'| \, \mathcal{H}_0 \, |s\rangle \, \hat{a}_s + \tfrac{1}{2} \sum_{t,t'} \sum_{s,s'} \hat{a}^{\dagger}_{s'} \hat{a}^{\dagger}_{t'} (s', t'|\mathcal{V}|s, t) \hat{a}_t \hat{a}_s + \cdots . \tag{7.103}$$

Occupation of energy eigenstates

Interestingly, the construction operators were introduced without specification of the representation $\{|s\rangle\}$. Hence, the expression (7.103) can be simplified by turning to a specific representation in which the occupation numbers refer to the occupation of the eigenstates $|s\rangle$ of $\mathcal{H}_0$ defined by

$$\mathcal{H}_0 \, |s\rangle = \varepsilon_s \, |s\rangle \, . \tag{7.104}$$

In this representation, the representation of $\mathcal{H}_0$, the one-body matrix is diagonal, $\langle s'| \, \mathcal{H}_0 \, |s\rangle = \varepsilon_s \delta_{ss'}$, and $\hat{H}^{(1)}$ becomes

$$\hat{H}^{(1)} = \sum_s \hat{a}^{\dagger}_s \langle s| \, \mathcal{H}_0 \, |s\rangle \, \hat{a}_s = \sum_s \varepsilon_s \hat{n}_s, \tag{7.105}$$

as could be written down without much knowledge of the underlying formalism. Thus we find for the full hamiltonian

$$\hat{H} = \sum_s \varepsilon_s \hat{n}_s + \tfrac{1}{2} \sum_{t,t'} \sum_{s,s'} \hat{a}^{\dagger}_{s'} \hat{a}^{\dagger}_{t'} (s', t'|\mathcal{V}|s, t) \hat{a}_t \hat{a}_s + \cdots . \tag{7.106}$$

7.6 Field operators

7.6.1 Position representation

Let us write the *total number operator* (7.98) in the position representation. Using the closure relation $\underline{1} = \int d\mathbf{r}\,|\mathbf{r}\rangle\langle\mathbf{r}|$ we obtain

$$\hat{N} = \int d\mathbf{r} \sum_{s's} \hat{a}^{\dagger}_{s'}\, \langle s'|\,\mathbf{r}\rangle\langle\mathbf{r}\,|s\rangle\, \hat{a}_s = \int d\mathbf{r} \sum_{s'} \varphi^{*}_{s'}(\mathbf{r})\hat{a}^{\dagger}_{s} \sum_{s} \varphi_s(\mathbf{r})\hat{a}_s, \tag{7.107}$$

where the $\langle\mathbf{r}\,|s\rangle = \varphi_s(r)$ are the wavefunctions of an arbitrary single-particle basis $\{|s\rangle\}$. With this transformation we introduced two *operator densities*

$$\hat{\psi}(\mathbf{r}) \equiv \sum_{s} \varphi_s(\mathbf{r})\hat{a}_s \quad \text{and} \quad \hat{\psi}^{\dagger}(\mathbf{r}) \equiv \sum_{s} \varphi^{*}_{s}(\mathbf{r})\hat{a}^{\dagger}_{s}, \tag{7.108}$$

which are called *field operators* in view of their dependence on position. In terms of these field operators the total number operator takes the form

$$\hat{N} = \int d\mathbf{r}\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r}), \tag{7.109}$$

which can be written as

$$\hat{N} = \int d\mathbf{r}\,\hat{n}(\mathbf{r}). \tag{7.110}$$

This defines the *density* operator $\hat{n}(\mathbf{r})$ as the diagonal part of the *density matrix* operator,

$$\hat{n}(\mathbf{r},\mathbf{r}') = \hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r}'). \tag{7.111}$$

The field operators are construction operators that create or annihilate particles at a given position. Let us demonstrate this for $\hat{\psi}^{\dagger}(\mathbf{r})$. This field operator is a creation operator because it is defined in terms of creation operators,

$$\hat{\psi}^{\dagger}(\mathbf{r})|0\rangle = \sum_{s} \varphi^{*}_{s}(\mathbf{r})\hat{a}^{\dagger}_{s}|0\rangle = \sum_{s} |s\rangle\langle s|\mathbf{r}\rangle = |\mathbf{r}\rangle. \tag{7.112}$$

Using the closure relation $\underline{1} = \sum_s |s\rangle\,\langle s|$ we found that $\hat{\psi}^{\dagger}(\mathbf{r})$ creates from the vacuum a particle in state $|\mathbf{r}\rangle$; i.e., a particle at position $\mathbf{r}$. Similarly we can show that $\hat{\psi}(\mathbf{r})$ is the corresponding annihilation operator (cf. Problem 7.8)

$$\hat{\psi}(\mathbf{r})|\mathbf{r}\rangle = |0\rangle. \tag{7.113}$$

The field operators are important quantities because (at least in principle) the positions of the particles can be measured to arbitrary accuracy in any many-body system, also when the concept of stationary single-particle states has lost meaning due to coupling by the interactions.

Example 7.2. Consider the number state $|N_0\rangle$, representing N_0 bosons in the single-particle ground state $\varphi_0(\mathbf{r})$. In this case the following relation holds,

$$\langle N_0 - 1|\hat{\psi}(\mathbf{r})|N_0\rangle = \sqrt{N_0}\varphi_0(\mathbf{r}). \tag{7.114}$$

This expression follows immediately from Eq. (7.108). As only a single single-particle state is occupied only a single term contributes. If $|\psi_N\rangle = |\tilde{n}_\gamma\rangle$ is a pure number state of the single-particle representation $\{|s\rangle\}$, with many single-particle states are occupied, the expression is replaced by the linear combination

$$\langle\psi_{N-1}|\hat{\psi}(\mathbf{r})|\psi_N\rangle = \sum_{s} \sqrt{n_s}\varphi_s(\mathbf{r}).$$

Problem 7.8. Show that $\hat{\psi}(\mathbf{r})|\mathbf{r}\rangle = |0\rangle$.

Solution. Inserting the closure relation $\sum_{s'} |s'\rangle \langle s'| = \underline{1}$ just behind the annihilation operator we obtain

$$\hat{\psi}(\mathbf{r})|\mathbf{r}\rangle = \sum_s \varphi_s(\mathbf{r})\hat{a}_s|\mathbf{r}\rangle = \sum_{s,s'} \varphi_s(\mathbf{r})\hat{a}_s|s'\rangle\langle s'|\mathbf{r}\rangle = \sum_{s,s'} \varphi_s(\mathbf{r})\delta_{s,s'}|0\rangle\varphi^*_{s'}(\mathbf{r}) = \sum_s |\varphi_s(\mathbf{r})|^2|0\rangle = |0\rangle.$$

Here we recognized in the last step the Parseval relation $\sum_s |\varphi_s(\mathbf{r})|^2 = 1$. □

7.6.2 Commutation relations for field operators

It is straightforward to show (cf. Problem 7.9) that the field operators $\hat{\psi}^\dagger(\mathbf{r})$ and $\hat{\psi}(\mathbf{r})$ satisfy commutation relations very similar to those of the construction operators $\hat{a}^\dagger_s$ and $\hat{a}_s$ (cf. Section 7.5.3)

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm = \delta(\mathbf{r}-\mathbf{r}') \; ; \qquad [\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')]_\pm = [\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm = 0. \tag{7.115}$$

Like previously, the commutators $(-)$ refer to to case of bosons and the anti-commutators $(+)$ to the case of fermions. Further we have for *both bosons and fermions*

$$[\hat{n}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')] = +\hat{\psi}^\dagger(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') \; ; \quad [\hat{n}(\mathbf{r}), \hat{\psi}(\mathbf{r}')] = -\hat{\psi}(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'). \tag{7.116}$$

Using the expression (7.110) for the total number operator the latter commutation relation leads to

$$[\hat{\psi}(\mathbf{r}), \hat{N}] = \hat{\psi}(\mathbf{r}). \tag{7.117}$$

Problem 7.9. Show that the boson $(-)$ and fermion $(+)$ field operators satisfy the following commutation relations

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm = \delta(\mathbf{r}-\mathbf{r}').$$

Solution. Starting from the definition we have

$$\begin{aligned}[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm &= \sum_q \varphi_q(\mathbf{r})\hat{a}_q \sum_s \varphi^*_s(\mathbf{r}')\hat{a}^\dagger_s \pm \sum_s \varphi^*_s(\mathbf{r}')\hat{a}^\dagger_s \sum_q \varphi_q(\mathbf{r})\hat{a}_q \\ &= \sum_{q,s} \varphi^*_s(\mathbf{r}')\varphi_q(\mathbf{r})\hat{a}_q\hat{a}^\dagger_s \pm \sum_{q,s} \varphi^*_s(\mathbf{r}')\varphi_q(\mathbf{r})\hat{a}^\dagger_s\hat{a}_q \\ &= \sum_{q,s} \varphi^*_s(\mathbf{r}')\varphi_q(\mathbf{r})[\hat{a}_q, \hat{a}^\dagger_s]_\pm \\ &= \sum_s \langle\mathbf{r}|s\rangle\langle s|\mathbf{r}'\rangle.\end{aligned}$$

In the last step we used the commutation relation $[\hat{a}_q, \hat{a}^\dagger_s]_\pm = \delta_{q,s}$. Substituting the closure relation $\sum_s |s\rangle \langle s| = \underline{1}$ we arrive at $[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm = \langle\mathbf{r}|\mathbf{r}'\rangle = \delta(\mathbf{r}-\mathbf{r}')$. □

7.6.3 Number density

For a many-body system in the state $|\psi_N\rangle$ the *number-density* is given by $\langle\psi_N|\hat{n}(\mathbf{r})|\psi_N\rangle$. Using the definitions (7.108) the density coperator can be expressed in the occupation number representation of the single-particle representation $\{|s\rangle\}$; ,

$$\hat{n}(\mathbf{r}) = \sum_s \varphi^*_s(\mathbf{r})\hat{a}^\dagger_s \sum_t \varphi_t(\mathbf{r})\hat{a}_t = \sum_s |\varphi_s(\mathbf{r})|^2\hat{a}^\dagger_s\hat{a}_s + {\sum_{s,t}}' \varphi^*_s(\mathbf{r})\varphi_t(\mathbf{r})\hat{a}^\dagger_s\hat{a}_t, \tag{7.118}$$

where the prime indicates that $t \neq s$. We separated the operators into a sum of two contributions: (a) a part diagonal in the number representation of $\{|s\rangle\}$. For pure number states, $|\psi_N\rangle = |\tilde{n}_\gamma\rangle$, we calculate

$$\langle\psi_N|\hat{n}(\mathbf{r})|\psi_N\rangle = \sum_s |\varphi_s(\mathbf{r})|^2\langle\tilde{n}_\gamma|\hat{n}_s|\tilde{n}_\gamma\rangle = \sum_s |\varphi_s(\mathbf{r})|^2 n_s = \bar{n}(\mathbf{r}), \tag{7.119}$$

which corresponds to an eigenvalue equal to the quantum mechanical average (probability density). (b) the cross terms in this representation,

$$\sum_{s,t}{}' \varphi_s^*(\mathbf{r})\varphi_t(\mathbf{r})\hat{a}_s^\dagger\hat{a}_t = \hat{n}(\mathbf{r}) - \sum_s |\varphi_s(\mathbf{r})|^2\hat{n}_s. \tag{7.120}$$

For pure number states the cross term contribution vanishes. For linear combinations of number states the cross terms correspond to *density fluctuations* about the average.

7.6.4 The hamiltonian expressed in field operators

It is instructive to write the matrix elements $\langle s'|\,\mathcal{H}_0\,|s\rangle$ and $(s',t'|\mathcal{V}|s,t)$ in the position representation,

$$\hat{H}^{(1)} = \sum_{s,s'}\int d\mathbf{r}'d\mathbf{r}\,\hat{a}_{s'}^\dagger\,\langle s|\,\mathbf{r}'\rangle\langle\mathbf{r}'|\mathcal{H}_0|\mathbf{r}\rangle\langle\mathbf{r}\,|s\rangle\,\hat{a}_s \tag{7.121}$$

Writing this expression in the form

$$\hat{H}^{(1)} = \int d\mathbf{r}'d\mathbf{r}\sum_{s'}\varphi_{s'}^*(\mathbf{r}')\hat{a}_{s'}^\dagger\langle\mathbf{r}'|\mathcal{H}_0|\mathbf{r}\rangle\sum_s\varphi_s(\mathbf{r})\hat{a}_s \tag{7.122}$$

we recognize the field operators and $\hat{H}^{(1)}$ takes the form

$$\hat{H}^{(1)} = \int d\mathbf{r}'d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r}')\langle\mathbf{r}'|\mathcal{H}_0|\mathbf{r}\rangle\hat{\psi}(\mathbf{r}). \tag{7.123}$$

Since $\mathcal{H}_0$ is diagonal in the position representation, $\langle\mathbf{r}'|\mathcal{H}_0|\mathbf{r}\rangle = \mathcal{H}_0(\mathbf{p},\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$, the one-body hamiltonian reduces to

$$\hat{H}^{(1)} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\mathcal{H}_0(\mathbf{p},\mathbf{r})\hat{\psi}(\mathbf{r}). \tag{7.124}$$

Here $\mathcal{H}_0(\mathbf{p},\mathbf{r})$ is the single-particle hamiltonian in the Schrödinger representation ($\mathbf{p} \to -i\hbar\boldsymbol{\nabla}$, $\underline{\mathbf{r}} \to \mathbf{r}$). Importantly, $\mathcal{H}_0(\mathbf{p},\mathbf{r})$ does *not* commute with the field operators because the laplacian does not commute with the functions of the basis set $\{\varphi_s(\mathbf{r})\}$. In Problem 7.10 we derive the commutation relation

$$[\hat{\psi}(\mathbf{r}),\hat{H}^{(1)}] = \mathcal{H}_0(\mathbf{p},\mathbf{r})\hat{\psi}(\mathbf{r}), \tag{7.125}$$

which holds for both bosons and fermions.

We proceed with the interaction term from Eq. (7.103),

$$\hat{H}^{(2)} = \tfrac{1}{2}\sum_{t,t's,s'}\int d\mathbf{r}_1'd\mathbf{r}_2'd\mathbf{r}_1d\mathbf{r}_2\hat{a}_{s'}^\dagger\hat{a}_{t'}^\dagger(s',t'|\mathbf{r}_1',\mathbf{r}_2')(\mathbf{r}_1',\mathbf{r}_2'|\mathcal{V}(\underline{\mathbf{r}}_1-\underline{\mathbf{r}}_2)|\mathbf{r}_1,\mathbf{r}_2)(\mathbf{r}_1,\mathbf{r}_2|s,t)\hat{a}_t\hat{a}_s. \tag{7.126}$$

Since the operator $\mathcal{V}(\underline{\mathbf{r}}_i - \underline{\mathbf{r}}_j)$ is diagonal in the position representation we have

$$\hat{H}^{(2)} = \tfrac{1}{2}\sum_{t,t's,s'}\int d\mathbf{r}_1'd\mathbf{r}_2'd\mathbf{r}_1d\mathbf{r}_2\hat{a}_{s'}^\dagger\hat{a}_{t'}^\dagger\langle t'|\mathbf{r}_2'\rangle\langle s'|\mathbf{r}_1'\rangle\mathcal{V}(\mathbf{r}_1-\mathbf{r}_2)\langle\mathbf{r}_1'|\mathbf{r}_1\rangle\langle\mathbf{r}_2'|\mathbf{r}_2\rangle\langle\mathbf{r}_2|t\rangle\langle\mathbf{r}_1|s\rangle\hat{a}_t\hat{a}_s, \tag{7.127}$$

where $\mathcal{V}(\mathbf{r}_1-\mathbf{r}_2)$ is not an operator but a function of the relative position of two arbitrary particles (denoted 1 and 2). Since $\langle\mathbf{r}'|\mathbf{r}\rangle=\delta(\mathbf{r}-\mathbf{r}')$ and $\langle\mathbf{r}|s\rangle=\varphi_s(\mathbf{r})$ the operator $\hat{H}^{(2)}$ by integration over $\mathbf{r}_1'$ and $\mathbf{r}_2'$ Eq. (7.127) reduces to

$$\hat{H}^{(2)}=\tfrac{1}{2}\sum_{t,t's,s'}\int d\mathbf{r}_1d\mathbf{r}_2\hat{a}_{s'}^{\dagger}\varphi_{s'}^{*}(\mathbf{r}_1)\hat{a}_{t'}^{\dagger}\varphi_{t'}^{*}(\mathbf{r}_2)\mathcal{V}(\mathbf{r}_1-\mathbf{r}_2)\hat{a}_t\varphi_t(\mathbf{r}_2)\hat{a}_s\varphi_s(\mathbf{r}_1). \tag{7.128}$$

Note that the indices s and s' (t and t') are attached to particle 1 (2). Eq. (7.128) is different in this respect. As long as $\mathcal{V}(\mathbf{r}_1-\mathbf{r}_2)$ is a simple function of $\mathbf{r}_1-\mathbf{r}_2$ (e.g., not depending on a gradient with respect to position) it commutes with the functions of the set $\{\varphi_s(\mathbf{r})\}$ and Eq. (7.128) simplifies to the form

$$\hat{H}^{(2)}=\tfrac{1}{2}\int d\mathbf{r}_1d\mathbf{r}_2\mathcal{V}(\mathbf{r}_1-\mathbf{r}_2)\hat{\psi}^{\dagger}(\mathbf{r}_1)\hat{\psi}^{\dagger}(\mathbf{r}_2)\hat{\psi}(\mathbf{r}_2)\hat{\psi}(\mathbf{r}_1). \tag{7.129}$$

Note that the relation between summation index and particle index has resulted in the *particular order* in which the position variables $\mathbf{r}_1$ and $\mathbf{r}_2$ appear in Eq. (7.129).

Problem 7.10. Show that the following commutation relation holds for both fermions and bosons,

$$[\hat{\psi}(\mathbf{r}),\hat{H}^{(1)}]=\mathcal{H}_0(\mathbf{p},\mathbf{r})\hat{\psi}(\mathbf{r}).$$

Solution. First we write the commutator in the form

$$[\hat{\psi}(\mathbf{r}),\hat{H}^{(1)}]=\int d\mathbf{r}'[\hat{\psi}(\mathbf{r}),\hat{H}^{(1)}(\mathbf{r}')],$$

where $\hat{H}^{(1)}(\mathbf{r}')=\hat{\psi}^{\dagger}(\mathbf{r}')\mathcal{H}_0(\mathbf{p},\mathbf{r}')\hat{\psi}(\mathbf{r}')$ is the construction operator density for the one-body hamiltonian $\mathcal{H}_0(\mathbf{p},\mathbf{r})$. Using the commutation relations $[\hat{\psi}(\mathbf{r}),\hat{\psi}(\mathbf{r}')]_{\pm}=0$ and $[\mathcal{H}_0(\mathbf{p},\mathbf{r}'),\hat{\psi}(\mathbf{r})]=0$ we find

$$\begin{aligned}\int d\mathbf{r}'[\hat{\psi}(\mathbf{r}),\hat{H}^{(1)}(\mathbf{r}')]&=\int d\mathbf{r}'[\hat{\psi}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\mathcal{H}_0(\mathbf{p},\mathbf{r}')\hat{\psi}(\mathbf{r}')-\hat{\psi}^{\dagger}(\mathbf{r}')\mathcal{H}_0(\mathbf{p},\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})]\\&=\int d\mathbf{r}'[\hat{\psi}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\mathcal{H}_0(\mathbf{p},\mathbf{r}')\hat{\psi}(\mathbf{r}')\pm\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r})\mathcal{H}_0(\mathbf{p},\mathbf{r}')\hat{\psi}(\mathbf{r}')]\\&=\int d\mathbf{r}'[\hat{\psi}(\mathbf{r}),\hat{\psi}^{\dagger}(\mathbf{r}')]_{\pm}\mathcal{H}_0(\mathbf{p},\mathbf{r}')\hat{\psi}(\mathbf{r}').\end{aligned}$$

Substituting $[\hat{\psi}(\mathbf{r}'),\hat{\psi}^{\dagger}(\mathbf{r}')]_{\pm}=\delta(\mathbf{r}-\mathbf{r}')$ and integrating over $\mathbf{r}'$ we obtain the desired expression. □

7.6.5 Time-dependent field operators - second quantized form

Let us consider the hamiltonian of an ideal gas (non-interacting many-body system),

$$H=\sum_i-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2+\mathcal{U}(\mathbf{r}_i)=\sum_i\mathcal{H}_0(\mathbf{p}_i,\mathbf{r}_i). \tag{7.130}$$

In terms of field operators this hamiltonian can be written in the form $\hat{H}=\hat{H}^{(1)}$,

$$\hat{H}^{(1)}=\int d\mathbf{r}\hat{\psi}^{\dagger}(\mathbf{r})\mathcal{H}_0(\mathbf{p},\mathbf{r})\hat{\psi}(\mathbf{r}), \tag{7.131}$$

where the one-body construction operator $\hat{H}^{(1)}$ is expressed in terms of the field operators $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}^{\dagger}(\mathbf{r})$ defined by Eqs. (7.108). Let

$$\hat{\psi}(\mathbf{r},t)\equiv\hat{\psi}_H(t)=e^{i\hat{H}^{(1)}t/\hbar}\hat{\psi}(\mathbf{r})e^{-i\hat{H}^{(1)}t/\hbar} \tag{7.132}$$

be the Heisenberg operator corresponding to $\hat{\psi}(\mathbf{r})$. Because $\hat{\psi}(\mathbf{r})$ does not contain an explicit time dependence ($\partial\hat{\psi}(\mathbf{r})/\partial t = 0$), the Heisenberg equation of motion is given by Eq. (B.80) and since the evolution operator commutes with $\hat{H}^{(1)}$ we have

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r},t) = [\hat{\psi}(\mathbf{r},t),\hat{H}^{(1)}] = e^{i\hat{H}^{(1)}t/\hbar}[\hat{\psi}(\mathbf{r}),\hat{H}^{(1)}]e^{-i\hat{H}^{(1)}t/\hbar}. \tag{7.133}$$

Applying Eq. (7.125) we obtain

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r},t) = \mathcal{H}_0(\mathbf{p},\mathbf{r})\hat{\psi}(\mathbf{r},t). \tag{7.134}$$

With this equation we have regained for the Heisenberg equation of motion the form of the Schrödinger equation! This has become known as the *second* quantization form and, more in general, to the not very helpful name *second quantization* for the construction operator formalism.

7.7 Correlation functions

7.7.1 Introduction

We define first-order (one-body), second-order (two-body), third-order (three-body), etc. correlation operators depending on the number of particles involved in the correlation,

$$\begin{aligned}
\hat{n}(\mathbf{r},\mathbf{r}') &= \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}'),\\
\hat{n}^{(2)}(\mathbf{r},\mathbf{r}') &= \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r}),\\
\hat{n}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'') &= \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}^\dagger(\mathbf{r}'')\hat{\psi}(\mathbf{r}'')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r}),
\end{aligned}$$

and analogously for higher-order correlations. For a many-body system in an *arbitrary* state, $|\psi_N\rangle$, the corresponding density matrices are defined as the expectation value of the correlation operators in that state

$$\begin{aligned}
\rho^{(1)}(\mathbf{r},\mathbf{r}') &= \langle\psi_N|\hat{n}(\mathbf{r},\mathbf{r}')|\psi_N\rangle,\\
\rho^{(2)}(\mathbf{r},\mathbf{r}') &= \langle\psi_N|\hat{n}^{(2)}(\mathbf{r},\mathbf{r}')|\psi_N\rangle,\\
\rho^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'') &= \langle\psi_N|\hat{n}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')|\psi_N\rangle,
\end{aligned}$$

and analogously for higher order. These density matrices are correlation functions representing the distribution of one body, two bodies, three bodies, etc.. Importantly, these correlation functions are well defined, irrespective of the presence or absence or strength of the interparticle interactions but, in general, the actual calculation will be a major task.

In the coming section we discuss some interesting cases for which explicit expressions can be obtained. In Section 7.7.2 we discuss the one-body correlation functions for the ideal Fermi gas at $T = 0\,\mathrm{K}$ and the ideal Bose gas for $T < T_c$, where T_c is the critical temperature for Bose-Einstein condensation (see Section 9.2). For the ideal Fermi gas we can obtain a closed expression because the groundstate of the system can be represented by a simple number state, $|\psi_N\rangle \to |\mathrm{DFG}\rangle$. We show that the correlation is of the order of the inverse Fermi wavevector k_F^{-1}. For the degenerate Bose gas we have to follow a different approach because, at finite temperature, the best we can do is use a statistical distribution over the energy levels. For the *ideal* Bose gas the situation is still favorable because the statistical distribution can be expressed in terms of the occupation numbers of the single-particles states. As these occupation numbers are given by the well-known Bose-Einstein distribution function we can obtain a closed expression for the single particle correlation function of a degenerate ideal Bose gas. This correlation function shows the famous off-diagonal long-range order provided the single-particle groundstate (condensate) is macroscopically occupied. For *interacting*

Bose gases this approach fails because the single-particle state are coupled by the interactions. So what is the relevance of Bose-Einstein condensation for a quantum fluid if the interactions are strong? This question has been debated for many years in relation to the superfluidity of liquid ^{4}He below the so-called lambda transition at $T_\lambda \approx 2.17\,\mathrm{K}$. In 1956 Oliver Penrose and Lars Onsager pointed out that the eigenstates of the statistical operator remain well defined irrespective of the strength of the interaction because the statistical operator contains the full hamiltonian [54]. Therefore, although the concept of occupation of free-particle states has lost its meaning, off-diagonal long-range order can still be present and serve as an indicator for superfluidity. As we show in Section 7.7.3 off-diagonal long-range order is present if a macroscopic fraction of the particles have identical momentum. This criterium for superfluidity is supported by the Bogoliubov theory for the weakly-interacting Bose gas.

In Section 7.7.4 we turn to the two-body correlation functions. These are called pair-correlation functions because they describe the distribution of the particles remaining after removal of one particle from the system. For the ideal Fermi gas at $T = 0\,\mathrm{K}$ we use again the number state $|\mathrm{DFG}\rangle$ and obtain zero probability to find two fermion (in the same internal state at the same position. This manifests itself as a dip in the pair-correlation function (repulsive statistics) which is known as the Fermi hole. For the ideal Bose gas below T_c we use again the Bose-Einstein distribution function. Characteristically, we find no correlations between the atoms in the condensate and attractive correlations for those in the thermal cloud.

7.7.2 First-order correlations - density matrix - single-particle correlation function

For a many-body system in the state $|\psi_N\rangle$, the expectation value

$$\rho^{(1)}(\mathbf{r},\mathbf{r}') = \langle\psi_N|\hat{n}(\mathbf{r},\mathbf{r}')|\psi_N\rangle \tag{7.135}$$

is called the *one-body density matrix* or *single-particle correlation function* of the system in state $|\psi_N\rangle$. To evaluate the density matrix we have to choose a representation. Substituting the definitions (7.108) the operator takes the form

$$\hat{n}(\mathbf{r},\mathbf{r}') = \sum_s \varphi_s^*(\mathbf{r})\hat{a}_s^\dagger \sum_t \varphi_t(\mathbf{r}')\hat{a}_t = \sum_s \varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}')\hat{a}_s^\dagger\hat{a}_s + {\sum_{s,t}}' \varphi_s^*(\mathbf{r})\varphi_t(\mathbf{r}')\hat{a}_s^\dagger\hat{a}_t, \tag{7.136}$$

which is convenient for calculating the density matrix in the number representation of $\{|s\rangle\}$. For *pure* number states, $|\psi_N\rangle \to |\tilde{n}_\gamma\rangle$ (see Section 7.5.3), the cross terms of $\hat{n}(\mathbf{r},\mathbf{r}')$ do not contribute and the correlation function takes the form

$$\rho^{(1)}(\mathbf{r},\mathbf{r}') = \langle\tilde{n}_\gamma|\hat{n}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle = \sum_s \varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}')\langle\tilde{n}_\gamma|\hat{a}_s^\dagger\hat{a}_s|\tilde{n}_\gamma\rangle = \sum_s \varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}')n_s. \tag{7.137}$$

Ideal fermions

As an instructive example we calculate the density matrix for the *groundstate* of a one-component ideal Fermi gas of N particles per quantization volume V. By one-component we mean that all fermions are in the same internal state. Hence, the kinetic state of the gas has to be antisymmetric and can be represented by a single Slater determinant of N fermions. In the occupation number representation this groundstate is denoted by

$$|\mathrm{DFG}\rangle \equiv |n_0, n_1, \cdots\rangle \;\; \text{with} \;\; n_s = \begin{cases} 1 & \text{for } s \le N \\ 0 & \text{for } s > N, \end{cases} \tag{7.138}$$

where DFG stands for Degenerate Fermi Gas. The single-particle correlation function for the $|\mathrm{DFG}\rangle$ is defined as the expectation value

$$\rho^{(1)}(\mathbf{r},\mathbf{r}')=\langle\mathrm{DFG}|\hat{n}(\mathbf{r},\mathbf{r}')|\mathrm{DFG}\rangle=\sum_{s=0}^{N}\varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}')\langle\mathrm{DFG}|\hat{n}_s|\mathrm{DFG}\rangle.$$

For a *homogeneous* gas the states can be represented by plane waves ($s\to\mathbf{k}$),

$$\varphi_{\mathbf{k}}(\mathbf{r})=\frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{7.139}$$

Thus, the density matrix takes the form

$$\rho^{(1)}(\mathbf{r},\mathbf{r}')=\frac{1}{V}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}\langle\mathrm{DFG}|\hat{n}_{\mathbf{k}}|\mathrm{DFG}\rangle. \tag{7.140}$$

Furthermore, if the quantization volume is sufficiently large we obtain a quasi continuum of momentum states for which we may replace the state summation by a phase space integration - see Eq. (1.15)

$$\sum_{\mathbf{k}}\to\frac{V}{(2\pi)^3}\int d\mathbf{k}, \tag{7.141}$$

and, taking into account the occupied levels of the Fermi sea, we obtain

$$\rho^{(1)}(\mathbf{r},\mathbf{r}')=\frac{1}{(2\pi)^3}\int_{k\le k_F}d\mathbf{k}\,e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}. \tag{7.142}$$

Note that this is a function of $r=|\mathbf{r}'-\mathbf{r}|$. Therefore, we simplify the notation by writing $\rho^{(1)}(r)$ for the correlation function. After $\mathbf{k}$ integration we obtain (see Problem 7.11)

$$\rho^{(1)}(r)=\frac{2k_F^3}{(2\pi)^2}\frac{\sin(k_Fr)-k_Fr\cos(k_Fr)}{(k_Fr)^3}. \tag{7.143}$$

This function plotted in Fig. 7.1. For small k_Fr the function can be expanded in powers of (k_Fr)

$$\rho^{(1)}(r)=\frac{k_F^3}{6\pi^2}\left\{1-\tfrac{1}{10}(k_Fr)^2+\cdots\right\}. \tag{7.144}$$

Since for $r\to0$ the density matrix reduces to the number density, $\rho^{(1)}(0)=n=N/V$, we find that the latter is given by the well-known expression

$$n=\frac{k_F^3}{6\pi^2}. \tag{7.145}$$

This shows that, in a fully-degenerate *uniform* one-component ideal Fermi gas, the mean interparticle spacing is about as large as the inverse Fermi wavevector

$$n^{-1/3}\sim k_F^{-1}. \tag{7.146}$$

The correlation length calculates to

$$\ell_c^{(1)}\equiv\int_0^\infty\rho^{(1)}(r)/\rho^{(1)}(0)\,dr=\tfrac{3}{4}\pi k_F^{-1}. \tag{7.147}$$

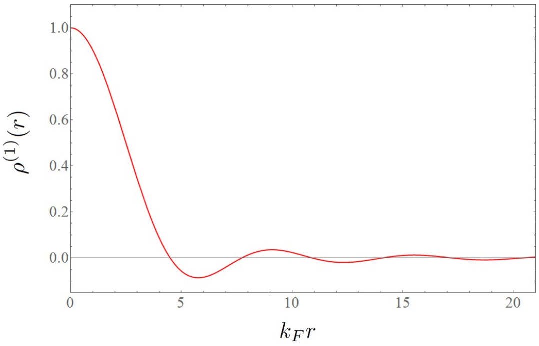

Figure 7.1: Single-particle correlation function (normalized to the density) for a fully degenerate Fermi sea of non-interacting particles. For the correlation length we calculate $\ell_c^{(1)} = \frac{3}{4}\pi k_F^{-1}$, which is comparable to the mean interparticle spacing.

Let us discuss our findings. For this purpose we first consider the one-body density matrix for a *single* particle in the eigenstate $|\varphi_s\rangle$,

$$\rho^{(1)}(\mathbf{r},\mathbf{r}') = \langle\varphi_s|\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}')|\varphi_s\rangle. \tag{7.148}$$

In this case, the density matrix represents the overlap between the states

$$\hat{\psi}(\mathbf{r}')|\varphi_s\rangle = \varphi_s(\mathbf{r}')|0\rangle \quad \text{and} \quad \hat{\psi}(\mathbf{r})|\varphi_s\rangle = \varphi_s(\mathbf{r})|0\rangle, \tag{7.149}$$

which evaluates to

$$\rho^{(1)}(\mathbf{r},\mathbf{r}') = \varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}'). \tag{7.150}$$

For the plane wave basis this becomes a wave uniformly distributed over space,

$$\rho^{(1)}(\mathbf{r},\mathbf{r}') = \frac{1}{V}e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})},$$

being 1 for $\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r}) = 0,\ \pm 2\pi,\ \pm 4\pi, \cdots$. For the N-body density matrix of the $|\text{DFG}\rangle$ this density matrix is given by

$$\rho^{(1)}(\mathbf{r},\mathbf{r}') = \sum_{\substack{\mathbf{k}\\(k\le k_F)}} e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}, \tag{7.151}$$

which is unity for $\mathbf{r}'=\mathbf{r}$ but falls off rapidly for growing $\mathbf{r}'-\mathbf{r}$,

$$\rho^{(1)}(\mathbf{r},\mathbf{r}') \to 0 \quad \text{for } |\mathbf{r}-\mathbf{r}'| \to \infty. \tag{7.152}$$

In the limit of an unrestricted sum over $\mathbf{k}$ the density matrix becomes the Dirac deltafunction. The one-body density matrix is a measure for the *single-particle correlations* in the system. The distance over which the correlations are substantial is called the *correlation length* $\ell_c^{(1)}$. For many-body fermionic systems $\ell_c^{(1)}$ is small because many Fourier components contribute to the number states. As can be seen in Fig. 7.1, the correlation length is of the order of the mean interparticle spacing, $\ell_c^{(1)} \sim k_F^{-1}$.

Problem 7.11. Show that the density matrix of a fully-degenerate uniform one-component Fermi gas can be written in the form

$$\rho^{(1)}(r) = \frac{2k_F^3}{(2\pi)^2}\frac{\sin(k_F r) - k_F r\cos(k_F r)}{(k_F r)^3}.$$

Solution. Starting from Eq. (7.142) we rewrite the integral in the form

$$\rho^{(1)}(\mathbf{r}'-\mathbf{r})=\frac{1}{(2\pi)^3}\int_0^{k_F}dk\int d\Omega k^2 e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}.$$

Defining $r=|\mathbf{r}'-\mathbf{r}|$ and θ as the angle enclosing the vectors $\mathbf{k}$ and $\mathbf{r}'-\mathbf{r}|$ the integral is written as

$$\rho^{(1)}(r)=\frac{2\pi}{(2\pi)^3}\int_0^{k_F}dk\,k^2\int_0^{\pi}d\theta e^{ikr\cos\theta}.$$

Changing to the dummy variable $\cos\theta\to x$ the integral becomes

$$\rho^{(1)}(r)=\frac{1}{(2\pi)^2}\int_0^{k_F}dk\,k^2\int_1^{-1}dx\,e^{ikrx}=\frac{2}{(2\pi)^2}\int_0^{k_F}dk\,k^2\frac{[e^{ikr}-e^{-ikr}]}{2ikr}.$$

Recycling the dummy variable, $kr\to x$, we obtain

$$\rho^{(1)}(r)=\frac{2}{(2\pi)^2}\frac{1}{r^3}\int_0^{k_F r}dx\,x\sin x,$$

which becomes, after integration by parts, the desired expression. □

Ideal bosons

Let us repeat the calculation but now for a degenerate ideal gas of spinless bosons. This a state of the system in which the single-particle ground state is macroscopically populated, while the occupation of the other states remains of order unity. In general this will be a thermal state. The one-body density matrix is given by the trace

$$\rho^{(1)}(\mathbf{r},\mathbf{r}')=\sum_{\{\tilde{n}_\gamma\}}\langle\tilde{n}_\gamma|\hat{\rho}\,\hat{n}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle, \tag{7.153}$$

which represents the average with the quantum statistical operator,

$$\hat{\rho}=\mathcal{Z}_{gr}^{-1}e^{-(\hat{H}-\mu\hat{N})/k_BT}. \tag{7.154}$$

Here T is the temperature and μ the chemical potential of the system; $\mathcal{Z}_{gr}$ is the grand canonical partition sum, which assures the unit normalization of the statistical distribution (see Chapter 8). As (for the ideal gas) $\hat{\rho}$ is diagonal in the occupation number representation of $\mathcal{H}_0$, the one-body density matrix can be written in the form

$$\rho^{(1)}(\mathbf{r},\mathbf{r}')=\sum_{\{\tilde{n}_\gamma\}}\langle\tilde{n}_\gamma|\hat{\rho}|\tilde{n}_\gamma\rangle\langle\tilde{n}_\gamma|\hat{n}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle, \tag{7.155}$$

where $\langle\tilde{n}_\gamma|\hat{n}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle$ is the density matrix for the number state state $|\tilde{n}_\gamma\rangle$. As $\langle\tilde{n}_\gamma|\hat{n}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle$ is diagonal, we may neglect the cross terms in Eq. (7.136) and the density matrix becomes

$$\rho^{(1)}(\mathbf{r},\mathbf{r}')=\sum_s\varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}')\langle\hat{n}_s\rangle. \tag{7.156}$$

The quantity $\langle\hat{n}_s\rangle$ is the quantum-statistical average of the occupation of state $|s\rangle$ (see Section 8.3.2), which evaluates to the well-know Bose-Einstein distribution function

$$\langle\hat{n}_s\rangle=\sum_{\{\tilde{n}_\gamma\}}\langle\tilde{n}_\gamma|\hat{\rho}|\tilde{n}_\gamma\rangle\langle\tilde{n}_\gamma|\hat{n}_s|\tilde{n}_\gamma\rangle=\frac{1}{z^{-1}e^{\varepsilon_s/k_BT}-1}. \tag{7.157}$$

In particular, one finds for the single-particle groundstate ($s = 0$)

$$\bar{n}_0 \equiv N_0 = \frac{z}{1-z} \simeq \frac{k_B T}{-\mu}. \tag{7.158}$$

Note that μ is macroscopically small but nonzero (otherwise N_0 diverges, which is unphysical). The quantity $z \equiv e^{\mu/k_B T}$ is the called the *fugacity* of the system. This function of the chemical potential (μ) offers convenience for algebraic manipulation of the Bose-Einstein distribution functions (see e.g., Problem 7.12). Separating the groundstate from the excited states the density matrix becomes

$$\rho^{(1)}(\mathbf{r}, \mathbf{r}') = N_0 \varphi_0^*(\mathbf{r}) \varphi_0(\mathbf{r}') + \rho_T^{(1)}(\mathbf{r}, \mathbf{r}'), \tag{7.159}$$

where $\rho_T^{(1)}(\mathbf{r}, \mathbf{r}')$ is the thermal contribution to the density matrix,

$$\rho_T^{(1)}(\mathbf{r}, \mathbf{r}') = \sum_{s \neq 0} \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r}') \langle \hat{n}_s \rangle. \tag{7.160}$$

Although the same result as for $\rho^{(1)}(\mathbf{r}, \mathbf{r}')$ is obtained for the pure number state $|N_0, \bar{n}_1, \bar{n}_2, \cdots\rangle$, it should be emphasized that the statistical average has a totally different physical meaning.

For a *homogeneous* gas the states can be represented by plane waves ($s \to \mathbf{k}$),

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{V^{1/2}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{7.161}$$

Thus, the density matrix takes the form

$$\rho^{(1)}(\mathbf{r}, \mathbf{r}') = \frac{N_0}{V} + \frac{1}{V} \sum_{\mathbf{k} \neq 0} n_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}. \tag{7.162}$$

If the quantization volume is sufficiently large we obtain a quasi continuum of momentum states for which we may replace the state summation by a phase space integration, see Eq. (7.141), and we obtain

$$\rho_T^{(1)}(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int d\mathbf{k}\, n_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}. \tag{7.163}$$

Substituting for $n_{\mathbf{k}}$ the Bose-Einstein distribution function - see Eq. (8.69) ,

$$n(k) = \frac{1}{z^{-1} e^{\hbar^2 k^2 / 2m k_B T} - 1}, \tag{7.164}$$

and evaluating the integral (see Problem 7.12), we find for the thermal contribution to the single particle correlation function

$$\rho_T^{(1)}(r) = \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{3/2}} \exp[-\frac{\pi r^2}{\ell \Lambda^2}]. \tag{7.165}$$

The full single particle correlation function is given by

$$\rho^{(1)}(r) = \frac{N_0}{V} + \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{3/2}} \exp[-\frac{\pi r^2}{\ell \Lambda^2}] \tag{7.166}$$

In the limit $r \to 0$ the density matrix yields the total density. For $z \to 1$ it becomes

$$\rho^{(1)}(0) = \frac{N_0}{V} + \frac{2.612\cdots}{\Lambda^3}. \tag{7.167}$$

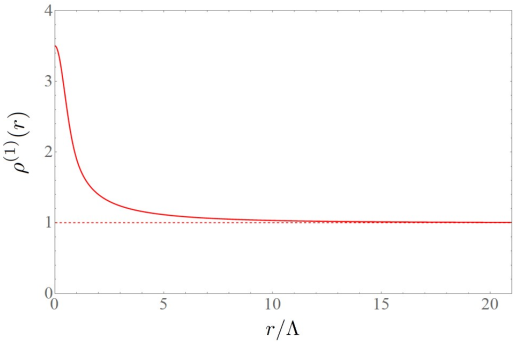

Figure 7.2: Single-particle correlation function (normalized to the condensate density) showing off-diagonal long-range order ($\ell_c^{(1)} \to \infty$) caused by the presence of the condensate. The correlation length in the thermal cloud is $\ell_c^{(1)}(T) \sim \Lambda$ but diverges for $z \to 1$.

The first term represents the condensate density. In the second term we recognize the critical density for BEC ($n_c = \zeta(3/2)\Lambda^{-3}$, see Section 9.2) for a homogeneous gas in the thermodynamic limit ($N, V \to \infty$, for $(N - N_0)/V = n_c$). The full density matrix is sketched in Fig. 7.2. Note that it does not decay to zero but to a constant value determined by the condensate density. This phenomenon is known as *off-diagonal long-range order* and is regarded as an indicator for the presence of a condensate (importantly, also for interacting quantum systems - cf. Section 7.7.3). For the ideal gas the correlation length evaluates to

$$\ell_c^{(1)} \equiv \int_0^\infty \rho_T^{(1)}(r)/\rho_T^{(1)}(0)\, dr = \tfrac{1}{2}\Lambda[g_1(z)/g_{3/2}(z)], \tag{7.168}$$

which is of order Λ but diverges for $z \to 1$ (the functions g_1 and $g_{3/2}$ are defined in Appendix C.4). This is characteristic for second-order (i.e., continuous) phase transitions and arises from an algebraic decay of the correlation function for $r \to \infty$ (see Problem 7.13).

Problem 7.12. Show that the density matrix for the thermal component of a degenerate ideal Bose gas can be written in the form

$$\rho_T^{(1)}(r) = \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{3/2}} \exp[-\frac{\pi r^2}{\ell \Lambda^2}],$$

where Λ is the thermal wavelength.

Solution. Starting from Eq. (7.163) we rewrite the integral in the form

$$\rho_T^{(1)}(r) = \frac{1}{(2\pi)^3} \int_0^\infty dk \int d\Omega k^2 n(k)\, e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})} = \frac{2\pi}{(2\pi)^3} \int_0^\infty dk\, k^2 n(k) \int_0^\pi d\theta e^{ikr\cos\theta}.$$

Introducing the dummy variable $\cos\theta \to x$, the integral becomes

$$\rho_T^{(1)}(r) = \frac{1}{(2\pi)^2} \int_0^\infty dk\, k^2 n(k) \int_1^{-1} dx\, e^{ikrx} = \frac{2}{(2\pi)^2} \int_0^\infty dk\, \frac{k^2}{z^{-1} e^{\hbar^2 k^2/2mk_BT} - 1} \frac{[e^{ikr} - e^{-ikr}]}{2ikr}.$$

Recycling the dummy variable, $\hbar^2 k^2/2mk_BT \to x$, we obtain

$$\rho_T^{(1)}(r) = \frac{1}{\pi\Lambda^2} \frac{1}{r} \int_0^\infty dx\, \frac{\sin(2\sqrt{\pi x}\, r/\Lambda)}{z^{-1} e^x - 1}.$$

This integral is rewritten with the aid of the fugacity expansion (8.91),

$$\rho_T^{(1)}(r) = \frac{1}{\pi\Lambda^2}\frac{1}{r}\sum_{\ell=1}^{\infty} z^{\ell} \int_0^{\infty} dx\, e^{-\ell x} \sin(2\sqrt{\pi x}\, r/\Lambda).$$

Evaluating the integral we find the desired result. □

Problem 7.13. Show that for degenerate Bose gases ($z \to 1$) the one-body correlation function falls off *algebraically* at large distances,

$$\rho_T^{(1)}(r) \sim \frac{1}{\Lambda^2}\frac{1}{r} \quad \text{for} \quad r \to \infty,$$

where Λ is the thermal wavelength.

Solution. Starting from Eq. (7.163) we use the approach of Problem 7.12 to write $\rho_T^{(1)}(r)$ in the form

$$\rho_T^{(1)}(r) = \frac{1}{\pi\Lambda^2}\frac{1}{r}\int_0^{\infty} dx\, \frac{\sin(2\sqrt{\pi x}\, r/\Lambda)}{z^{-1}e^{x} - 1},$$

where $x = \hbar^2 k^2/2mk_BT$. In view of its oscillatory behavior the sine only contributes substantially to the integral for $x \lesssim (1/4\pi)(\Lambda/r)^2$. For distances much larger than the thermal wavelength ($r \gg \Lambda$) this corresponds to values $x \ll 1$, which implies that (for $z \to 1$) the integral may be approximated by

$$\rho_T^{(1)}(r) \simeq \frac{1}{\pi\Lambda^2}\frac{1}{r}\int_0^{\infty} dx\, \frac{\sin(2\sqrt{\pi x}\, r/\Lambda)}{x} = \frac{1}{\Lambda^2}\frac{1}{r}.$$ □

7.7.3 Generalization to interacting systems - off-diagonal long-range order

The concept of off-diagonal long-range order derives its genuine importance from the *interacting* many-body quantum systems. In the presence of interactions, the stationary wavefunctions of the individual atoms are no longer defined as they have become coupled by the interactions. In search for the relevance of Bose-Einstein condensation in the presence of interactions Penrose and Onsager pointed out that the statistical operator (density matrix) remains well defined irrespective of the strength of the interactions because the statistical operator contains the full hamiltonian [54].

So let us consider a many-body system in the eigenstate $\psi_N(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ of the many-body hamiltonian of identical bosonic particles. The one-body density matrix of this state is given by the expectation value

$$\rho^{(1)}(\mathbf{r}, \mathbf{r}') = \langle \psi_N | \hat{n}(\mathbf{r}, \mathbf{r}') | \psi_N \rangle. \tag{7.169}$$

In the position representation this expression becomes

$$\rho^{(1)}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \int d\mathbf{r}'_1 \cdots d\mathbf{r}'_N \langle \psi_N | \mathbf{r}_1, \cdots, \mathbf{r}_N) \\ (\mathbf{r}_1, \cdots, \mathbf{r}_N | \hat{n}(\mathbf{r}, \mathbf{r}') | \mathbf{r}'_1, \cdots, \mathbf{r}'_N)(\mathbf{r}'_1, \cdots, \mathbf{r}'_N | \psi_N \rangle. \tag{7.170}$$

For $(\mathbf{r}_1, \cdots, \mathbf{r}_N | \hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r}') | \mathbf{r}'_1, \cdots, \mathbf{r}'_N)$ to be nonzero, annihilation of a particle at position $\mathbf{r}'_i$ (this is the particle with index $i \in \{1, \cdots, N\}$ in the product state) has to be compensated by recreating this particle at position $\mathbf{r}'_i$,

$$(\mathbf{r}_1, \cdots, \mathbf{r}_N | \hat{n}(\mathbf{r}, \mathbf{r}') | \mathbf{r}'_1, \cdots, \mathbf{r}'_N) = \delta(\mathbf{r}_1 - \mathbf{r}'_1) \cdots \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}'_i) \cdots \delta(\mathbf{r}'_N - \mathbf{r}_N). \tag{7.171}$$

As we are integrating over all positions and the particles are identical we obtain the same result for all particles (because $|\psi_N\rangle$ is symmetric under exchange of any two particles). This means that we are free to choose $i = 1$ and obtain

$$\rho^{(1)}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \, \psi_N^*(\mathbf{r}, \cdots, \mathbf{r}_N)\psi_N(\mathbf{r}', \cdots, \mathbf{r}_N).$$

This shows that the one-body distribution function $\rho^{(1)}(\mathbf{r}, \mathbf{r}')$ is well defined, irrespective of the strength of the interactions. Its shape is determined by quantum correlations as well as interparticle forces.

Knowing the one-body distribution function, we ask for its momentum content. For this purpose we write the field operator in the momentum representation

$$\hat{\psi}(\mathbf{k}) = \frac{1}{\sqrt{V}} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{\psi}(\mathbf{r}). \tag{7.172}$$

The operator for the momentum density is given by

$$\hat{n}(\mathbf{k}) = \hat{\psi}^\dagger(\mathbf{k})\hat{\psi}(\mathbf{k}). \tag{7.173}$$

In complete analogy with the number density, the operator for the total number of particles follows by integration over all momentum states (see Problem 7.14)

$$\hat{N} = \int \hat{n}(\mathbf{k}) d\mathbf{k}. \tag{7.174}$$

In search for the relation with the density matrix we use the definition (7.172) to write the momentum density operator in the form

$$\hat{n}(\mathbf{k}) = \frac{1}{V} \int d\mathbf{r} d\mathbf{r}' e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})} \hat{n}(\mathbf{r}, \mathbf{r}'). \tag{7.175}$$

Changing variables, $\mathbf{r}' - \mathbf{r} \to \mathbf{s}$ and $\frac{1}{2}(\mathbf{r}' + \mathbf{r}) \to \mathbf{R}$ (see Appendix A.7), the operator takes the form

$$\hat{n}(\mathbf{k}) = \lim_{V\to\infty} \frac{1}{V} \int d\mathbf{R} d\mathbf{s} e^{i\mathbf{k}\cdot\mathbf{s}} \hat{n}(\mathbf{R} + \tfrac{1}{2}\mathbf{s}, \mathbf{R} - \tfrac{1}{2}\mathbf{s}). \tag{7.176}$$

Let us restrict ourselves to the eigenstates $|\psi_N\rangle$ of uniform isotropic systems. In this case the density matrix is independent of $\mathbf{R}$ and the momentum distribution $n(\mathbf{k}) = \langle\psi_N|\hat{n}(\mathbf{k})|\psi_N\rangle$ is given by

$$n(\mathbf{k}) = \int d\mathbf{s} e^{i\mathbf{k}\cdot\mathbf{s}} \rho^{(1)}(\mathbf{r}, \mathbf{r}'). \tag{7.177}$$

Changing variables, $\mathbf{s} \to \mathbf{r}' - \mathbf{r}$ this becomes

$$n(\mathbf{k}) = \int d\mathbf{r}' e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})} \rho^{(1)}(\mathbf{r}, \mathbf{r}'). \tag{7.178}$$

Multiplying both sides with $e^{i\mathbf{k}\cdot\mathbf{r}}$ this integral takes the form of an eigenvalue equation for the density operator (cf. B.3),

$$\int d\mathbf{r}' \rho^{(1)}(\mathbf{r}, \mathbf{r}') \, e^{i\mathbf{k}\cdot\mathbf{r}'} = n(\mathbf{k}) \, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{7.179}$$

This expression shows that the many-body system can be analyzed in terms of the density of momentum states of the particles, $n(\mathbf{k})$. The Fourier decomposition has replaced the the basis of free-particle momentum states used in the ideal gas. This immediately implies that by observation of off-diagonal long-range order a macroscopic fraction of the atoms has to occupy the same momentum state. This points to BEC or a BEC-like phenomenon and suggest that off-diagonal long-range order can serve as an indicator for BEC in both non-interacting and interacting quantum systems. In the weakly interacting case this conjecture can be verified analytically. Penrose and Onsager demonstrated that this criterium also applies to models describing superfluid liquid ^{4}He [54].

Problem 7.14. Verify the relation $\int d\mathbf{k}\hat{n}(\mathbf{k}) = \hat{N}$.

Solution. Using Eq. (7.175) we have

$$\int d\mathbf{k}\hat{n}(\mathbf{k}) = \frac{1}{V}\int d\mathbf{r}d\mathbf{r}'\int d\mathbf{k}e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}\hat{n}(\mathbf{r},\mathbf{r}').$$

Using the expression for the Dirac deltafunction,

$$\frac{1}{V}\int \mathbf{dk}e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})} = \delta(\mathbf{r}'-\mathbf{r}) \tag{7.180}$$

we find the desired result

$$\int d\mathbf{k}\hat{n}(\mathbf{k}) = \int d\mathbf{r}d\mathbf{r}'\delta(\mathbf{r}'-\mathbf{r})\hat{n}(\mathbf{r},\mathbf{r}') = \int d\mathbf{r}\hat{n}(\mathbf{r},\mathbf{r}) = \hat{N}. \qquad \square$$

7.7.4 Second-order correlations - two-body density matrix - pair correlation function

The idea of the density matrix can be generalized to characterize higher-order correlations. In this spirit we define the *two-body density matrix*,

$$\hat{n}^{(2)}(\mathbf{r},\mathbf{r}') \equiv \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r}). \tag{7.181}$$

For a many-body system in the state $|\psi_N\rangle$, the expectation value

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \langle\psi_N|\hat{n}^{(2)}(\mathbf{r},\mathbf{r}')|\psi_N\rangle \tag{7.182}$$

is the called the *pair-correlation function* of the system in state $|\psi_N\rangle$. To reveal the physical meaning of this quantity we notice that the two-body density matrix is equal to the one-body density matrix *after removal of a particle*,

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \langle\psi_N|\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\psi_N\rangle = \langle\psi_N'|\hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r}')|\psi_N'\rangle = \bar{n}(\mathbf{r}'), \tag{7.183}$$

where

$$|\psi_N'\rangle \equiv \hat{\psi}(\mathbf{r})|\psi_N\rangle. \tag{7.184}$$

This shows that $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ is nothing else but the density distribution of the remaining particles in the system and corresponds to the distribution of pairs in the state $|\psi_N\rangle$. It also explains the name *pair correlation function.*

To evaluate the two-body density matrix we substitute the decomposition (7.108) for calculating the two-body density matrix in the number representation of $\{|s\rangle\}$,

$$\hat{n}^{(2)}(\mathbf{r},\mathbf{r}') = \sum_{t,t',s,s'}\varphi_{s'}^*(\mathbf{r})\varphi_{t'}^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\,\hat{a}_{s'}^\dagger\hat{a}_{t'}^\dagger\hat{a}_t\hat{a}_s. \tag{7.185}$$

For *pure* number states, $|\psi_N\rangle \to |\tilde{n}_\gamma\rangle$, the only nonzero contributions from the state summation (7.185) are those terms in which all states annihilated by the $\hat{a}_t\hat{a}_s$ are recreated by the $\hat{a}_{s'}^\dagger\hat{a}_{t'}^\dagger$. For $l \neq s$ these are the terms with either $s' = s$ and $t' = t$ or $t' = s$ and $s' = t$. For $s = t$ there is no exchange; i.e., only a single option remains to reconstruct the number state. Thus, the expression for the *two-body density matrix* reduces to the form

$$\begin{aligned}\rho^{(2)}(\mathbf{r},\mathbf{r}') \equiv \sum_s\{&\varphi_s^*(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_s(\mathbf{r}')\varphi_s(\mathbf{r})\langle\tilde{n}_\gamma|\hat{a}_s^\dagger\hat{a}_s^\dagger\hat{a}_s\hat{a}_s|\tilde{n}_\gamma\rangle\\ &+{\sum_{t,s}}'\{\varphi_s^*(\mathbf{r})\varphi_t^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\langle\tilde{n}_\gamma|\hat{a}_s^\dagger\hat{a}_t^\dagger\hat{a}_t\hat{a}_s|\tilde{n}_\gamma\rangle\\ &+\varphi_t^*(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\langle\tilde{n}_\gamma|\hat{a}_t^\dagger\hat{a}_s^\dagger\hat{a}_t\hat{a}_s|\tilde{n}_\gamma\rangle\}\},\end{aligned} \tag{7.186}$$

where the prime stands for the exclusion of $s = t$ from the double summation.

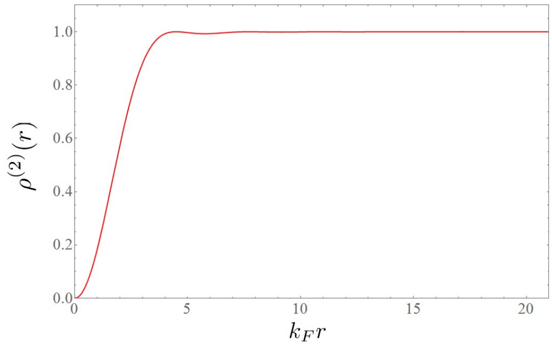

Figure 7.3: Pair correlation function (normalized to the density squared) for a fully degenerate Fermi sea of non-interacting particles. This pair correlation function vanishes for $r \to 0$, which reflects the absence of fermions (in the same internal state) within a "Pauli excluded" volume of size k_F^{-3} around each fermion. For the correlation length we find $\ell_c^{(2)} \sim k_F^{-1}$.

Ideal fermions

First we focus again on the fermions. Before evaluating the two-body density matrix we bring in recollection that two fermions in the same internal state cannot be at the same position. As we shall find, this shows up in the relative distribution of the particles. To demonstrate this we use again for the groundstate of the degenerate Fermi gas the state $|\mathrm{DFG}\rangle$ defined by Eq. (7.138) in Section 7.7.2,

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \langle \mathrm{DFG}|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\mathrm{DFG}\rangle. \tag{7.187}$$

As the $|\mathrm{DFG}\rangle$ is a pure number state, the expression for the *two-body density matrix* follows from Eq. (7.186),

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \sum_{t,s}{}' \{\varphi_s^*(\mathbf{r})\varphi_t^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\langle \mathrm{DFG}|\hat{a}_s^{\dagger}\hat{a}_t^{\dagger}\hat{a}_t\hat{a}_s|\mathrm{DFG}\rangle \\ + \varphi_t^*(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\langle \mathrm{DFG}|\hat{a}_t^{\dagger}\hat{a}_s^{\dagger}\hat{a}_t\hat{a}_s|\mathrm{DFG}\rangle\}. \tag{7.188}$$

We excluded the term $s = t$ from the summation because doubly occupied fermionic states do not exist. Since, we have $\hat{n}_s = \hat{a}_s^{\dagger}\hat{a}_s$ and for fermions $\hat{a}_t^{\dagger}\hat{a}_s = -\hat{a}_s\hat{a}_t^{\dagger}$ (since $s \neq t$ for fermions), we find with the aid of the commutation relation (7.82)

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \sum_{t,s}{}' \{|\varphi_t(\mathbf{r}')|^2|\varphi_s(\mathbf{r})|^2 - \varphi_t^*(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\}\langle \mathrm{DFG}|\hat{n}_t\hat{n}_s|\mathrm{DFG}\rangle. \tag{7.189}$$

For a *homogeneous* Fermi gas the states can be represented by plane waves,

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{7.190}$$

Setting $s \to \mathbf{k}$ and $t \to \mathbf{q}$ we obtain

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \frac{1}{V^2}\sum_{\mathbf{q},\mathbf{k}}{}' \left\{1 - e^{-i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}e^{i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})}\right\}\langle \mathrm{DFG}|\hat{n}_{\mathbf{q}}\hat{n}_{\mathbf{k}}|\mathrm{DFG}\rangle. \tag{7.191}$$

Substituting $\langle \mathrm{DFG}|\hat{n}_{\mathbf{q}}\hat{n}_{\mathbf{k}}|\mathrm{DFG}\rangle = \langle \mathrm{DFG}|\hat{n}_{\mathbf{q}}|\mathrm{DFG}\rangle\langle \mathrm{DFG}|\hat{n}_{\mathbf{k}}|\mathrm{DFG}\rangle$ and using the relation (7.140) we obtain

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \frac{N(N-1)}{V^2} - \left[\rho^{(1)}(\mathbf{r},\mathbf{r}')\right]^2. \tag{7.192}$$

This shows that the second-order correlation function is closely related to the first-order one. Substituting Eq. (7.143) we arrive at

$$\rho^{(2)}(r) = \frac{N(N-1)}{V^2}\left\{1 - \left(3\frac{\sin(k_F r) - k_F r\cos(k_F r)}{(k_F r)^3}\right)^2\right\}. \tag{7.193}$$

This function is plotted in Fig. 7.3. Note that the pair correlation function vanishes for $r \to 0$, which reflects the absence of fermions (in the same internal state) within a "Pauli excluded" volume of size k_F^{-3} around each fermion. This excluded volume is often referred to as the *Fermi hole* surrounding the fermions in the Fermi sea.

Ideal bosons

For the bosonic case we shall use the same approach as introduced for the one-body correlations in Section 7.7.2. The two-body density matrix is given by the trace

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \sum_{\{\tilde{n}_\gamma\}} \langle \tilde{n}_\gamma|\hat{\rho}\,\hat{n}^{(2)}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle, \tag{7.194}$$

which represents the average with the quantum statistical operator (7.154). As $\hat{\rho}$ is diagonal in the occupation number representation of $\mathcal{H}_0$, the two-body density matrix can be written in the form

$$\rho_T^{(2)}(\mathbf{r},\mathbf{r}') = \sum_{\{\tilde{n}_\gamma\}} \langle \tilde{n}_\gamma|\hat{\rho}|\tilde{n}_\gamma\rangle\langle \tilde{n}_\gamma|\hat{n}^{(2)}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle. \tag{7.195}$$

where $\langle \tilde{n}_\gamma|\hat{n}^{(2)}(\mathbf{r},\mathbf{r}')|\tilde{n}_\gamma\rangle$ is the two-body density matrix for the number state state $|\tilde{n}_\gamma\rangle$. As the $|\tilde{n}_\gamma\rangle$ is a pure number state, the expression for the *two-body density matrix* follows from Eq. (7.186) and becomes after thermal averaging,

$$\begin{aligned}\rho^{(2)}(\mathbf{r},\mathbf{r}') = \sum_s |\varphi_s(\mathbf{r}')|^2|\varphi_s(\mathbf{r})|^2\langle \hat{a}_s^\dagger\hat{a}_s^\dagger\hat{a}_s\hat{a}_s\rangle \\ + \sum_{t,s}{}' \{\varphi_s^*(\mathbf{r})\varphi_t^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\langle \hat{a}_s^\dagger\hat{a}_t^\dagger\hat{a}_t\hat{a}_s\rangle \\ + \varphi_t^*(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\langle \hat{a}_t^\dagger\hat{a}_s^\dagger\hat{a}_t\hat{a}_s\rangle\},\end{aligned} \tag{7.196}$$

where

$$\langle \hat{A}\rangle \equiv \sum_{\{\tilde{n}_\gamma\}} \langle \tilde{n}_\gamma|\hat{\rho}|\tilde{n}_\gamma\rangle\langle \tilde{n}_\gamma|\hat{A}|\tilde{n}_\gamma\rangle.$$

Comparing $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ with the fermionic case we find that the fermionic constraint $s \neq t$ is absent. Since, we have $\hat{n}_s = \hat{a}_s^\dagger\hat{a}_s$ and for bosons $\hat{n}_t\hat{a}_s = -\hat{a}_s\delta_{s,t} + \hat{a}_s\hat{n}_t$, we find with the aid of the commutation relation (7.82)

$$\begin{aligned}\rho^{(2)}(\mathbf{r},\mathbf{r}') = \sum_s |\varphi_s(\mathbf{r}')|^2|\varphi_s(\mathbf{r})|^2\langle \hat{n}_s(\hat{n}_s - 1)\rangle \\ + \sum_{t,s}{}' \{|\varphi_t(\mathbf{r}')|^2|\varphi_s(\mathbf{r})|^2 + \varphi_t^*(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_t(\mathbf{r}')\varphi_s(\mathbf{r})\}\langle \hat{n}_t\hat{n}_s\rangle.\end{aligned} \tag{7.197}$$

For a *homogeneous* Bose gas the states can be represented by plane waves,

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{7.198}$$

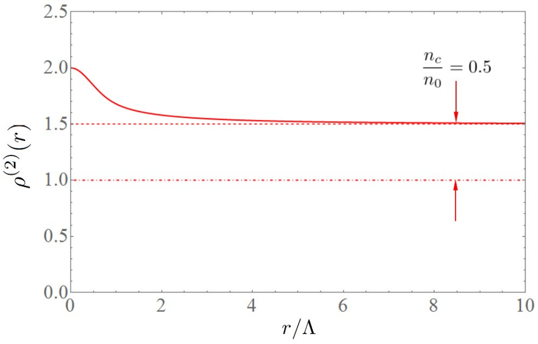

Figure 7.4: Pair correlation function (normalized to the condensate density squared) for a degenerate Bose gas of non-interacting particles. In this example the condensate fraction is taken to be 2/3. The pair-correlation length diverges ($\ell_c^{(2)} \to \infty$) due to the presence of the condensate. For the thermal component we find $\ell_c^{(2)}(T) \sim \Lambda$.

Setting $s \to \mathbf{k}$ and $t \to \mathbf{q}$ we obtain

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \frac{1}{V^2}\sum_{\mathbf{k}}\langle\hat{n}_{\mathbf{k}}(\hat{n}_{\mathbf{k}}-1)\rangle + \frac{1}{V^2}{\sum_{\mathbf{q},\mathbf{k}}}' \left\{1+e^{-i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}e^{i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})}\right\}\langle\hat{n}_{\mathbf{q}}\hat{n}_{\mathbf{k}}\rangle. \tag{7.199}$$

In case only the single-particle groundstate is macroscopically occupied this expression may be approximated by

$$\rho^{(2)}(r) \simeq \frac{N_0(N_0-1)}{V^2} + \frac{N_0}{V^2}{\sum_{\mathbf{k}}}' \left\{1+e^{-i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}\right\}\langle\hat{n}_{\mathbf{k}}\rangle \tag{7.200}$$

After continuum transition and recalling Eq. (7.163) we obtain

$$\rho^{(2)}(r) \simeq \frac{N_0(N_0-1)}{V^2} + \frac{N_0(N-N_0)}{V^2} + \frac{N_0}{V}\rho_T^{(1)}(r). \tag{7.201}$$

Substituting $n = N/V$ and $n_0 = N_0/V$ and using

$$n - n_0 = n_c \simeq \frac{2.612}{\Lambda^3} \tag{7.202}$$

we arrive at

$$\rho^{(2)}(r) \simeq n_0^2\left\{1+(n_c/n_0)[1+\rho_T^{(1)}(r)]\right\}. \tag{7.203}$$

This function is plotted in Fig. 7.4. Note that the probability to find two *thermal* bosons at the same position is twice as large as the probability to find them at large separation.

7.7.5 Occupation of momentum eigenstates

In the case of *homogeneous* fluids the eigenfunctions of $\mathcal{H}_0$ correspond to plane waves,

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{7.204}$$

These are also eigenstates of the momentum representation. Hence, $\hat{H}^{(2)}$ can also be expressed in the occupation number representation of the momentum eigenstates $|\mathbf{k}\rangle$,

$$\hat{H}^{(2)} = \tfrac{1}{2}\sum_{\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2'}\hat{a}^\dagger_{\mathbf{k}_1'}\hat{a}^\dagger_{\mathbf{k}_2'}\hat{a}_{\mathbf{k}_2}\hat{a}_{\mathbf{k}_1}\frac{1}{V^2}\int d\mathbf{r}_1 d\mathbf{r}_2 e^{i\left(\mathbf{k}_1-\mathbf{k}_1'\right)\cdot\mathbf{r}_1}e^{i\left(\mathbf{k}_2-\mathbf{k}_2'\right)\cdot\mathbf{r}_2}\mathcal{V}(\mathbf{r}_1-\mathbf{r}_2). \tag{7.205}$$

Turning to center of mass ($\mathbf{R}$) and relative ($\mathbf{r}$) coordinates (cf. Appendix A.7), we have $\mathbf{r}_1 = \mathbf{R} + \mathbf{r}/2$, $\mathbf{r}_2 = \mathbf{R} - \mathbf{r}/2$ and the expression for $\hat{H}^{(2)}$ becomes

$$\hat{H}^{(2)} = \tfrac{1}{2} \sum_{\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2'} \hat{a}^\dagger_{\mathbf{k}_1'} \hat{a}^\dagger_{\mathbf{k}_2'} \hat{a}_{\mathbf{k}_2} \hat{a}_{\mathbf{k}_1} \frac{1}{V^2} \int d\mathbf{R} e^{i\left(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_1'-\mathbf{k}_2'\right)\cdot\mathbf{R}} \int d\mathbf{r} e^{i\left(\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_1'+\mathbf{k}_2'\right)\cdot\mathbf{r}/2} \mathcal{V}(\mathbf{r}). \quad (7.206)$$

Note that this expression is zero unless the two-body operator conserves momentum

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2' = (\mathbf{k}_1 + \mathbf{q}) + (\mathbf{k}_2 - \mathbf{q}). \quad (7.207)$$

Thus, the summation over $\mathbf{k}_1, \mathbf{k}_1', \mathbf{k}_2, \mathbf{k}_2'$ can be replaced by a summation over $\mathbf{k}_1, \mathbf{k}_2, \mathbf{q}$ and the expression for $\hat{H}^{(2)}$ reduces to

$$\hat{H}^{(2)} = \tfrac{1}{2} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{q}} \hat{a}^\dagger_{\mathbf{k}_1+\mathbf{q}} \hat{a}^\dagger_{\mathbf{k}_2-\mathbf{q}} \hat{a}_{\mathbf{k}_2} \hat{a}_{\mathbf{k}_1} \frac{1}{V} \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \mathcal{V}(\mathbf{r}). \quad (7.208)$$

For realistic short-range interatomic potentials the Fourier transform

$$\widetilde{\mathcal{V}}(\mathbf{q}) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \mathcal{V}(\mathbf{r}) \quad (7.209)$$

cannot be restricted to low values of $\mathbf{q}$ because the potential steeply varies at distances $r \ll r_0$, where r_0 is the range of the potential. For ultracold dilute gases this problem can be circumvented because in the low-energy limit ($kr_0 \ll 1$) the scattering amplitude becomes energy independent and for isotropic scatterers all effects of the interaction can be represented by a single parameter, the s-wave scattering length a - see Chapter 3. In that case we can replace the potential $\mathcal{V}(\mathbf{r})$ by an effective potential $\mathcal{V}_{\text{eff}}(r)$ that lacks the hard core of the real system but yields the same value for a. In this case $\mathbf{q}$ is always small and the exponent $e^{-i\mathbf{q}\cdot\mathbf{r}}$ always close to unity except for large values of $\mathbf{r}$ ($r \gg r_0$) where short-range potentials are negligibly small. Hence, we may approximate

$$\widetilde{\mathcal{V}}(\mathbf{q}) \simeq \widetilde{\mathcal{V}}_{\text{eff}}(0). \quad (7.210)$$

In this limit the expression for $\hat{H}^{(2)}$ becomes

$$\hat{H}^{(2)} = \frac{g}{2V} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{q}} \hat{a}^\dagger_{\mathbf{k}_1+\mathbf{q}} \hat{a}^\dagger_{\mathbf{k}_2-\mathbf{q}} \hat{a}_{\mathbf{k}_2} \hat{a}_{\mathbf{k}_1}, \quad (7.211)$$

where

$$g = \int d\mathbf{r} \mathcal{V}_{\text{eff}}(r) \quad (7.212)$$

is called the coupling constant of the interaction. This expression is only valid for ultracold dilute gases, where the size of the scattering length is much smaller that the mean particle spacing,

$$|a| \ll n^{-1/3}. \quad (7.213)$$

A particularly convenient form for the effective potential is the pseudo potential introduced in Section 3.8. In that section we show that the coupling constant and the scattering length are related by the expression

$$g = 4\pi\hbar^2 a/m. \quad (7.214)$$

8

Quantum statistics

8.1 Introduction

To describe the time evolution of an isolated quantum gas, in principle, all we need to know is the many-body wavefunction plus the hamiltonian operator. Of course, in practice, these quantities will be known only to limited accuracy. Therefore, just as in the case of classical gases, we have to rely on statistical methods to describe the properties of a quantum gas. This means that we are interested in the probability of occupation of quantum many-body states. In view of the convenience of the occupation number representation we ask in particular for the probability of occupation P_γ of the number states $|\tilde{n}_\gamma\rangle$. The canonical ensemble introduced in Section 1.2.4 is not suited for this purpose because it presumes a fixed number of atoms N, whereas the ensemble of number states $\{|\tilde{n}_\gamma\rangle\}$ is defined in Grand Hilbert space in which the number of atoms is not fixed. This motivates us to introduce an important variant of the canonical ensemble which is known as the grand canonical ensemble.

8.2 Grand canonical distribution

In the grand canonical approach we consider a small system which can exchange not only heat but also atoms with a large reservoir. Like in the canonical case a small system is split off as a part of a one-component gas of N_{tot} identical atoms at temperature T (total energy E_{tot}). We can visualize the situation as a cloud of trapped atoms connected asymptotically to a homogeneous gas at very low density, a bit reminiscent of the conditions for evaporative cooling (see Section 1.4.1). We are interested in conditions in which the quantum resolution limit is reached in the center of the cloud and the cloud has to be treated as an interacting quantum many-body system. In the reservoir the density can be made arbitrarily low, so the reservoir atoms may be treated quasi-classically.

According to the statistical principle, the probability $P_0(E,N)$ that the trapped gas (the subsystem) has total energy between E and $E+\delta E$ and consists of a number of trapped atoms between N and $N+\delta N$ is proportional to the number $\Omega^{(0)}(E,N)$ of states accessible to the *total* system in which the subsystem matches the conditions for E and N,

$$P_0(E,N) = C_0\Omega^{(0)}(E,N),$$

where C_0 is a normalization constant. Because the atoms of the subsystem do not interact with the atoms of the reservoir (except for a vanishingly fraction of the atoms near the edge of the trap) the probability $P_0(E,N)$ can be written as the *product* of the number of quantum mechanical N-body states $\Omega_N(E)$ with energy near E times the number of microstates $\Omega(E^*,N^*)$ of energy near $E^* = E_{tot} - E$ accessible to the $N^* = N_{tot} - N$ atoms of the rest of the gas,

$$P_0(E,N) = C_0\Omega(E,N)\,\Omega(E_{tot}-E, N_{tot}-N). \tag{8.1}$$

If the total number of atoms is very large ($N_{tot} \ggg 1$) the trapped number will always be much smaller than the number in the remaining gas, $N \lll N^*$. Similarly, the amount of heat involved is small, $E \lll E^*$. Thus the distribution $P_0(E, N)$ can be calculated by treating the remaining gas as both a *heat reservoir* and a *particle reservoir* for the small system. The ensemble of subsystems with energy between E and $E + \delta E$ and atom number between N and $N + \delta N$ is called the *grand canonical ensemble*.

The probability P_γ of finding the small system in a specific, properly symmetrized, many-body *energy* eigenstate $|\tilde{n}_\gamma\rangle$ is given by

$$P_\gamma = C_0 \Omega_\gamma (E_\gamma, N_\gamma) \Omega (E_{tot} - E_\gamma, N_{tot} - N_\gamma) = C_0 \Omega (E^*, N^*), \tag{8.2}$$

where we used $\Omega_\gamma (E_\gamma, N_\gamma) = 1$ because the state of the subsystem is fully specified.

Like in the case of the canonical distribution we turn to a logarithmic scale by introducing the function $S^* = k_B \ln \Omega(E^*, N^*)$. Because $E \ll E_{tot}$ and $N \ll N_{tot}$ we may approximate $\ln \Omega(E^*, N^*)$ with a Taylor expansion to first order in E^* and N^*,

$$\ln \Omega(E^*, N^*) = \ln \Omega (E_{tot}, N_{tot}) - [\partial \ln \Omega(E^*, N^*)/\partial E^*]_{N^*} E_\gamma - [\partial \ln \Omega(E^*, N^*)/\partial N^*]_{E^*} N_\gamma.$$

Introducing the quantity $\beta \equiv [\partial \ln \Omega(E^*, N^*)/\partial E^*]_{N^*}$ we infer $k_B\beta = (\partial S^*/\partial E^*)_{N^*}$. Similarly we introduce the quantity $\alpha \equiv [\partial \ln \Omega(E^*, N^*)/\partial N^*]_{E^*}$, which implies $k_B\alpha = (\partial S^*/\partial N^*)_{E^*}$. In terms of these quantities we obtain for the probability to find the small system in the state $|\tilde{n}_\gamma\rangle$

$$P_\gamma = C_\gamma \Omega (E_{tot}, N_{tot}) e^{-\beta E_\gamma - \alpha N_\gamma} = \mathcal{Z}_{gr}^{-1} e^{-\beta E_\gamma - \alpha N_\gamma}. \tag{8.3}$$

This is called the *grand canonical distribution*, subject to the closure condition $\sum_\gamma P_\gamma = 1$. The closure is normalized by the *Grand partition sum.*

$$\mathcal{Z}_{gr} = \sum_\gamma e^{-\beta E_\gamma - \alpha N_\gamma}. \tag{8.4}$$

It differs from the canonical partition sum in that the summation over all many-body states $|\tilde{n}_\gamma\rangle$ is *unrestricted*; i.e., it not only includes states of different energy but also states of different number of atoms. The Grand partition sum can be separated into a double summation in which we first sum over all possible states $|N, \tilde{n}_\gamma\rangle$ of N atoms and subsequently over all possible values of N,

$$\mathcal{Z}_{gr} = \sum\nolimits_N e^{-\alpha N} \sum\nolimits_\gamma^{(N)} e^{-\beta E_\gamma} = \sum\nolimits_N e^{-\alpha N} Z_N. \tag{8.5}$$

Here Z_N is recognized as the canonical partition sum for a subsystem of N atoms. The superscript (N) indicates that the sum over γ is *restricted* to all many-body states of N atoms. In the quantum gases the distribution over the states depends on the temperature (actually, on the level of quantum degeneracy). This is similar to the temperature dependence of chemical equilibrium between states and is most conveniently handled with the aid of a chemical potential.

Recognizing in $S^* = k_B \ln \Omega(E^*, N^*)$ a function of E^*, N^* and $\mathcal{U}$ in which $\mathcal{U}$ is kept constant, we identify S^* with the *entropy* of the reservoir. Thus, the most probable state of the total system is seen to corresponds to the state of maximum entropy, $S^* + S = \max$, where S is the entropy of the small system. Next we recall the thermodynamic relation

$$dS = \frac{1}{T} dU - \frac{1}{T} đW - \frac{\mu}{T} dN, \tag{8.6}$$

where $đW$ is the *mechanical work* done on the small system, U its *internal energy*, μ the *chemical potential* and T the *temperature* of the system. Since $dS = -dS^*$, $dN = -dN^*$ and $dU = -dE^*$ for conditions of maximum entropy, we identify $k_B\beta = (\partial S^*/\partial E^*)_{\mathcal{U},N^*} = (\partial S/\partial U)_{\mathcal{U},N}$ and $\beta = 1/k_BT$. Further we identify $k_B\alpha = (\partial S^*/\partial N^*)_{E^*} = (\partial S/\partial N)_U$ with $\alpha = -\mu/k_BT$. For *homogeneous* systems a small quantity of mechanical work can be expressed as $đW = -pdV$, where p is the *pressure* and V the *volume* of the system.

8.2.1 The statistical operator

To introduce the statistical operator we consider the operator A, which represents an observable of a given system. Averaged over the grand canonical ensemble of that system, the quantum statistical average of A is given by - see Eq. (B.108)

$$\bar{A} \equiv \langle\!\langle A \rangle\!\rangle = \sum_{\gamma} w_{\gamma} \langle \hat{A} \rangle_{\gamma}, \tag{8.7}$$

where

$$w_{\gamma} = \mathcal{Z}_{gr}^{-1} e^{-(E_{\gamma}-\mu N_{\gamma})/k_B T} \tag{8.8}$$

is the probability (8.3) of finding the system in the Fock state $|\tilde{n}_{\gamma}\rangle$, where $\{|\tilde{n}_{\gamma}\rangle\}$ is the occupation number representation of the hamiltonian $\hat{H}$, and

$$\langle \hat{A} \rangle_{\gamma} \equiv \langle \tilde{n}_{\gamma} | \hat{A} | \tilde{n}_{\gamma} \rangle \tag{8.9}$$

is the quantum mechanical expectation value of $\hat{A}$ for this state.

Formally, see Eq. (B.110), the grand canonical ensemble average $\langle\!\langle A \rangle\!\rangle$ can be obtained with the aid of the *statistical operator*,

$$\hat{\varrho} = \sum_{\gamma} w_{\gamma} |\tilde{n}_{\gamma}\rangle\langle\tilde{n}_{\gamma}| = \mathcal{Z}_{gr}^{-1} e^{-(\hat{H}-\mu\hat{N})/k_B T}, \tag{8.10}$$

where $\hat{H}$ and $\hat{N}$ are the hamiltonian and total number operator, respectively, and

$$\mathcal{Z}_{gr} = \mathrm{tr}\, e^{-(\hat{H}-\mu\hat{N})/k_B T} \tag{8.11}$$

is the grand-canonical partition sum (in representation-free form). Using the statistical operator, the quantum statistical average of the observable A is given by - see Eq. (B.112)

$$\bar{A} \equiv \langle\!\langle A \rangle\!\rangle = \mathrm{tr}\, \hat{\varrho} \hat{A}. \tag{8.12}$$

To demonstrate that Eq. (8.12) represents indeed the average value of the observable A we choose the energy representation $|\tilde{n}_{\gamma}\rangle$, which is the representation based on the eigenstates of $\hat{H}$. In this representation $\hat{\varrho}$ is diagonal and Eq. (8.12) reduces to

$$\bar{A} = \sum_{\gamma} \langle \tilde{n}_{\gamma} | \hat{\varrho} | \tilde{n}_{\gamma} \rangle \langle \tilde{n}_{\gamma} | \hat{A} | \tilde{n}_{\gamma} \rangle = \sum_{\gamma} w_{\gamma} \langle \hat{A} \rangle_{\gamma}. \tag{8.13}$$

8.3 Ideal quantum gases

8.3.1 Gibbs factor

An important application of the grand canonical ensemble is to calculate the average occupation $\overline{n}_s$ of a given single-particle state $|s\rangle$ of energy ε_s in an *ideal* quantum gas,

$$\overline{n}_s = \mathrm{tr}\, \hat{\varrho} \hat{n} = \mathcal{Z}_{gr}^{-1} \sum_{\gamma} \langle \tilde{n}_{\gamma} | \, e^{-(\hat{H}-\mu\hat{N})/k_B T} \hat{n}_s \, | \tilde{n}_{\gamma} \rangle \,, \tag{8.14}$$

where the ensemble closure is normalized by the grand canonical partition sum,

$$\mathcal{Z}_{gr} = \sum_{\gamma} \langle \tilde{n}_{\gamma} | \, e^{-(\hat{H}-\mu\hat{N})/k_B T} \, | \tilde{n}_{\gamma} \rangle \,. \tag{8.15}$$

To calculate $\overline{n}_s$ we choose the representation of $\hat{H}$, where (in the absence of interactions) the hamiltonian is given by Eq. (7.105). Thus we have

$$\hat{H}-\mu\hat{N}=\sum_s\hat{n}_s(\varepsilon_s-\mu) \tag{8.16}$$

and the statistical operator is given by

$$\hat{\varrho}=\mathcal{Z}_{gr}^{-1}\prod_s e^{-\hat{n}_s(\varepsilon_s-\mu)/k_BT}. \tag{8.17}$$

Substituting this expression into Eq. (8.14) we obtain

$$\overline{n}_s=\mathcal{Z}_{gr}^{-1}\sum_{n_1,n_2,\cdots}\langle n_1,\cdots,n_s,\cdots|\,e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_BT}\hat{n}_s\,|n_1,\cdots,n_s,\cdots\rangle\,, \tag{8.18}$$

where the sums over the occupations $n_1,n_{2,}\cdots$ run (independently) from zero up, unrestricted for the case of bosons and restricted to the maximum value 1 for the case of fermions. Separating the sum over the occupations of state s from the sums over the occupations of all other states we obtain after evaluation of the matrix elements

$$\overline{n}_s=\mathcal{Z}_{gr}^{-1}\sum_{n_s}n_se^{-n_s(\varepsilon_s-\mu)/k_BT}\sum_{n_1,n_2,\cdots}{}^{(n_s)}e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_BT}. \tag{8.19}$$

The superscript at the summation $\sum^{(n_s)}$ indicates that the contribution of state $|s\rangle$ is excluded from the sum. Similarly, the grand canonical partition sum can be written as

$$\mathcal{Z}_{gr}=\sum_{n_s}e^{-n_s(\varepsilon_s-\mu)/k_BT}\sum_{n_1,n_2,\cdots}{}^{(n_s)}e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_BT}. \tag{8.20}$$

Combining Eqs. (8.20) and (8.19) we can eliminate the sum over all other states and obtain for the average thermal occupation of state $|s\rangle$

$$\overline{n}_s=\frac{\sum_{n_s}n_se^{-n_s(\varepsilon_s-\mu)/k_BT}}{\sum_{n_s}e^{-n_s(\varepsilon_s-\mu)/k_BT}}, \tag{8.21}$$

where the sum runs over all allowed occupations of the state $|s\rangle$. This expression shows that, *for given* μ, the average thermal occupation $\overline{n}_s$ is completely determined by ε_s, T and μ. For a system of N particles, the value of μ is fixed by the condition

$$\sum_s\overline{n}_s=N. \tag{8.22}$$

Generalizing Eq. (8.21) to obtain the average occupation of an arbitrary state of energy ε we write

$$\bar{n}(\varepsilon;T,\mu)=\sum_n nP(n), \tag{8.23}$$

where

$$P(n)=\mathcal{Z}^{-1}e^{-n(\varepsilon-\mu)/k_BT} \tag{8.24}$$

is the probability to find n atoms in the *same* state of energy ε, with closure condition $\sum_n P(n)=1$ and partition sum

$$\mathcal{Z}=\sum_n e^{-n(\varepsilon-\mu)/k_BT}. \tag{8.25}$$

Comparing the probability of occupation n_1 with n_2 for a given state of energy ε we find that their probability ratio is given by the *Gibbs factor*

$$P(n_2)/P(n_1)=e^{-\Delta n(\varepsilon-\mu)/k_BT}, \tag{8.26}$$

with $\Delta n = n_2 - n_1$.

For identical bosons there is no restriction on the occupation of a given state and $\mathcal{Z}$ has the form of a geometrical series with ratio $r = e^{-(\varepsilon-\mu)/k_BT}$,

$$\mathcal{Z}_{\mathrm{BE}} = \sum\nolimits_{n=0}^{\infty} r^n = \frac{1}{1-r} \quad (r<1)\,. \tag{8.27}$$

Note that this series only converges if the ratio r is less than unity; i.e., for $\mu < \varepsilon$. For identical fermions the occupation n of a given state is restricted to 0 or 1 and

$$\mathcal{Z}_{\mathrm{FD}} = \sum\nolimits_{n=0}^{1} r^n = 1 + r. \tag{8.28}$$

Comparing Eq. (8.27) with (8.28) we see that the grand canonical partition sums for Bose and Fermi systems coincide in the limit $r \ll 1$; i.e., for $k_BT \ll (\varepsilon - \mu)$. For a given value of ε this is the case for a sufficiently large *negative* value of μ.

8.3.2 Bose-Einstein statistics

We are now in a position to calculate the average occupation of an arbitrary single-particle state $|s\rangle$ of energy ε_s. For a system of identical bosons there is no restriction on the occupation of the states. So, using Eq. (8.24) with $\mathcal{Z} = \mathcal{Z}_{\mathrm{BE}}$, the average occupation is given by

$$\bar{n}_s = \sum_{n=0}^{\infty} nP_s(n) = \mathcal{Z}_{\mathrm{BE}}^{-1} \sum_{n=0}^{\infty} ne^{-n(\varepsilon_s-\mu)/k_BT} = \mathcal{Z}_{\mathrm{BE}}^{-1} \sum_{n=0}^{\infty} nr_s^n, \tag{8.29}$$

where $r_s = e^{-(\varepsilon_s-\mu)/k_BT}$. Using Eq. (8.27) the summation can be rewritten in the form

$$\sum\nolimits_{n=0}^{\infty} nr^n = r\sum\nolimits_{n=0}^{\infty} nr^{n-1} = r\frac{\partial \mathcal{Z}_{\mathrm{BE}}}{\partial r} = \frac{r}{(1-r)^2} = \frac{r}{(1-r)}\mathcal{Z}_{\mathrm{BE}} \quad (r<1)\,. \tag{8.30}$$

So, for $r = r_s < 1$ we obtain

$$\bar{n}_s = \frac{r_s}{(1-r_s)} = \frac{1}{e^{(\varepsilon_s-\mu)/k_BT} - 1} \equiv f_{\mathrm{BE}}(\varepsilon_s). \tag{8.31}$$

Note that $\bar{n}_s$ depends (for given values of T and μ) only on the *energy* of the state $|s\rangle$. Eq. (8.31) defines the *Bose-Einstein (BE) distribution function* $f_{\mathrm{BE}}(\varepsilon)$ for the thermal occupation of single-particle states of given energy. The average total number of atoms of the ensemble is given by

$$\sum\nolimits_s \bar{n}_s = \bar{N}. \tag{8.32}$$

To apply the grand canonical ensemble to a gas of N identical atoms at temperature T we use the condition

$$\sum\nolimits_s \bar{n}_s = N \tag{8.33}$$

to determine the value of μ at which the BE-distribution function yields the correct occupation of all states. As μ has to be a function of temperature, we ask for the properties of this function. We recall the condition $r_s < 1$ (or equivalently $\mu < \varepsilon_s$) from the derivation of Eq. (8.31). This condition also makes sense from the physical point of view: $r_s > 1$ is unacceptable as it would imply a negative thermal occupation. As this objection holds for *any* state we require $\mu \leq \varepsilon_0 \leq \varepsilon_s$, where ε_0 is the energy of the single atom ground-state $|s=0\rangle$. However, also $\mu = \varepsilon_0$ is unacceptable because it makes $P_{s=0}(n)$ independent of n. This is unphysical as it implies the absence of a unique solution for the state of the gas in thermal equilibrium (for instance its density or momentum distribution).

Thus, we require $\mu < \varepsilon_0$. Choosing the zero of the energy scale such that $\varepsilon_0 = 0$ we arrive at the conclusion that *in the case of bosons the chemical potential has to be negative*, $\mu < 0$.

Interestingly, although the condition $\mu < 0$ assures that the occupation of all states remains regular it does not prevent the ground state occupation N_0 from becoming anomalously large ($N_0 \simeq N$) *at finite temperature.* This happens if the condition $-\mu \lll \varepsilon_1 \ll k_BT$ can be satisfied. In this case we have

$$N_0 = \frac{1}{e^{-\mu/k_BT} - 1} \simeq \frac{k_BT}{-\mu}, \tag{8.34}$$

which diverges for $\mu \to 0$ while the occupation of all excited states $|s \neq 0\rangle$ remains finite, $n_s = k_BT/\varepsilon_s$. However, $-\mu$ cannot become arbitrarily small. Since $N_0 < N$ we require

$$-\mu/k_BT > 1/N. \tag{8.35}$$

Note that Eqs. (8.34) and (8.35) are simultaneously satisfied for $1/N < -\mu/k_BT \ll 1$, which is possible for systems with a large number of bosons ($N \ggg 1$). In classical statistics (Boltzmann statistics) macroscopic occupation of the ground state can also occur but *only* in the zero temperature limit ($k_BT \ll \varepsilon_1$).

The phenomenon in which a macroscopic fraction of a Bose gas collects in the ground state is known as *Bose-Einstein condensation* (BEC) and the macroscopically occupied ground state is called the *condensate*. The atoms in the excited states are said to occupy the *thermal cloud*. Knowing that N_0 grows like $1/\mu$ for decreasing chemical potential does not give us a sharp criterion for the onset of BEC. Actually, it does not even tell us whether BEC will occur or not. As will appear in the next sections, this depends crucially on the density of states of the system. In extreme cases such as in one-dimensional (1D) gases or in the homogeneous two-dimensional (2D) gas BEC turns out to be absent. Therefore, the occurrence of BEC should be distinguished from the occurrence of *quantum degeneracy*. By the latter we mean the *deviation from classical statistics* and this occurs whenever the degeneracy parameter ($n\Lambda^3$ in 3D and $n_2\Lambda^2$ in 2D) exceeds unity.

8.3.3 Fermi-Dirac statistics

For a system of identical fermions the occupation n of a given state is restricted to the values 0 or 1, so using Eq. (8.24) the average occupation of state $|s\rangle$ is given by

$$\bar{n}_s = \sum_{n=0}^{1} nP_s(n) = \mathcal{Z}_{\mathrm{FD}}^{-1} e^{-(\varepsilon_s - \mu)/k_BT} = \frac{r_s}{(1 + r_s)}. \tag{8.36}$$

Substituting $r_s \equiv e^{-(\varepsilon_s - \mu)/k_BT}$ we obtain

$$\bar{n}_s = \frac{1}{e^{(\varepsilon_s - \mu)/k_BT} + 1} \equiv f_{\mathrm{FD}}(\varepsilon_s). \tag{8.37}$$

This relation defines the *Fermi-Dirac (FD) distribution function* $f_{\mathrm{FD}}(\varepsilon)$ for the thermal occupation of single-particle states of given energy. Note that $\bar{n}_s < 1$ for any finite temperature. For $\mu \gg k_BT$ we have $\bar{n}_s \approx 1$ for $\varepsilon_s \leq \mu$ and $\bar{n}_s \ll 1$ for $\varepsilon_s > \mu$. This is the limit of strong quantum degeneracy for fermions.

8.3.4 Density distributions of quantum gases - semi-classical approximation in 3D

For inhomogeneous gases the quantum statistics will not only affect the distribution over states but also the distribution in configuration space. To analyze this behavior we consider a quantum gas with a macroscopic number of atoms, $N \ggg 1$, confined in the external potential $\mathcal{U}(\mathbf{r})$. The sum over the average occupations $\bar{n}_s$ of all single-particle states must add up to the total number of trapped atoms. Therefore, we require

$$N = \sum_s \bar{n}_s = \sum_s \frac{1}{e^{(\varepsilon_s-\mu)/k_BT} \pm 1}, \tag{8.38}$$

where the ± sign distinguishes between Bose-Einstein $(-)$ and Fermi-Dirac $(+)$ statistics. For sufficiently high temperatures many single-particle levels will be occupied and their average occupation will be small, $n_s \ll N$. For fermions this is the case for all temperatures. For bosons we have to restrict ourselves to temperatures k_BT much larger than the characteristic trap level splitting $\hbar\omega$ and exclude, for the time being, the presence of a condensate. Under these conditions the quantum gases are characterized by a quasi-continuous Bose-Einstein or Fermi-Dirac distribution function. Therefore, like in Section 1.3.1, the discrete summation over states in Eq. (8.38) may be replaced by the integration $(2\pi\hbar)^{-3}\int d\mathbf{p}d\mathbf{r}$ over phase space,

$$N = \frac{1}{(2\pi\hbar)^3}\int \frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT} \pm 1} d\mathbf{r}d\mathbf{p}, \tag{8.39}$$

with the energy of the states given by the classical one-body hamiltonian,

$$\varepsilon_s = H_0(\mathbf{r},\mathbf{p}) = p^2/2m + \mathcal{U}(\mathbf{r}) \tag{8.40}$$

In principle it is not allowed to integrate over the full phase space because the zero point motion lifts the energy of the ground state above the minimum of the classical hamiltonian, $\varepsilon_0 > H_0(0,0)$. In practice we simply extend the integral to the full phase space by setting $\varepsilon_0 \simeq H_0(0,0) = 0$, because for $k_BT \gg \hbar\omega$ only a small error is made by neglecting the discrete structure of the spectrum. This shows that the description has remained mostly classical. Only the quantum mechanical condition on the level occupation (i.e., the quantum statistics) affects the results.

8.3.4.1 Local density approximation

Along the lines of Section 1.3.1 we note that the total number of atoms N must equal the integral over the density distribution,

$$N = \int n(\mathbf{r})d\mathbf{r}. \tag{8.41}$$

This suggest to make a *local density approximation*. For given temperature and chemical potential $n(\mathbf{r})$ is obtained by integrating the integrand of Eq. (8.39) only over momentum space

$$n(\mathbf{r}) = \frac{1}{(2\pi\hbar)^3}\int_0^\infty \frac{4\pi p^2}{e^{(p^2/2m+\mathcal{U}(\mathbf{r})-\mu)/k_BT} \pm 1} dp, \tag{8.42}$$

where the ± sign distinguishes between BE $(-)$ and FD $(+)$ statistics. In particular, we obtain for the density in the minimum of the trap $(\mathbf{r}=0)$

$$n_0 = \frac{1}{(2\pi\hbar)^3}\int \frac{4\pi p^2}{e^{(p^2/2m-\mu)/k_BT} \pm 1} dp. \tag{8.43}$$

Note that this result is obtained *irrespective* of the shape of the trap and coincides with the result for a homogeneous gas [4].[1] To proceed we make the integral dimensionless by introducing reduced variables,

$$n(\mathbf{r}) = \frac{1}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\epsilon^{1/2}}{\tilde{z}(\mathbf{r})^{-1}e^{\epsilon} \pm 1} d\epsilon = \frac{1}{\Lambda^3} F_{3/2}^{\mathrm{FD/BE}}[\tilde{z}(\mathbf{r})]. \tag{8.44}$$

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[1] Note that this well-known result does not hold for reduced dimensionality.

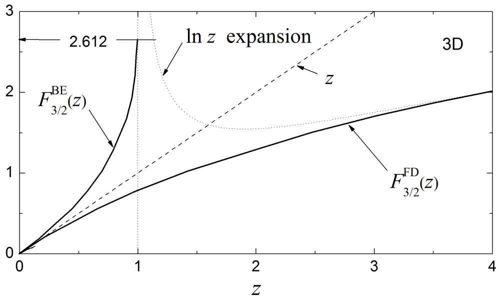

Figure 8.1: Bose-Einstein (BE) and Fermi-Dirac (FD) integrals as a function of the fugacity z for the three-dimensional case. For comparison also the linear dependence of Maxwell-Boltzmann statistics is shown. The dotted line corresponds to the expansion (8.98) for fermions.

Here

$$\epsilon = p^2/2mk_BT \tag{8.45}$$

is called the *reduced kinetic energy*; the chemical potential has been reduced by introducing the (local and global) *fugacity*,

$$\tilde{z}(\mathbf{r}) = ze^{-\mathcal{U}(\mathbf{r})/k_BT}, \quad \text{with } z \equiv e^{\mu/k_BT}. \tag{8.46}$$

In terms of these reduced quantities the local density can be written in the compact form

$$n(\mathbf{r}) = \frac{1}{\Lambda^3} F_{3/2}^{\mathrm{FD/BE}}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]. \tag{8.47}$$

The $F_{3/2}^{\mathrm{FD/BE}}$ integrals are monotonically increasing functions of z as shown in Fig. 8.1. From Eq. (8.47) we infer that these integrals can be interpreted as the *local degeneracy parameters* for the cases of BE and FD statistics. To deal with inhomogeneity, the degeneracy of trapped gases is defined by the degeneracy parameter in the trap center,

$$D = n_0\Lambda^3 = F_{3/2}^{\mathrm{FD/BE}}(z). \tag{8.48}$$

The $F_{3/2}^{\mathrm{FD/BE}}$ integrals belong to the more general class of *quantum statistical integrals* defined by

$$F_{\alpha}^{\mathrm{FD/BE}}(z) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{\epsilon^{\alpha-1}}{z^{-1}e^{\epsilon} \pm 1} d\epsilon. \tag{8.49}$$

Properties of these integrals are summarized Section 8.3.8 and Appendix C.3.

8.3.5 Semi-classical approximation - dependence on dimensionality

The discussion of the previous section is readily extended to arbitrary dimension d by the map

$$\sum_s \to \frac{1}{(2\pi\hbar)^{\mathrm{d}}} \int d\mathbf{p}d\mathbf{r}, \tag{8.50}$$

where $\mathbf{p}$ and $\mathbf{r}$ represent vectors in d dimensions. For given temperature and chemical potential $n(\mathbf{r})$ is again obtained by integrating the integrand of Eq. (8.39) over momentum space,

$$n(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{\mathrm{d}}} \int_0^{\infty} \frac{c_d p^{(\mathrm{d}-1)}}{e^{(p^2/2m+\mathcal{U}(\mathbf{r})-\mu)/k_BT} \pm 1} dp, \tag{8.51}$$

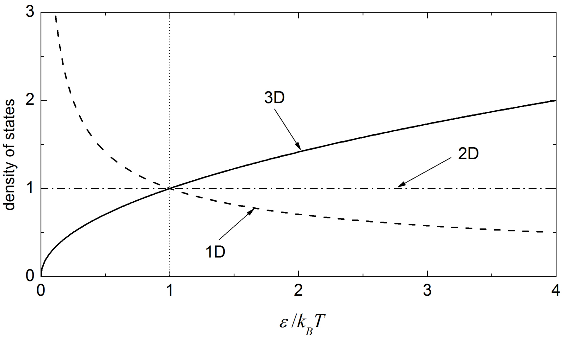

Figure 8.2: Density of states versus energy for homogeneous clouds in 1, 2 and 3 dimensions. For d >2 the density of states favors the contribution of states with kinetic energy larger than k_BT and for d <2 that of states with kinetic energy smaller than k_BT. For d $=2$ the density of states is flat. The absence of states at low energy favors BEC.

where $c_d = 4\pi, 2\pi, 1$ for d $= 3, 2, 1$, respectively. Changing integration variable by turning to the dimensionless kinetic energy $\epsilon = p^2/2mk_BT$ we obtain

$$n(\mathbf{r}) = \frac{1}{\Lambda^{\mathrm{d}}} F_{\mathrm{d}/2}^{\mathrm{FD/BE}}\left(ze^{-\mathcal{U}(\mathbf{r})/k_BT}\right). \tag{8.52}$$

The functions

$$F_{\mathrm{d}/2}^{\mathrm{FD/BE}}(z) = \frac{1}{\Gamma(\mathrm{d}/2)} \int_0^\infty \frac{\epsilon^{\mathrm{d}/2-1}}{z^{-1}e^{\epsilon} \pm 1} d\epsilon \tag{8.53}$$

differ in the energy dependence of the density of states $\rho(\epsilon) = \epsilon^{\mathrm{d}/2-1}$ as shown in Fig. 8.2. For d $= 2$ the density of states is constant and $F_1^{\mathrm{FD/BE}}(z)$ represents the flat integral over the quantum distributions. For d > 2 the density of states favors the contribution of states with kinetic energy larger than k_BT and for d < 2 that of states with kinetic energy smaller than k_BT.

8.3.6 Grand partition sum

In Section 1.2.5 we discussed how the thermodynamic properties of trapped classical gases can be obtained systematically once we have an expression for the canonical partition integral Z_N. The grand partition sum $\mathcal{Z}_{gr}$ plays a similar role for the quantum gases. In preparation for the discussion of this topic in Section 8.3.7 we first derive expressions for $\mathcal{Z}_{gr}$ for the cases of BE- and FD-statistics. Starting from the definition

$$\mathcal{Z}_{gr} = \sum_{n_1, n_2, \cdots} e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_BT}, \tag{8.54}$$

we note that we can sequentially factor-out the contributions of all single-particle states, just as was done for state s in Eq. (8.55),

$$\mathcal{Z}_{gr} = \prod_s \sum_{n_s} e^{-n_s(\varepsilon_s-\mu)/k_BT}. \tag{8.55}$$

This is only possible since we are dealing with unrestricted sums. Introducing the quantity

$$r_s \equiv e^{-(\varepsilon_s-\mu)/k_BT} \tag{8.56}$$

Eq. (8.55) can be further simplified to the form

$$\mathcal{Z}_{gr} = \prod_s \sum_{n_s} r_s^{n_s}. \tag{8.57}$$

- For identical bosons there is no restriction on the occupation n_s of a given state s and we recognize in r_s the ratio of a geometrical series. After summation we obtain,

$$\mathcal{Z}_{gr} = \prod_s \frac{1}{1 - r_s} \qquad \text{(bosons)}. \tag{8.58}$$

- For identical fermions the state occupations n_s are restricted to the values $0, 1$ and we have only two terms in the sum,

$$\mathcal{Z}_{gr} = \prod_s (1 + r_s) \qquad \text{(fermions)}. \tag{8.59}$$

- Combining Eqs. (8.58) and (8.59) we obtain a single formula,

$$\ln \mathcal{Z}_{gr} = \pm \sum_s \ln (1 \pm r_s), \tag{8.60}$$

  where the ± sign distinguishes between Fermi-Dirac $(+)$ and Bose-Einstein $(-)$ statistics.

Let us derive an expression for $\ln \mathcal{Z}_{gr}$ in the semi-classical approximation. Replacing the summation over all states by the integration $(2\pi\hbar)^{-3} \int d\mathbf{p}d\mathbf{r}$ over phase space we obtain

$$\ln \mathcal{Z}_{gr} = \frac{1}{(2\pi\hbar)^3} \int \ln \left(1 \pm z e^{-H_0(\mathbf{p},\mathbf{r})/k_BT}\right) d\mathbf{p}d\mathbf{r}, \tag{8.61}$$

where $H_0(\mathbf{r}, \mathbf{p})$ is again the one-body hamiltonian (1.35). For *inhomogeneous* gases we write $\ln \mathcal{Z}_{gr}$ in the form

$$\ln \mathcal{Z}_{gr} = \Lambda^{-3} \int F_{5/2}[z e^{-\mathcal{U}(\mathbf{r})/k_BT}] d\mathbf{r}, \tag{8.62}$$

where the local contribution to $\ln \mathcal{Z}_{gr}$ is given by

$$\ln \tilde{\mathcal{Z}}_{gr}(\mathbf{r}) = \Lambda^{-3} F_{5/2}[z e^{-\mathcal{U}(\mathbf{r})/k_BT}]. \tag{8.63}$$

For *homogeneous* gases we have $\mathcal{U}(\mathbf{r}) = 0$ and integrating (8.62) over configuration space we obtain

$$\ln \mathcal{Z}_{gr} = \left(V/\Lambda^3\right) F_{5/2}(z). \tag{8.64}$$

Introducing $\alpha = \sqrt{2mk_BT}$ and changing to the integration variable $\epsilon = (p/\alpha)^2$ the function $F_{5/2}(z)$ can be written as

$$\begin{aligned} F_{5/2}(z) &= \frac{\Lambda^3}{(2\pi\hbar)^3} \int_0^\infty \ln \left(1 \pm z e^{-(p/\alpha)^2}\right) 4\pi p^2 dp \\ &= \frac{1}{\Gamma(3/2)} \int_0^\infty \ln \left(1 \pm z e^{-\epsilon}\right) \epsilon^{1/2} d\epsilon, \end{aligned} \tag{8.65}$$

which can be rewritten by partial integration in the form of the integral representation of the polylogarithm (see Appendix C.3),

$$F_{5/2}(z) = \frac{1}{\Gamma(5/2)} \int_0^\infty \frac{\epsilon^{3/2}}{z^{-1} e^\epsilon \pm 1} d\epsilon. \tag{8.66}$$

8.3.6.1 Example: BE and FD distributions

As a (first) demonstration of the central role of $\ln\mathcal{Z}_{gr}$ in the grand canonical approach we rederive the expressions for the average thermal occupation $\overline{n}_s$ in bosonic and fermionic quantum gases. Rewriting Eq. (8.21) in the form

$$\overline{n}_s = \frac{r_s \sum_{n_s} n_s r_s^{n_s-1}}{\sum_{n_s} r_s^{n_s}} \frac{\prod\limits_{t\neq s} \sum_{n_t} r_t^{n_t}}{\prod\limits_{t\neq s} \sum_{n_t} r_t^{n_t}}, \tag{8.67}$$

we recognize in the denominator $\mathcal{Z}_{gr}$, see Eq. (8.57), and in the numerator a derivative of $\mathcal{Z}_{gr}$,

$$\overline{n}_s = \frac{r_s}{\mathcal{Z}_{gr}} \frac{\partial \mathcal{Z}_{gr}}{\partial r_s} = r_s \partial \ln \mathcal{Z}_{gr}/\partial r_s. \tag{8.68}$$

Substituting Eq. (8.60) yields in one line the BE $(-)$ and FD $(+)$ distribution functions,

$$\overline{n}_s = \frac{r_s}{1 \pm r_s} = \frac{1}{e^{(\varepsilon_s-\mu)/k_BT} \pm 1}. \tag{8.69}$$

8.3.7 Link to the thermodynamics - semi-classical approximation

In this section we explore how the thermodynamic properties can be obtained from the grand partition sum. We restrict ourselves again to temperatures k_BT much larger than the characteristic trap level splitting $\hbar\omega$ and exclude the presence of a condensate. The starting point is to identify the grand canonical average of the total energy E of a system with the thermodynamic internal energy U of that system,

$$U = \bar{E} = \sum_s \varepsilon_s \bar{n}_s = \sum_s \frac{\varepsilon_s}{e^{(\varepsilon_s-\mu)/k_BT} \pm 1}. \tag{8.70}$$

In the semi-classical approximation this becomes

$$U = \int u(\mathbf{r}) d\mathbf{r} = \frac{1}{(2\pi\hbar)^3} \int \frac{H_0(\mathbf{r},\mathbf{p})}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT} \pm 1} d\mathbf{p}d\mathbf{r}, \tag{8.71}$$

where the local energy density $u(\mathbf{r})$ is given by

$$u(\mathbf{r}) = k_BT\frac{1}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int \frac{\epsilon^{3/2}}{z^{-1}e^{\mathcal{U}(\mathbf{r})/k_BT}e^{\epsilon} \pm 1} d\epsilon + \frac{\mathcal{U}(\mathbf{r})}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int \frac{\epsilon^{1/2}}{z^{-1}e^{\mathcal{U}(\mathbf{r})/k_BT}e^{\epsilon} \pm 1} d\epsilon. \tag{8.72}$$

Here we recognize two F integrals,

$$u(\mathbf{r}) = \tfrac{3}{2}k_BT\frac{1}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}] + \mathcal{U}(\mathbf{r})\frac{1}{\Lambda^3}F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]. \tag{8.73}$$

Using the recursion relation for polylogarithms (C.18) we find that Eq. (8.73) is equivalent to

$$\begin{aligned} u(\mathbf{r}) = {} & -k_BT\frac{1}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}] \\ & + T\left(\frac{\partial}{\partial T}k_BT\frac{1}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]\right)_{\mathcal{U},\mu} + \mu\frac{1}{\Lambda^3}F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]. \end{aligned} \tag{8.74}$$

In the first two terms we recognize the expression (8.63) for $\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})$. In the last term we recognize the local density, but rather than writing $\mu n(\mathbf{r})$ we note that the local density can also be expressed in terms of $\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})$ (see Problem 8.1),

$$n(\mathbf{r}) = \left(\frac{\partial}{\partial\mu}k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})\right)_{\mathcal{U},T}, \tag{8.75}$$

Thus Eq. (8.74) can be written in a form containing only $k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})$ and its derivatives,

$$u(\mathbf{r}) = -k_BT\ln\tilde{\mathcal{Z}}_{gr} + T[\partial(k_BT\ln\tilde{\mathcal{Z}}_{gr})/\partial T]_{\mathcal{U},\mu} + \mu\partial(k_BT\ln\tilde{\mathcal{Z}}_{gr})/\partial\mu]_{\mathcal{U},T}. \tag{8.76}$$

This expression suggests to introduce the quantity

$$\tilde{\Omega}(\mathbf{r}) = -k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r}) \quad\Leftrightarrow\quad \tilde{\mathcal{Z}}_{gr}(\mathbf{r}) = e^{-\tilde{\Omega}(\mathbf{r})/k_BT}. \tag{8.77}$$

By substitution of Eq. (8.63) $\tilde{\Omega}(\mathbf{r})$ can be expressed in the form

$$\tilde{\Omega}(\mathbf{r}) = -\frac{k_BT}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]. \tag{8.78}$$

We are now in a position to make the connection to thermodynamics. First we shall do this for the *homogeneous* gas. In this case $\mathcal{U}(\mathbf{r}) \equiv 0$ the conditions on the trap shape are replaced by conditions on the volume of the gas, V. Eq. (8.76) can be written in the form $\Omega = U + T\left(\partial\Omega/\partial T\right)_{V,\mu} + \mu\left(\partial\Omega/\partial\mu\right)_{V,T}$. Comparing this relation with the thermodynamic relation

$$\Omega = U - TS - \mu N \tag{8.79}$$

we recognize in Ω the *grand potential* Ω, which is a function of T, μ and V (for inhomogeneous systems $\mathcal{U}$). Further, we identify

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T}. \tag{8.80}$$

Other thermodynamic quantities are obtained by combining the thermodynamic relation for changes of the grand potential $d\Omega = dU - TdS - SdT - \mu dN - Nd\mu$ with that for the internal energy $dU = đW + TdS + \mu dN$ into the expression $d\Omega = đW - SdT - Nd\mu$. In particular the pressure follows from the expression for the mechanical work $đW = -pdV$,

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}. \tag{8.81}$$

Hence, Ω is obtained by integrating p over the volume (for given value of T and μ),

$$\Omega = -\int_V \left(\partial\Omega/\partial V\right)_{T,\mu} d\mathbf{r}. \tag{8.82}$$

Evaluating the integral we obtain

$$\Omega = -pV. \tag{8.83}$$

In other words, in a homogeneous gas the pressure is simply an other name for the Grand potential per unit volume (up to a sign),

$$p = -\Omega/V \equiv -\tilde{\Omega}(\mathbf{r}), \tag{8.84}$$

for all $\mathbf{r} \in V$.

To discuss *inhomogeneous* systems we presume the local density approximation to be valid; i.e., we write Ω as the integral over a local grand potential, $\Omega = -\int_V \tilde{\Omega}(\mathbf{r})d\mathbf{r}$, and use the relation

$$p = -\tilde{\Omega}(\mathbf{r}) \tag{8.85}$$

for the local pressure. Using Eq. (8.85) in combination with Eqs. (8.78) and (8.47) we obtain for the equation of state

$$p = \frac{F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]}{F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]}n(\mathbf{r})k_BT. \tag{8.86}$$

Note that the prefactor $F_{5/2}/F_{3/2}$ represents the quantum correction to the classical ideal gas law. Similar to Ω and U, all extensive quantities can be expressed as an integral over their corresponding local density and (8.79) becomes

$$p = -u(\mathbf{r}) + Ts(\mathbf{r}) + \mu n(\mathbf{r}). \tag{8.87}$$

The *entropy density* and *number density* follow from the pressure with

$$s(\mathbf{r}) = (\partial p/\partial T)_{\mathcal{U},\mu} \quad \text{and} \quad n(\mathbf{r}) = (\partial p/\partial \mu)_{\mathcal{U},T}\,. \tag{8.88}$$

Substituting Eq. (8.78) we obtain for the entropy density

$$s(\mathbf{r}) = \tfrac{5}{2}\frac{k_B}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}] - \frac{1}{\Lambda^3}F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]\frac{\mu-\mathcal{U}(\mathbf{r})}{k_BT}. \tag{8.89}$$

Problem 8.1. Show that the relation between the local density and $\mathcal{Z}_{gr}$ is given by

$$n(\mathbf{r}) = \left(\frac{\partial}{\partial\mu}k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})\right)_{\mathcal{U},T}.$$

Solution. Starting from the r.h.s. of Eq. (8.75) we have for constant $\mathcal{U}(\mathbf{r})$ and T

$$\frac{\partial}{\partial\mu}k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r}) = k_BT\frac{1}{\Lambda^3}\frac{\partial}{\partial\mu}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}].$$

Noting the property $(\partial\tilde{z}/\partial\mu)_{\mathcal{U},T} = \tilde{z}/k_BT$ the above expression becomes for constant $\mathcal{U}(\mathbf{r})$ and T

$$k_BT\frac{1}{\Lambda^3}\frac{\partial}{\partial\tilde{z}}F_{5/2}(\tilde{z})\frac{\partial\tilde{z}(\mathbf{r})}{\partial\mu} = \frac{1}{\Lambda^3}F_{3/2}(\tilde{z}) = n(\mathbf{r}),$$

where Eq. (8.47) was used in the final step. □

8.3.8 Series expansions for the quantum gases

To deal with the BE and FD integrals a number of mathematical tools is at our disposal, which can be ordered with respect to the value of the fugacity.

8.3.8.1 a. the case $0 < z \leq 1$

For $\mu/k_BT \leq 0$ the fugacity is small and we can rewrite both the BE and FD integrals in the form

$$F_\alpha^{\mathrm{FD/BE}}(z) = \frac{1}{\Gamma(\alpha)}\int_0^\infty \frac{\epsilon^{\alpha-1}}{z^{-1}e^\epsilon \pm 1}d\epsilon. \tag{8.90}$$

Since $z \leq 1$ and $e^{-\epsilon} \leq 1$ the denominator of the integrand can be expanded in powers of $ze^{-\epsilon}$,

$$\frac{ze^{-\epsilon}}{1 \pm ze^{-\epsilon}} = ze^{-\epsilon}[1 \mp ze^{-\epsilon} + \left(ze^{-\epsilon}\right)^2 \mp \cdots] = \mp\sum_{\ell=1}(\mp z)^\ell e^{-\ell\epsilon} \tag{8.91}$$

and substituting this expansion into Eq. (8.90) we obtain after swapping summation and integration

$$F_\alpha^{\mathrm{FD/BE}}(z) = \mp\sum_{\ell=1}(\mp z)^\ell \frac{1}{\Gamma(\alpha)}\int_0^\infty e^{-\ell\epsilon}\epsilon^{\alpha-1}d\epsilon. \tag{8.92}$$

Note that this swap is allowed because the series *converges uniformly* for $0 < z \leq 1$. Evaluating the integral gives

$$\frac{1}{\Gamma(\alpha)}\int_0^\infty e^{-\ell\epsilon}\epsilon^{\alpha-1}d\epsilon = \frac{1}{\ell^\alpha}. \tag{8.93}$$

Thus we obtain

$$F_\alpha^{\mathrm{BE}}(z) = \sum_{\ell=1} \frac{z^\ell}{\ell^\alpha} \equiv g_\alpha(z) = \mathrm{Li}_\alpha(z) \tag{8.94a}$$

$$F_\alpha^{\mathrm{FD}}(z) = \sum_{\ell=1} (-)^{\ell+1}\frac{z^\ell}{\ell^\alpha} \equiv f_\alpha(z) = -\mathrm{Li}_\alpha(-z), \tag{8.94b}$$

where $\mathrm{Li}_\alpha(z)$ is the polylogarithm (see Appendix C.3). These expressions are known as the *fugacity expansions* of the BE-function $g_\alpha(z)$ and FD-function $f_\alpha(z)$.

8.3.8.2 b. the case $0 \leq (1-z) \ll 1$

Highly degenerate bosonic gases are characterized by the condition $0 \leq -\mu/k_BT \ll 1$. In this case the integral $F_\alpha^{\mathrm{BE}}(z)$ can be expanded in powers of $-\ln z = -\mu/k_BT \ll 1$ (see Appendix C.4). In particular we have

$$F_{3/2}^{\mathrm{BE}}(z) = \zeta(3/2) + \Gamma(-1/2)\sqrt{-\ln z} + \cdots \tag{8.95}$$

$$F_{5/2}^{\mathrm{BE}}(z) = \zeta(5/2) - \zeta(3/2)\left(-\ln z\right) + \Gamma\left(-3/2\right)\left(-\ln z\right)^{3/2} + \cdots \tag{8.96}$$

valid for $-\mu \ll k_BT$. Note that these expressions satisfy the recursion relations (C.18). Note further that these relations break down for $z > 1$ (see Fig. 8.1). In the limit $z \to 1$ the functions $F_\alpha^{\mathrm{BE}}(z)$ turn into the Riemann zeta function,

$$\lim_{z\to 1} F_\alpha^{\mathrm{BE}}(z) = \zeta(\alpha). \tag{8.97}$$

8.3.8.3 c. the case $z \gg 1$

Highly degenerate fermionic gases are characterized by the condition $\mu/k_BT \gg 1$. For $z > 1$ the expansion (8.91) does not converge. However, for $z \gg 1$, the integral $F_{3/2}^{\mathrm{FD}}(z)$ can be expanded in powers of $(\ln z)^{-1} = k_BT/\mu \ll 1$ (see Appendix C.5),

$$F_{3/2}^{\mathrm{FD}}(z) = \frac{4}{3\sqrt{\pi}}\left(\ln z\right)^{3/2}\left[1 + \frac{\pi^2}{8}\left(\ln z\right)^{-2} + \cdots\right] \tag{8.98}$$

$$F_{5/2}^{\mathrm{FD}}(z) = \frac{8}{15\sqrt{\pi}}\left(\ln z\right)^{5/2}\left[1 + \frac{5\pi^2}{8}\left(\ln z\right)^{-2} + \cdots\right]. \tag{8.99}$$

Note that these expansions satisfy the recursion relations (C.18) and nicely express the logarithmic divergence of the integrals $F_{3/2}^{\mathrm{FD}}(z)$ and $F_{5/2}^{\mathrm{FD}}(z)$. The approximation of $F_{3/2}^{\mathrm{FD}}(z)$ by the first two terms of Eq. (8.98) is shown as the dotted line in Fig. 8.1. Note that this approximation is already excellent for $z \gtrsim 4$ (i.e., $\mu/k_BT \gtrsim \ln 4 \approx 1.3$).

9

The ideal Bose gas

9.1 Introduction

In this section we analyze the ideal Bose gas in more detail, in particular the phenomenon of Bose-Einstein Condensation (BEC). Like in previous chapters we consider a gas of N trapped atoms confined by an external potential $\mathcal{U}(\mathbf{r})$ with characteristic level splitting $\hbar\omega$ and studied at temperatures T where many states are populated ($k_BT \gg \hbar\omega$). The system is described by the hamiltonian

$$\mathcal{H} = \sum_i \mathcal{H}_0(\mathbf{p}_i, \mathbf{r}_i), \tag{9.1}$$

representing the sum of single-particle contributions,

$$\mathcal{H}_0(\mathbf{p}, \mathbf{r}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \mathcal{U}(\mathbf{r}). \tag{9.2}$$

The single-particle energy eigenstates $|s\rangle$ and eigenvalues ε_s are defined by $\mathcal{H}_0\,|s\rangle = \varepsilon_s\,|s\rangle$. As we are dealing with bosons, the occupation of the state s is given by the BE-distribution

$$f_{\mathrm{BE}}(\varepsilon_s; \mu, T) = \frac{1}{e^{(\varepsilon_s-\mu)/k_BT} - 1}. \tag{9.3}$$

For given ε_s and T this distribution is a regular, monotonically increasing function of μ on the interval $-\infty < \mu < 0$, which diverges in the case of the ground state ($\varepsilon_s = \varepsilon_0 = 0$) when μ approaches zero (see also Section 8.3.2),

$$\frac{1}{e^{-\mu/k_BT} - 1} \simeq \frac{1}{-\mu/k_BT} \text{ for } \mu \to 0. \tag{9.4}$$

As the occupation can impossibly exceed the total number of available atoms N we note that in *finite* systems the chemical potential remains nonzero, $-\mu/k_BT \geq 1/N$. Excluding the ground state, the BE-distribution is a quasi-continuous function of ε_s (even for $-\mu \ll k_BT$) as is illustrated in Fig. 9.1. In the absence of a condensate, i.e. for $-\mu/k_BT \gg 1/N$, this allows us to make the semi-classical approximation (8.39), in which the summation over single-particle states is replaced by an integral over phase space (see Section 8.3.4). Clearly, this approximation brakes down with the onset of BEC, i.e. for $-\mu \ll k_BT$, when the ground-state occupation N_0 grows disproportionately as compared to the occupation of adjacent excited states. The work-around is well known: as only the ground-state becomes macroscopically populated it suffices to single-out the ground state from the summation (8.38). In this way we obtain the *semi-classical approximation* in which only the summation over excited states is treated quasi-classically,

$$N = N_0 + {\sum_s}' \bar{n}_s = \frac{1}{e^{-\mu/k_BT} - 1} + \frac{1}{(2\pi\hbar)^3}\int \frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT} - 1} d\mathbf{r}d\mathbf{p}. \tag{9.5}$$

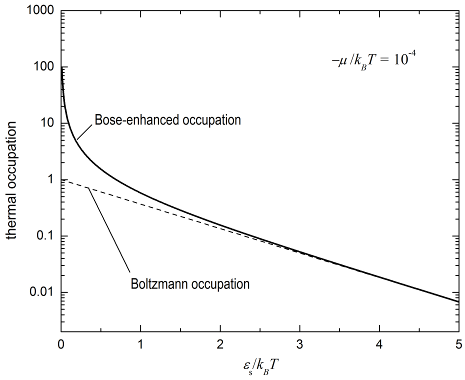

Figure 9.1: Average thermal occupation $\bar{n}_s \equiv f_{\mathrm{BE}}(\varepsilon_s;\mu,T)$ of states of energy ε_s for $-\mu/k_BT = 10^{-4}$ (solid line). The occupation of the lowest levels ($\varepsilon_s < k_BT$) is strongly enhanced as compared to the classical (Boltzmann) occupation (dashed line). This is known as quantum degeneracy. The lowest plotted energy corresponds to $\varepsilon_1 = k_BT/100$, a typical value for the first excited state in harmonic traps at $T \simeq T_c$.

The summation over the occupations of the excited states yields by definition the number of atoms in the *thermal cloud*,

$$\sum_s{}' \bar{n}_s \equiv N' = N - N_0. \tag{9.6}$$

As is readily verified, like the N_0-term also the BE-integral in Eq. (9.5) is a regular, monotonically increasing function of μ on the interval $-\infty < \mu < 0$ and because N_0 diverges for $\mu \to 0$ the Eq. (9.5) can be satisfied for any value of N and T by choosing the appropriate value for μ. The occupation of the thermal cloud can be written as

$$N' = \int n'(\mathbf{r})d\mathbf{r}, \tag{9.7}$$

where

$$n'(\mathbf{r}) = \frac{1}{\Lambda^3} F_{3/2}^{\mathrm{BE}}[\tilde{z}(\mathbf{r})] = \frac{1}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\epsilon^{1/2}}{\tilde{z}(\mathbf{r})^{-1}e^{\epsilon}-1}d\epsilon, \tag{9.8}$$

with $\epsilon = p^2/2mk_BT$ the reduced kinetic energy and $\tilde{z}(\mathbf{r})$ the local *fugacity* defined in Eq. (8.46).

As the chemical potential is always negative, the fugacity is bounded to the interval $0 < z < 1$. Since also $\exp[-p^2/2mk_BT]$ is bounded to this interval we can use the fugacity expansion (8.94a) for the BE-integral in Eq. (9.5),

$$N = N_0 + N' = \frac{z}{1-z} + \frac{1}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2}}\int e^{-\ell\mathcal{U}(\mathbf{r})/k_BT}d\mathbf{r}. \tag{9.9}$$

In the intergral we recognize the effective volume defined for a Boltzmann gas in Section 1.3.1,

$$V_{\ell e}(T) = \int e^{-\ell\mathcal{U}(\mathbf{r})/k_BT}d\mathbf{r} = V_e(T/\ell). \tag{9.10}$$

In accordance with Eq. (1.48) this is the effective volume V_e of a *classical* cloud at temperature T/ℓ. Although this volume is not visible in quantum gases its use is convenient from the mathematical point of view.

For spherical power-law traps with trap parameter γ the effective volume is given by Eq. (1.73),

$$V_e(T) = \alpha_{\mathrm{PL}}T^\gamma = \ell^\gamma V_e(T/\ell), \tag{9.11}$$

and the number of atoms in the thermal cloud can be written as

$$N' = \frac{V_e}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2+\gamma}}. \tag{9.12}$$

Note the dependence on the trap parameter. In contrast the degeneracy parameter of the thermal cloud is independent of γ; setting $\mathbf{r}=0$ in Eq. (9.8) we find

$$n'_0\Lambda^3 = \sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2}} \equiv g_{3/2}(z), \tag{9.13}$$

where $n'_0 \equiv n'(0)$ is the *local* density at the trap minimum.[1] Note that Eq. (9.13) does not depend on $\mathcal{U}(\mathbf{r})$. Therefore, the degeneracy parameter of the thermal cloud has the same convergence limit ($z \to 1 \Leftrightarrow \mu \to 0$), *irrespective* of the trap shape. This convenient rule is well known; therefore, it is important to be aware that it does *not* hold for cases of reduced dimensionality.

9.2 Regimes of quantum degeneracy

9.2.1 Classical regime - $n_0\Lambda^3 \ll 1$

At constant n'_0 the l.h.s. of Eq. (9.13) decreases monotonically for increasing temperature T. Therefore, the corresponding fugacity z has to become smaller until in the classical limit ($D \to 0$) only the first term contributes significantly to the series, $\sum_{\ell=1}^{\infty} z^\ell/\ell^{3/2} \simeq z$. Hence, in the *classical limit*, where $n'_0 = n_0$ the fugacity is found to coincide with the degeneracy parameter

$$z \underset{T\to\infty}{\simeq} n_0\Lambda^3 \quad \Leftrightarrow \quad \mu = k_B T \ln[n_0\Lambda^3]. \tag{9.14}$$

Apparently, in the classical limit μ must have a large negative value to assure that the Bose-Einstein distribution function corresponds to the proper number of atoms. In Chapter 1 expression (9.14) was obtained for the classical gas starting from the Helmholtz free energy (see Problem 1.13). Furthermore, for $z \to 0$ only the first term of the fugacity expansion is significant and the density distribution reduces to

$$n(\mathbf{r}) = n'(\mathbf{r}) = n_0 e^{-\mathcal{U}(\mathbf{r})/k_B T}. \tag{9.15}$$

Hence, z has dropped out of the expression, which makes it independent of N. Therefore, the distribution has become indendent of the occupation of the states.

9.2.2 The onset of quantum degeneracy - $1 \lesssim n_0\Lambda^3 < 2.612$

Decreasing the temperature of a trapped gas the chemical potential increases until at a critical temperature, T_c, the fugacity expansion reaches its convergence limit ($z \to 1$) and the density is given by

$$n(\mathbf{r}) = n'(\mathbf{r}) = \frac{1}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{1}{\ell^{3/2+\gamma}}e^{-\ell\mathcal{U}(\mathbf{r})/k_B T}. \tag{9.16}$$

Note that only in the trap center all terms of the expansion contribute to the density. Off-center the higher-order terms are exponentially suppressed with respect to the lower ones. This reflects the property of the Bose statistics to favor the occupation of the most occupied states. For the trap center we have at T_c

$$D = n_0\Lambda^3 = \sum_{\ell=1}^{\infty}\frac{1}{\ell^{3/2}} \equiv \zeta(3/2) \approx 2.612. \tag{9.17}$$

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[1] Beware that $n'_0 \equiv n'(0) = \zeta(3/2)\, n_0 \neq N'/V_e$. The central density is enhanced by the Bose statistics.

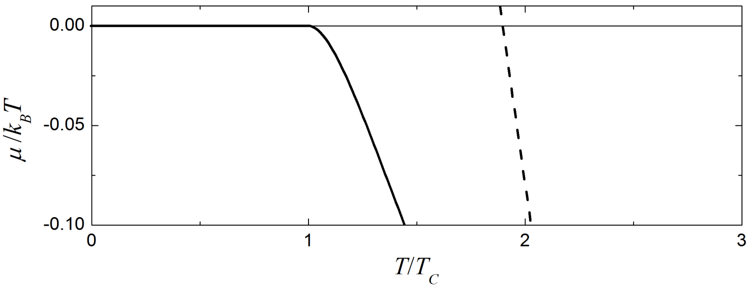

Figure 9.2: Chemical potential as a function of temperature for a homogeneous Bose gas close to T_c (solid line). For comparison the classical expression (9.14) is also plotted (dashed line).

We thus established that the parameter $D = n_0\Lambda^3$, where $n_0 = n(0)$ is the density at the trap center, is indeed a good indicator for the presence of quantum degeneracy; i.e., for the deviation from classical statistics. Hence, in 3D T_c only depends on the density in the trap center and *not on the trap shape.*

9.2.3 Fully degenerate Bose gas - homogeneous case

In this section we have a closer look at what happens close to T_c. First we consider the homogeneous gas for which the general expression (9.9) reduces to

$$N = N_0 + N' = \frac{z}{1-z} + \frac{V}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2}}. \tag{9.18}$$

For $T \lesssim T_c$ the chemical potential is always close to zero. Therefore, in the degenerate regime the Bose function is best represented by the expansion (8.95) in powers of $(-\ln z) = -\mu/k_BT$,

$$N = \frac{k_BT}{-\mu} + \frac{V}{\Lambda^3}\left[\zeta(3/2) + \zeta(1/2)\sqrt{\frac{-\mu}{k_BT}} + \cdots\right] \quad \text{for } (\mu \uparrow 0). \tag{9.19}$$

Just above T_c, i.e. for $1/N \lll -\mu/k_BT \ll 1$, the chemical potential can be expressed as

$$\mu = -k_BT\left(\frac{\zeta(3/2) - n_0\Lambda^3}{\zeta(1/2)}\right)^2, \tag{9.20}$$

which is plotted in Fig. 9.2.

As expected, the chemical potential increases with decreasing temperature. For $-\mu \lesssim k_BT$ the curve deviates from the classical expression (9.14) shown as the dashed line in Fig. 9.2. For $-\mu \ll k_BT$, the fugacity expansion approaches its convergence limit and the thermal term of Eq. (9.19) can no longer account for all atoms. For a large but finite number of atoms ($N \ggg 1$) this happens at a *non-zero* temperature $T = T_c$, where μ has a small but finite negative value and the following expression is satisfied,

$$N = \frac{k_BT}{-\mu} + \frac{V}{\Lambda_c^3}\left[\zeta(3/2) + \zeta(1/2)\sqrt{\frac{-\mu}{k_BT_c}} + \cdots\right] \simeq \frac{V}{\Lambda_c^3}\zeta(3/2) \simeq N'. \tag{9.21}$$

9.2.3.1 Bose-Einstein condensation

Lowering the temperature below T_c the ground state occupation starts to grow from $N_0 = -k_BT/\mu \ll N$ to macroscopic values, which marks the onset of Bose-Einstein condensation. Extracting the temperature from Eq. (9.21) we obtain the well know expression for T_c in a homogeneous 3D system,

$$k_BT_c \simeq 3.31\left(\hbar^2/m\right)n_0^{2/3}. \tag{9.22}$$

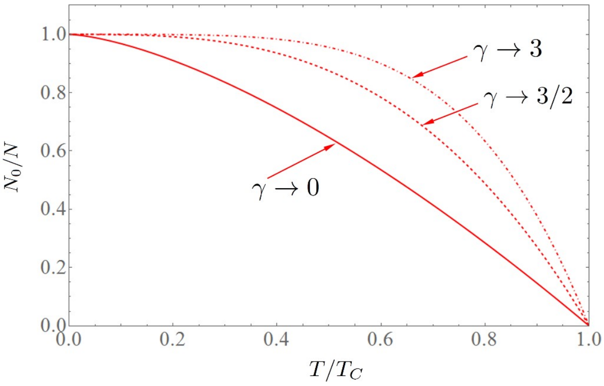

Figure 9.3: Condensate fraction as a function of T/T_c for three types of traps: homogeneous square well ($\gamma = 0$); harmonic trap ($\gamma = 3/2$); linear trap ($\gamma = 3$).

Below T_c the *non-condensed fraction* is given by

$$N' = (V/\Lambda^3)\zeta(3/2). \tag{9.23}$$

Dividing this expression by Eq. (9.21) we obtain

$$N'/N = \zeta(3/2)/n\Lambda^3 = (T/T_c)^{3/2}\,, \tag{9.24}$$

which implies that below T_c the number of atoms in the condensate has to be $N_0 = N - N' = -k_BT/\mu$ and that below T_c the *condensate fraction* is growing in accordance with

$$N_0/N = 1 - N'/N = 1 - (T/T_c)^{3/2}\,. \tag{9.25}$$

This is illustrated in Fig. 9.3. Far below T_c the condensate fraction is close to unity ($N_0 \simeq N$) and the chemical potential reaches its limiting value,

$$\mu = k_BT\ln(1 - 1/N_0) \simeq -k_BT/N. \tag{9.26}$$

Note that μ is zero for all practical purposes provided $N \ggg 1$ and truly zero only in the *thermodynamic limit* ($N, V \to \infty$, $N/V = n_0$).

9.2.4 BEC in isotropic power-law traps

The above analysis can be generalized to inhomogeneous gases. Restricting ourselves to power-law traps, the total number of atoms can be expressed in the form (9.9) and is for trap parameter γ given by

$$N = N_0 + N' = \frac{z}{1-z} + \frac{V_e}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2+\gamma}}, \tag{9.27}$$

where V_e is the effective volume defined by Eq. (1.73). For $T \leq T_c$ we have $z \simeq 1$ and the number of atoms in the *thermal cloud* is given by

$$N' = \frac{V_e}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{1}{\ell^{3/2+\gamma}} \leq N. \tag{9.28}$$

Dividing by the expression for the total number of atoms at T_c,

$$N = N' = \frac{V_e(T_c)}{\Lambda_c^3}\sum_{\ell=1}^{\infty}\frac{1}{\ell^{3/2+\gamma}}, \tag{9.29}$$

we obtain

$$N'/N = (T/T_c)^{3/2+\gamma}, \tag{9.30}$$

For the condensate fraction this implies

$$N_0/N = 1 - (T/T_c)^{3/2+\gamma}. \tag{9.31}$$

For $\gamma = 0$, $3/2$, 3 this is illustrated in Fig. 9.3.

9.2.5 BEC in systems with a power-law density of states

The analysis can be further generalized with the aid of the density of states $\rho(\varepsilon)$ of the system, introduced in Section 1.3.3. For this purpose we write the total number of atoms in the thermal cloud as

$$N' = \sum_s{}' \bar{n}_s = \sum_{\ell=1}^{\infty} z^{\ell} \frac{1}{(2\pi\hbar)^2} \int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT} d\mathbf{r} d\mathbf{p} = \sum_{\ell=1}^{\infty} z^{\ell} Z_1(T/\ell), \tag{9.32}$$

where Z_1 is the one-body canonical partition function introduced in Chapter 1. For trapping potentials, isotropic or anisotropic, with a density of states of the type

$$\rho(\varepsilon) = A\varepsilon^{1/2+\gamma} \tag{9.33}$$

Eq. (9.32) can be expressed in the form

$$N' = \sum_{\ell=1}^{\infty} z^{\ell} \int_0^{\infty} e^{-\ell\varepsilon/k_BT} \rho(\varepsilon) d\varepsilon, \tag{9.34}$$

where we used Eq. (1.84). For $T \leq T_c$ we have $z = 1$ and the expression for N' becomes

$$N' = A \sum_{\ell=1}^{\infty} \int_0^{\infty} e^{-\ell\varepsilon/k_BT} \varepsilon^{1/2+\gamma} d\varepsilon = A\,(k_BT)^{3/2+\gamma} \sum_{\ell=1}^{\infty} \int_0^{\infty} e^{-\ell x} x^{1/2+\gamma} dx. \tag{9.35}$$

Hence, using the integral relation (C.14) Eq. (9.35) reduces to

$$N' = A\,(k_BT)^{3/2+\gamma}\,\Gamma(3/2+\gamma) g_{3/2+\gamma}(z) \tag{9.36}$$

and Eq. (9.31) for the condensate fraction is seen to hold for all traps with a density of states of the type (9.33).

9.2.6 Example: BEC in harmonic traps

As an example we consider the harmonically trapped ideal Bose gas (trap parameter $\gamma = 3/2$) at temperatures $k_BT \gg \hbar\bar{\omega}$, where $\bar{\omega}/2\pi$ is the average oscillation frequency of a single trapped atom, with $\bar{\omega} = (\omega_x\omega_y\omega_z)^{1/3}$. For this system we have a quasi-continuous level occupation and the semi-classical single-particle partition function is given by $Z_1 = (k_BT/\hbar\bar{\omega})^3$ - see Eq. (1.86).

The density profile of the thermal cloud is found by substituting $\mathcal{U}(\mathbf{r}) = \frac{1}{2}m\omega^2r^2$ into Eq. (9.16),

$$n'(\mathbf{r}) = \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} \frac{z^{\ell}}{\ell^{3/2}} \exp[-\ell \frac{m\omega^2r^2}{2k_BT}]. \tag{9.37}$$

The profile of a fully saturated ($z = 1$) Bose-Einstein distribution is shown in Fig. 9.4. Note that the cloud is gaussian for $m\omega^2r^2 \gg k_BT$, which means that the tail of the distribution remains quasi

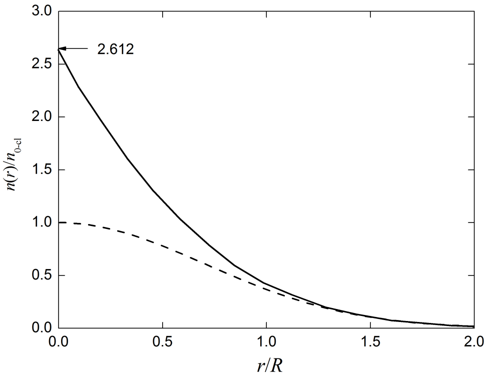

Figure 9.4: The density profile of a fully saturated ($z = 1$) thermal cloud of bosons in an isotropic harmonic trap (solid line). For comparison the gaussian profile of a classical gas is also drawn (dashed line); $R = \sqrt{2kT/m\omega^2}$ is the thermal radius of the classical cloud.

classical, irrespective of the value of z. Clearly, the center of the cloud is the interesting part. Here the density is enhanced, a plausible precursor for BEC.

The onset of BEC occurs when the fugacity expansion reaches its convergence limit $z \to 1$. This process is best analyzed starting from Eq. (9.9), which takes for harmonic traps the form

$$N = \frac{z}{1-z} + (k_B T/\hbar\omega)^3 \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^3}. \tag{9.38}$$

The convergence limit of the series is given by

$$\lim_{z\to 1} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^3} = g_3(1) = \zeta(3) \approx 1.202. \tag{9.39}$$

Thus at T_c we find with the aid of Eq. (9.38) $N = (k_B T_c/\hbar\omega)^3 \zeta(3)$, which can be written in the form of an expression for T_c,

$$k_B T_c = [N/\zeta(3)]^{1/3} \hbar\omega \simeq N^{1/3}\hbar\omega. \tag{9.40}$$

With this expression we calculate that for a million atoms in a harmonic trap the critical temperature corresponds to 100× the harmonic oscillator spacing. Thus we verified that down to T_c the condition $k_B T \gg \hbar\omega$ remains satisfied. Note that this holds for *any* harmonic trap and only as long as $N \ggg 1$ and the ideal gas condition is satisfied ($\upsilon_0 n_0 \ll k_B T_c$).

For $T \leq T_c$ Eq. (9.38) takes the form

$$N = N_0 + (k_B T/\hbar\omega)^3 \zeta(3) = N_0 + (T/T_c)^3 N, \tag{9.41}$$

where N_0 is the number of atoms in the oscillator ground-state (the condensate). Because the ground state is highly localized in the trap center, the condensation process results in a dramatic increase of the density in the center of the cloud and, in most cases, the ideal-gas approximation breaks down. Note that this density increase is a feature of the inhomogeneous gas. In homogeneous gases the density is constant and BEC manifests itself only in momentum space. Rewriting Eq. (9.41) we obtain for the for the condensate fraction of a harmonically trapped gas

$$N_0/N = 1 - (T/T_c)^3. \tag{9.42}$$

Note that at $T/T_c = 0.21$ the condensate fraction is already 99%.

Problem 9.1. Show that for one million bosons in a harmonic trap at T_c the *first* excited state has a hundred fold occupation.

Solution. The occupation of the lowest excited state, i.e. the state of energy $\varepsilon_1 = \hbar\omega \ll k_B T_c \simeq N^{1/3}\hbar\omega$, is given by

$$\bar{n}_1 = \frac{1}{e^{\varepsilon_1/k_B T_c} - 1} \simeq \frac{k_B T_c}{\hbar\omega} \simeq N^{1/3}.$$

For $N = 10^6$ this implies that $\bar{n}_1 = 100$. □

9.3 Release of trapped clouds - momentum distribution of bosons

For a gas of bosons above T_c the momentum distribution is given by

$$n(\mathbf{p}) = \sum_{\ell=1}^{\infty} z^{\ell} \frac{1}{(2\pi\hbar)^3} \int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_B T} d\mathbf{r} = \frac{1}{(2\pi\hbar)^3} \sum_{\ell=1}^{\infty} z^{\ell} e^{-\ell(p/\alpha)^2} V_e\,(T/\ell)\,, \tag{9.43}$$

where $\alpha = \sqrt{2mk_B T}$ and $V_e(T/\ell)$ is the effective volume of a *classical* cloud at temperature T/ℓ as defined in Eq. (9.10). Importantly, whatever the trap shape the momentum distribution is seen to be *isotropic*. This means that when releasing a trapped cloud by switching-off the trapping potential the cloud shape will always evolve into a spherical form. Once the cloud is much larger than its initial size only the radial distribution of the density reflects the properties of the original trap.

Substituting Eq. (9.11) into Eq. (9.43) we obtain for the momentum distribution

$$n(\mathbf{p}) = \frac{V_e\,(T)}{(2\pi\hbar)^3} \sum_{\ell=1}^{\infty} \frac{z^{\ell}}{\ell^{\gamma}} e^{-\ell(p/\alpha)^2} = \frac{N}{4\pi\alpha^3} \frac{1}{\frac{1}{4}\sqrt{\pi}} \frac{g_{\gamma}(ze^{-(p/\alpha)^2})}{g_{\gamma+3/2}(z)}, \tag{9.44}$$

where we used

$$N = \int n(\mathbf{p}) d\mathbf{p} = \frac{V_e\,(T)}{(2\pi\hbar)^3} 4\pi\alpha^3 \frac{1}{4}\sqrt{\pi}\, g_{\gamma+3/2}(z). \tag{9.45}$$

Since $\Lambda^3 = \pi^{-3/2}\,(2\pi\hbar/\alpha)^3$ the above expression coincides with Eq. (9.28). Interestingly, for *harmonic* traps ($\gamma = 3/2$) the momentum distribution (9.44) has exactly the same functional form as the density distribution (9.37).

To conclude this section we introduce the normalized momentum distribution

$$\mathrm{f}_{\mathrm{BE}}(\mathbf{p}) = n(\mathbf{p})/N = \frac{1}{4\pi\alpha^3} \frac{1}{\frac{1}{4}\sqrt{\pi}} \frac{g_{\gamma}(ze^{-(p/\alpha)^2})}{g_{\gamma+3/2}(z)}.$$

and give expressions for the variance and the average value of the momentum

$$\begin{aligned} \left\langle p^2 \right\rangle &= \int p^2 \mathrm{f}_{\mathrm{BE}}(\mathbf{p}) d\mathbf{p} = \alpha^2 \frac{\frac{3}{8}\sqrt{\pi} g_{\gamma+5/2}(z)}{\frac{1}{4}\sqrt{\pi} g_{\gamma+3/2}(z)} = 3mk_B T \frac{g_{\gamma+5/2}(z)}{g_{\gamma+3/2}(z)} \\ \left\langle p \right\rangle &= \int p\, \mathrm{f}_{\mathrm{BE}}(\mathbf{p}) d\mathbf{p} = \alpha \frac{\frac{1}{2} g_{\gamma+4}(z)}{\frac{1}{4}\sqrt{\pi} g_{\gamma+3/2}(z)} = \sqrt{8mk_B T/\pi} \frac{g_{\gamma+4}(z)}{g_{\gamma+3/2}(z)} \end{aligned}$$

Comparing the first and second moments we obtain

$$\left\langle p^2 \right\rangle / \left\langle p \right\rangle^2 = \frac{3\pi}{8} g_{\gamma+5/2}(z) g_{\gamma+3/2}(z) / \left[g_{\gamma+2}(z) \right]^2 ,$$

which implies that for harmonic traps the ratio $\left\langle p^2 \right\rangle / \left\langle p \right\rangle^2$ increases by $\sim 2.5\%$ when the fugacity changes from its value in the classical gas ($z \ll 1$) to that of the saturated Bose-Einstein distribution ($z = 1$). Clearly, this ratio is not a sensitive indicator for the onset of BEC.

9.4 Degenerate Bose gases without BEC

Interestingly, not any Bose gas necessarily undergoes BEC. This phenomenon depends on the density of states of the system. We illustrate this with a two-dimensional (2D) Bose gas; i.e., a gas of bosons confined to a plane. Like in Section 8.3.2 we require the sum over the average occupations $\bar{n}_s$ of all single-particle states to add up to the total number of trapped atoms,

$$N = \sum_s \bar{n}_s = \sum_{\ell=1}^{\infty} z^\ell \frac{1}{(2\pi\hbar)^2} \int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_B T} d\mathbf{r} d\mathbf{p}. \tag{9.46}$$

In 2D the phase space is 4-dimensional and after integration we obtain

$$N = \frac{1}{\Lambda^2} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell} \int e^{-\ell \mathcal{U}(\mathbf{r})/k_B T} d\mathbf{r}. \tag{9.47}$$

For the homogeneous gas of N bosons confined to an area A this expression reduces for $\mu \ll k_B T$ to

$$D = n\Lambda^2 = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell} = -\ln(1-z) \simeq -\ln(-\mu/k_B T), \tag{9.48}$$

where $n = N/A$ is the two-dimensional density. Because the fugacity expansion does not converge to a finite limit Eq. (9.48) shows that, at constant n, the 2D degeneracy parameter $D = n\Lambda^2$ can grow to any value without the occurrence of BEC. The ground state occupation grows steadily until at $T = 0$ all atoms are collected in the ground state.

The homogenous 2D Bose gas is seen to be a limiting case for BEC; even the slightest enhancement of the density of states will result in a finite T_c for Bose-Einstein condensation, also in two dimensions. This is easily demonstrated by including a trapping potential of the isotropic power-law type, $\mathcal{U}(\mathbf{r}) = w_0 r^{3/\gamma}$. In this case Eq. (9.47) can be written as

$$N = \frac{1}{\Lambda^2} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell} A_e(T/\ell) = \frac{A_e}{\Lambda^2} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{1+2\gamma/3}} = \frac{A_e}{\Lambda^2} g_{1+2\gamma/3}(z), \tag{9.49}$$

where $A_e = \alpha_{PL} T^{2\gamma/3}$ (see problem 9.2) is the classical effective area of the atom cloud. Hence, the condition for BEC in a 2D trap coincides with the existence of the convergence limit,

$$\lim_{z \to 1} g_{1+2\gamma/3}(z) = \zeta(1 + 2\gamma/3). \tag{9.50}$$

This limit exists for $\gamma > 0$, which shows that even the weakest power-law trap assures BEC in gas of bosons confined to a plane.

Similarly, it may be shown (see problem 9.3) that BEC occurs for 1D Bose gases in power-law traps with $\gamma > 3/2$. [1,2] Interestingly, unlike the 3D gas where the density in the trap center is also an indicator for the onset of BEC in lower dimensions this is *not* the case. For instance, as follows from Eq. (9.47) the 2D density in the trap center is independently of γ given by

$$n_0 = \frac{1}{\Lambda^2} \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell} \simeq -\frac{1}{\Lambda^2} \ln(-\mu/k_B T). \tag{9.51}$$

Hence, the density in the trap center locally diverges irrespective of the occurrence of BEC and is as such no indicator for BEC.

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[1] Note that for T_c very close to $T = 0$ the continuum approximation brakes down because the condition $kT > \hbar\omega$ is no longer satisfied. In this case the discrete structure of the excitation spectrum has to be taken into account.

[2] See W. Ketterle and N. J. van Druten, Phys. Rev. A **54**, 656 (1996) and D.S. Petrov, *Thesis*, University of Amsterdam, Amsterdam 2003 (unpublished).

Problem 9.2. Show that the effective area of a classical cloud in a 2D isotropic power-law trap is given by

$$A_e = \frac{2}{3}\pi r_e^2 \gamma \Gamma(2\gamma/3) \left(\frac{k_B T}{\mathcal{U}_0}\right)^{\frac{2}{3}\gamma},$$

where γ is the trap parameter and $\Gamma(z)$ is de Euler gamma function.

Solution. The effective area is defined as $A_e = \int e^{-\mathcal{U}(r)/k_B T} d\mathbf{r}$. Substituting $\mathcal{U}(\mathbf{r}) = w_0 r^{3/\gamma}$ for the potential of an isotropic power-law trap we find with $w_0 = \mathcal{U}_0 r_e^{-3/\gamma}$

$$V_e = \int e^{-w_0 r^{3/\gamma}/k_B T} 2\pi r dr = \frac{2}{3}\pi r_0^2 \gamma \left(\frac{k_B T}{\mathcal{U}_0}\right)^{\frac{2}{3}\gamma} \int e^{-x} x^{\frac{2}{3}\gamma - 1} dx,$$

where $x = (\mathcal{U}_0/k_B T)(r/r_e)^{3/\gamma}$ is a dummy variable. □

Problem 9.3. Show that BEC can be observed in a 1D Bose gas confined by a power-law potential if the trap parameter satisfies the condition $\gamma > 3/2$.

Solution. The total number of bosons confined by a power-law potential $\mathcal{U}(\mathbf{r}) = w_0 r^{3/\gamma}$ along a line can be written in form equivalent to Eq. (9.49):

$$N = \frac{1}{\Lambda}\sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{1/2}} L_e(T/\ell) = \frac{L_e}{\Lambda}\sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{1/2+\gamma/3}} = \frac{L_e}{\Lambda} g_{1/2+\gamma/3}(z),$$

where L_e is the classical effective length

$$L_e = \int e^{-w_0 r^{3/\gamma}/k_B T} dr = \frac{1}{3} r_0 \gamma \left(\frac{k_B T}{\mathcal{U}_0}\right)^{\frac{1}{3}\gamma} \int e^{-x} x^{\frac{1}{3}\gamma - 1} dx = \frac{1}{3} r_0 \gamma \left(\frac{k_B T}{\mathcal{U}_0}\right)^{\frac{1}{3}\gamma} \Gamma(1\gamma/3),$$

with $x = (\mathcal{U}_0/k_B T)(r/r_e)^{3/\gamma}$ a dummy variable. Like in the 3D and 2D case the condition for the existence of BEC is determined by the existence of a convergence limit of a $g_\alpha(z)$-function,

$$\lim_{z\to 1} g_{1/2+\gamma/3}(z) = \zeta(1/2 + \gamma/3).$$

In the 1D case the limit exists for $\gamma > 3/2$. Taking into account the discrete structure of the excitation spectrum it may be shown that BEC also occurs in harmonic traps.[7] □

10

Ideal Fermi gases

10.1 Introduction

In the case of fermionic gases the semi-classical approximation (8.39) is always valid because, as a result of Pauli exclusion, for $N \ggg 0$ the typical single-particle energy is always much larger than the characteristic level splitting $\hbar\omega$. The number of atoms is given by the Fermi-Dirac integral (8.39),

$$N = \frac{1}{(2\pi\hbar)^3} \int \frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT}+1} d\mathbf{r}d\mathbf{p}. \tag{10.1}$$

Because the integrand (the Fermi-Dirac distribution function) is a regular, monotonically increasing function of μ, the integral expression (10.1) can be satisfied for any temperature T by choosing the appropriate value for the chemical potential. This value can be positive or negative, depending on N and T.

For $\mu < 0$ the fugacity $z \equiv e^{\mu/k_BT}$ is a small positive number $(0 < z \leq 1)$ and the distribution function can be expanded in powers of $z \exp[-H_0(\mathbf{r},\mathbf{p})/k_BT]$,

$$\frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT}+1} = \sum_{\ell=1}^{\infty} (-)^{\ell+1} z^{\ell} e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT}. \tag{10.2}$$

Note that this *fugacity expansion* has the form of an alternating series. Substituting Eq. (10.2) into Eq. (10.1) we obtain after swapping summation and integration

$$N = \sum_{\ell=1}^{\infty} (-)^{\ell+1} z^{\ell} \frac{1}{(2\pi\hbar)^3} \int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT} d\mathbf{r}d\mathbf{p}. \tag{10.3}$$

Note that this swap is allowed because the series *converges uniformly* for $0 < z \leq 1$. Introducing the local density approximation (8.42) for the case of fermions in a trap $\mathcal{U}(\mathbf{r})$,

$$n(\mathbf{r}) = \sum_{\ell=1}^{\infty} (-)^{\ell+1} z^{\ell} \frac{1}{(2\pi\hbar)^3} \int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT} d\mathbf{p} = \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} (-)^{\ell+1} \frac{z^{\ell}}{\ell^{3/2}} e^{-\ell\mathcal{U}(\mathbf{r})/k_BT}. \tag{10.4}$$

In particular, at the trap minimum $(\mathbf{r} = 0)$ we have for the degeneracy parameter

$$D \equiv n_0\Lambda^3 = \sum_{\ell=1}^{\infty} (-)^{\ell+1} \frac{z^{\ell}}{\ell^{3/2}} \equiv f_{3/2}(z) = F_{3/2}(u) \quad \text{(for } 0 < z \leq 1\text{)}, \tag{10.5}$$

where $z \equiv e^{-u}$ with $u \equiv -\mu/k_BT$.

For $\mu > 0$ the series does not converge. Hence, a different approach is required to evaluate the Fermi-Dirac integral 10.1 (cf. section 10.4).

10.2 Classical regime $\left(n_0\Lambda^3 \ll 1\right)$

At constant n_0 the l.h.s. of Eq. (10.5) decreases monotonically for increasing temperature T. Therefore, the corresponding fugacity z has to become smaller until in the classical limit $(D \to 0)$ only the first term contributes significantly to the series, $\sum_{\ell=1}^{\infty}(-)^{\ell+1} z^\ell/\ell^{3/2} \simeq z$. Hence, just like for bosons, in the *classical limit* the fugacity is found to coincide with the degeneracy parameter

$$z \underset{T\to\infty}{\simeq} n_0\Lambda^3 \Leftrightarrow \mu = k_BT\ln[n_0\Lambda^3]. \tag{10.6}$$

In Chapter 1 expression (9.14) was obtained for the classical gas starting from the Helmholtz free energy (see Problem 1.13). Hence, in the classical limit the expressions for the chemical potentials of the quantum gases coincide with that of the Boltzmann gas, *i.e.*, μ is a large *negative* number.

10.3 The onset of quantum degeneracy $\left(n_0\Lambda^3 \simeq 1\right)$

Decreasing the temperature of a trapped fermionic gas the chemical potential increases monotonically until at the degeneracy temperature T_D the fugacity expansion reaches its limit of validity $(z = 1)$ in the trap center. At this temperature the density distribution is given by

$$\begin{aligned} n(\mathbf{r}) &= \frac{1}{\Lambda^3}\sum_{\ell=1}^{\infty}(-)^{\ell+1}\frac{z^\ell}{\ell^{3/2}}e^{-\ell\mathcal{U}(\mathbf{r})/k_BT} \\ &= \frac{1}{\Lambda^3}f_{3/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT}) \\ &= \frac{e^{-\mathcal{U}(\mathbf{r})/k_BT_D}}{\Lambda^3}\left\{1-\frac{1}{2^{3/2}}e^{-\mathcal{U}(\mathbf{r})/k_BT_D}+\frac{1}{3^{3/2}}e^{-2\mathcal{U}(\mathbf{r})/k_BT_D}-\cdots\right\}. \end{aligned}$$

Note that only in the trap center all terms of the expansion contribute to the density. Off-center the higher-order terms are exponentially suppressed with respect to the lower ones. Hence, the degeneracy is largest in the center and because the leading correction is negative the density is suppressed as compared to the classical Boltzmann gas. This reflects the Pauli exclusion of doubly occupied states. Like in the case of bosons the parameter $D = n_0\Lambda^3$ is a good indicator for the presence of quantum degeneracy. For the trap center we have at T_D

$$D = n_0\Lambda_D^3 = \sum_{\ell=1}^{\infty}\frac{(-)^{\ell+1}}{\ell^{3/2}} = (1-2^{-1/2})\zeta(3/2) \approx 0.765. \tag{10.7}$$

Hence, the degeneracy temperature is given

$$k_BT_D \simeq 7.51\left(\hbar^2/m\right)n_0^{2/3}$$

and depends only on the density in the trap center and *not on the trap shape.*

10.4 Fully degenerate Fermi gases

In this section we have a closer look at what happens below the degeneracy temperature T_D, where $\mu/k_BT \gg 1$ and $z \gg 1$. The number density is given by the Fermi-Dirac integral,

$$n(\mathbf{r}) = \frac{1}{(2\pi\hbar)^3}\int\frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT}+1}d\mathbf{p} = \frac{1}{\Lambda^3}F_{3/2}^{\mathrm{FD}}(\tilde{z}(\mathbf{r})), \tag{10.8}$$

where

$$\tilde{z}(\mathbf{r}) = ze^{-\mathcal{U}(\mathbf{r})/k_BT} \tag{10.9}$$

is the position dependent fugacity for a confinement potential $\mathcal{U}(\mathbf{r})$. For

$$\ln\tilde{z}\left(\mathbf{r}\right)=\frac{\mu\left(\mathbf{r}\right)}{k_BT}=\frac{\mu-\mathcal{U}\left(\mathbf{r}\right)}{k_BT}\gg 1 \tag{10.10}$$

we can use the expansion Eq.(8.98)

$$F_{3/2}^{\mathrm{FD}}(z)=\frac{4}{3\sqrt{\pi}}\left(\ln z\right)^{3/2}\left[1+\frac{\pi^2}{8}\left(\ln z\right)^{-2}+\cdots\right] \tag{10.11}$$

and the local density can be written in the form

$$n\left(\mathbf{r}\right)=\frac{1}{\Lambda^3}\frac{4}{3\sqrt{\pi}}\left(\frac{\mu\left(\mathbf{r}\right)}{k_BT}\right)^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu\left(\mathbf{r}\right)}\right)^2+\cdots\right]. \tag{10.12}$$

Eliminating the chemical potential we obtain

$$\mu\left(\mathbf{r}\right)=\frac{\hbar^2}{2m}\left[6\pi^2n\left(\mathbf{r}\right)\right]^{2/3}\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\mu\left(\mathbf{r}\right)}\right)^2+\cdots\right]. \tag{10.13}$$

Introducing the *Fermi energy* of the fully degenerate gas

$$\varepsilon_F\equiv\lim_{T\to 0}\mu\left(0\right)=\frac{\hbar^2}{2m}\left[6\pi^2n_0\right]^{2/3} \tag{10.14}$$

and defining the Fermi temperature as $\varepsilon_F\equiv k_BT_F$ the chemical potential of a homogeneous system can be written as

$$\mu=\varepsilon_F\left[1-\frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2+\cdots\right]\qquad(\text{for }T\to 0). \tag{10.15}$$

Note that the Fermi temperature is approximately equal to the degeneracy temperature introduced in Section 10.3, $T_F\simeq T_D$. For this reason, it makes little sense to distinguish between the two. In practice, only the Fermi temperature is used.

10.4.1 Thomas-Fermi approximation

The local density approximation in the zero-temperature limit is known as the Thomas-Fermi approximation

$$\mu\left(\mathbf{r}\right)=\varepsilon_F-\mathcal{U}(\mathbf{r})=\frac{\hbar^2}{2m}\left[6\pi^2n\left(\mathbf{r}\right)\right]^{2/3}. \tag{10.16}$$

The corresponding Thomas-Fermi profile is obtained by eliminating $n\left(\mathbf{r}\right)$ from this equation

$$n\left(\mathbf{r}\right)=\frac{1}{6\pi^2}\left\{\frac{2m}{\hbar^2}\left[\varepsilon_F-\mathcal{U}(\mathbf{r})\right]\right\}^{3/2}=n_0\left[1-\mathcal{U}(\mathbf{r})/\varepsilon_F\right]^{3/2}, \tag{10.17}$$

which is positive for $\mathcal{U}(\mathbf{r})<\varepsilon_F$.

For isotropic harmonic traps,

$$\mathcal{U}(r)=\tfrac{1}{2}m\omega^2r^2, \tag{10.18}$$

the total number of fermions can be expressed by the integral

$$N_0=n_0\int_0^{R_F}\left(1-\frac{m\omega^2}{2\varepsilon_F}r^2\right)^{3/2}4\pi r^2dr=4\pi n_0R_F^3\int_0^1\left(1-x^2\right)^{3/2}x^2dx=\frac{\pi^2}{8}n_0R_F^3,$$

where $\equiv (2\varepsilon_F/m\omega_0^2)^{1/2}$ is the Thomas-Fermi radius of the ideal Fermi gas.

More in general, for isotropic power-law traps,

$$\mathcal{U}(r) = \mathcal{U}_0\,(r/r_0)^{3/\gamma}\,, \tag{10.19}$$

the total number of Fermions can be expressed by the integral

$$N_0 = n_0 \int_0^{R_F} \left(1-(r/R_F)^{3/\gamma}\right)^{3/2} 4\pi r^2 dr = \pi^{3/2}\frac{\Gamma(1+\gamma)}{\Gamma(\frac{5}{2}+\gamma)} n_0 R_F^3,$$

where $R_F \equiv r_0\,(\varepsilon_F/\mathcal{U}_0)^{\gamma/3}$ is the Thomas-Fermi radius of the ideal Fermi gas.

10.4.2 Link to the thermodynamics - semi-classical approximation

To study the thermodynamic properties of ideal Fermi gases we restrict ourselves to temperatures k_BT much larger than the characteristic trap level splitting $\hbar\omega$. Identifying the grand canonical average of the total energy E with the thermodynamic internal energy U of a system we obtain

$$U = \bar{E} = \sum_s \varepsilon_s \bar{n}_s = \sum_s \frac{\varepsilon_s}{e^{(\varepsilon_s-\mu)/k_BT}+1}. \tag{10.20}$$

In the semi-classical approximation this becomes

$$U = \int u(\mathbf{r})d\mathbf{r} = \frac{1}{(2\pi\hbar)^3}\int \frac{H_0(\mathbf{r},\mathbf{p})}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT}+1} d\mathbf{p}d\mathbf{r}, \tag{10.21}$$

where the local energy density $u(\mathbf{r})$ is given by

$$u(\mathbf{r}) = k_BT\frac{1}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int \frac{\epsilon^{3/2}}{e^{\mathcal{U}(\mathbf{r})/k_BT}z^{-1}e^{\epsilon}+1}d\epsilon + \frac{\mathcal{U}(\mathbf{r})}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int \frac{\epsilon^{1/2}}{e^{\mathcal{U}(\mathbf{r})/k_BT}z^{-1}e^{\epsilon}+1}d\epsilon. \tag{10.22}$$

Here we recognize two polylogarithms,

$$u(\mathbf{r}) = \tfrac{3}{2}k_BT\frac{1}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}] + \mathcal{U}(\mathbf{r})\frac{1}{\Lambda^3}F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]. \tag{10.23}$$

What happens below the degeneracy temperature T_D, where $\mu/k_BT \gg 1$ and $z \gg 1$? Approximating the FD functions we obtain in the zero-temperature limit, 3

$$u(\mathbf{r}) = \left(\frac{2m}{\hbar^2}\right)^{3/2}\left\{\frac{1}{10\pi^2}[\mu-\mathcal{U}(\mathbf{r})]^{5/2} + \mathcal{U}(\mathbf{r})\frac{1}{16\pi^2}[\mu-\mathcal{U}(\mathbf{r})]^{3/2}\right\}. \tag{10.24}$$

Using the recursion relation for polylogarithms (C.18) we find that Eq. (10.23) is equivalent with

$$\begin{aligned} u(\mathbf{r}) = {} & -k_BT\frac{1}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}] \\ & + T\left(\frac{\partial}{\partial T}k_BT\frac{1}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]\right)_{\mathcal{U},\mu} + \mu\frac{1}{\Lambda^3}F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]. \end{aligned} \tag{10.25}$$

In the first two terms we recognize the expression (8.63) for $\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})$. In the last term we recognize the local density, but rather than writing $\mu n(\mathbf{r})$ we note that the local density can also be expressed in terms of $\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})$ (see Problem 8.1),

$$n(\mathbf{r}) = \left(\frac{\partial}{\partial\mu}k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})\right)_{\mathcal{U},T}, \tag{10.26}$$

Thus Eq. (10.25) can be written in a form containing only $k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r})$ and its derivatives,

$$u(\mathbf{r}) = -k_BT\ln\tilde{\mathcal{Z}}_{gr} + T[\partial(k_BT\ln\tilde{\mathcal{Z}}_{gr})/\partial T]_{\mathcal{U},\mu} + \mu\partial(k_BT\ln\tilde{\mathcal{Z}}_{gr})/\partial\mu]_{\mathcal{U},T}. \tag{10.27}$$

This expression suggests to introduce the quantity

$$\tilde{\Omega}(\mathbf{r}) = -k_BT\ln\tilde{\mathcal{Z}}_{gr}(\mathbf{r}) \quad\Leftrightarrow\quad \tilde{\mathcal{Z}}_{gr}(\mathbf{r}) = e^{-\tilde{\Omega}(\mathbf{r})/k_BT}. \tag{10.28}$$

By substitution of Eq. (8.63) $\tilde{\Omega}(\mathbf{r})$ can be expressed in the form

$$\tilde{\Omega}(\mathbf{r}) = -\frac{k_BT}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]. \tag{10.29}$$

We are now in a position to make the connection to thermodynamics. First we shall do this for the *homogeneous* gas. In this case $\mathcal{U}(\mathbf{r})\equiv 0$ the conditions on the trap shape are replaced by conditions on the volume of the gas, V. Eq. (10.27) can be written in the form $\Omega = U + T\,(\partial\Omega/\partial T)_{V,\mu} + \mu\,(\partial\Omega/\partial\mu)_{V,T}$. Comparing this relation with the thermodynamic relation

$$\Omega = U - TS - \mu N \tag{10.30}$$

we recognize in Ω the *grand potential* Ω, which is a function of T, μ and V (for inhomogeneous systems $\mathcal{U}$). Further, we identify

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T}. \tag{10.31}$$

Other thermodynamic quantities are obtained by combining the thermodynamic relation for changes of the grand potential $d\Omega = dU - TdS - SdT - \mu dN - Nd\mu$ with that for the internal energy $dU = đW + TdS + \mu dN$ into the expression $d\Omega = đW - SdT - Nd\mu$. In particular the pressure follows from the expression for the mechanical work $đW = -pdV$,

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}. \tag{10.32}$$

Hence, Ω is obtained by integrating p over the volume (for given value of T and μ),

$$\Omega = -\int_V (\partial\Omega/\partial V)_{T,\mu}\,d\mathbf{r}. \tag{10.33}$$

Evaluating the integral we obtain

$$\Omega = -pV. \tag{10.34}$$

In other words, in a homogeneous gas the pressure is simply an other name for the Grand potential per unit volume (up to a sign),

$$p = -\Omega/V \equiv -\tilde{\Omega}(\mathbf{r}), \tag{10.35}$$

for all $\mathbf{r}\in V$.

To discuss *inhomogeneous* systems we presume the local density approximation to be valid; i.e., we write Ω as the integral over a local grand potential, $\Omega = -\int_V \tilde{\Omega}(\mathbf{r})d\mathbf{r}$, and use the relation

$$p(\mathbf{r}) = -\tilde{\Omega}(\mathbf{r}) \tag{10.36}$$

for the local pressure. We first discuss temperatures well below the degeneracy temperature ($\mu/k_BT \gg 1$ and $z \gg 1$). Using the large-z approximation for $F_{5/2}$ we find

$$p(\mathbf{r}) = \left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{1}{15\pi^2}[\mu-\mathcal{U}(\mathbf{r})]^{5/2}\left[1+\frac{8\pi^2}{15}\left(\frac{k_BT}{\mu-\mathcal{U}(\mathbf{r})}\right)^2+\cdots\right]. \tag{10.37}$$

This expression represents the so-called Fermi pressure of the degenerate gas. In the trap center the expression for the pressure reduces to

$$p_0 = \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{15\pi^2}\mu^{5/2}\left[1+\frac{8\pi^2}{15}\left(\frac{T}{T_F}\right)^2+\cdots\right].$$

To analyze the case of finite temperature it is insightful to multiply and divide $\tilde{\Omega}(\mathbf{r})$ by $F_{3/2}$ since, recalling Eq. (10.8), this shows that the pressure can be expressed in the form

$$p(\mathbf{r}) = \frac{F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]}{F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]}n(\mathbf{r})k_BT. \tag{10.38}$$

Here the prefactor $F_{5/2}/F_{3/2}$ represents the quantum correction to the classical ideal gas law. For $T\to 0$ we can use the large-z approximation and obtain

$$p(\mathbf{r}) = \tfrac{2}{5}[\mu-\mathcal{U}(\mathbf{r})]n(\mathbf{r}). \tag{10.39}$$

Similar to Ω and U, all extensive quantities can be expressed as an integral over their corresponding local density and (10.30) becomes

$$p = -u(\mathbf{r}) + Ts(\mathbf{r}) + \mu n(\mathbf{r}). \tag{10.40}$$

The *entropy density* and *number density* follow from the pressure with

$$s(\mathbf{r}) = (\partial p/\partial T)_{\mathcal{U},\mu} \quad\text{and}\quad n(\mathbf{r}) = (\partial p/\partial \mu)_{\mathcal{U},T}\,. \tag{10.41}$$

Substituting Eq. (10.29) we obtain for the entropy density

$$s(\mathbf{r}) = \tfrac{5}{2}\frac{k_B}{\Lambda^3}F_{5/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}] - \frac{1}{\Lambda^3}F_{3/2}[ze^{-\mathcal{U}(\mathbf{r})/k_BT}]\frac{\mu-\mathcal{U}(\mathbf{r})}{k_BT}. \tag{10.42}$$

11

Weakly interacting bosons at zero temperature

11.1 Introduction

In this chapter we specialize to the case of bosons, in particular to a bosonic fluid of neutral atoms without spin confined in space by an external potential $\mathcal{U}(\mathbf{r})$ at $T = 0$ K. The famous example of such a fluid is liquid ^{4}He. Let us assume that the fluid may be described by the hamiltonian for a *pairwise interacting* many-body system,

$$H = H^{(1)} + H^{(2)} = \sum_i \mathcal{H}_0(\mathbf{p}_i, \mathbf{r}_i) + \tfrac{1}{2} {\sum_{i,j}}' \mathcal{V}(\mathbf{r}_i, \mathbf{r}_j), \tag{11.1}$$

where

$$\mathcal{H}_0(\mathbf{p}, \mathbf{r}) = -\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) \tag{11.2}$$

is the free particle hamiltonian. Let us further assume that the interatomic potential has a *short range* and may be approximated by the expression

$$\mathcal{V}(\mathbf{r}_i, \mathbf{r}_j) = g\,\delta(\mathbf{r}_i - \mathbf{r}_j), \tag{11.3}$$

where $g = \left(4\pi\hbar^2/m\right) a$ and a is called the *s-wave scattering length* (see Section 3.8). Such a potential is called a *contact potential.* It expresses the physical picture that the interatomic forces may be neglected except when the atoms are close to each other; i.e., during collisions. To determine the ground state of the fluid in the Schrödinger picture we have to solve the Schrödinger equation for the many-body hamiltonian H. This is a formidable task and can only be done numerically for a small number of atoms. Therefore, we take a different approach. Realizing that we are dealing with a quantum many-body system of identical particles we turn to the hamiltonian in second quantization,

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\mathcal{H}_0(\mathbf{p}, \mathbf{r})\hat{\psi}(\mathbf{r}) + \tfrac{1}{2}\int d\mathbf{r}d\mathbf{r}'\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\mathcal{V}(\mathbf{r}, \mathbf{r}')\,\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r}). \tag{11.4}$$

Substituting Eqs. (11.2) and (11.3) this becomes

$$\hat{H} = \int d\mathbf{r}\left[-\frac{\hbar^2}{2m}\hat{\psi}^\dagger(\mathbf{r})\nabla^2\hat{\psi}(\mathbf{r}) + \mathcal{U}(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}) + \tfrac{1}{2}g\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r})\hat{\psi}(\mathbf{r})\right]. \tag{11.5}$$

The interaction term $\hat{H}^{(2)}$ can be written in the form

$$\hat{H}^{(2)} = \tfrac{1}{2}g\int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\hat{n}(\mathbf{r})\hat{\psi}(\mathbf{r}). \tag{11.6}$$

Before proceeding, it is important to be aware of three commutation relations,

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(1)}] = \mathcal{H}_0(\mathbf{p}, \mathbf{r})\hat{\psi}(\mathbf{r}), \tag{11.7}$$

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(2)}] = g\,\hat{n}(\mathbf{r})\hat{\psi}(\mathbf{r}), \tag{11.8}$$

$$[\hat{\psi}(\mathbf{r}), \hat{N}] = \hat{\psi}(\mathbf{r}). \tag{11.9}$$

Note the *absence* of the factor $\frac{1}{2}$ on the r.h.s. of Eq. (11.8). Eq. (11.7) was derived in Problem 7.10. The other commutation relations can be derived analogously.

Problem 11.1. Derive the commutation relation

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(2)}] = g\,\hat{n}(\mathbf{r})\hat{\psi}(\mathbf{r}).$$

Note the *absence* of the prefactor $\frac{1}{2}$ on the r.h.s. of this commutation relation.

Problem 11.2. Derive the commutation relation

$$[\hat{\psi}(\mathbf{r}), \hat{N}] = \hat{\psi}(\mathbf{r}).$$

11.2 Gross-Pitaevskii equation

11.2.1 Heisenberg field operators and chemical potential

Having the hamiltonian at our disposal in terms of field operators $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}^\dagger(\mathbf{r})$, we can investigate the effect of the interactions on the N-body ground state $|G_N\rangle$ of the interacting quantum fluid, which is an eigenstate of the hamiltonian $\hat{H}$,

$$\hat{H}\,|G_N\rangle = E_0(N)\,|G_N\rangle\,.$$

The evolution of the system is described by the *Heisenberg equation of motion* for the field operators. Since neither the hamiltonian $\hat{H}$ nor the Schrödinger field operator $\hat{\psi}(\mathbf{r})$ have an explicit time dependence, the Heisenberg equation of motion is of the form (B.80),

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}_H(\mathbf{r}, t) = [\hat{\psi}_H(\mathbf{r}, t), \hat{H}], \tag{11.10}$$

where

$$\hat{\psi}_H(\mathbf{r}, t) = e^{i\hat{H}t/\hbar}\hat{\psi}(\mathbf{r})e^{-i\hat{H}t/\hbar} \tag{11.11}$$

is the Heisenberg field annihilation operator, with boundary condition $\hat{\psi}(\mathbf{r}) = \hat{\psi}_H(\mathbf{r}, 0)$. Since $\hat{\psi}_H(\mathbf{r}, t)$ does not conserve the particle number, its expectation values vanish identically; in particular, $\langle G_N|\hat{\psi}_H(\mathbf{r}, t)|G_N\rangle \equiv 0$. On the other hand, using the relation $\hat{H}\,|G_{N-1}\rangle = E_0(N-1)\,|G_{N-1}\rangle$, we can define a *nonzero* function

$$\psi_N(\mathbf{r}, t) \equiv \langle G_{N-1}|\hat{\psi}_H(\mathbf{r}, t)|G_N\rangle \tag{11.12}$$

as the solution of the differential equation

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi_N(\mathbf{r}, t) &= \langle G_{N-1}|\,\hat{\psi}_H(\mathbf{r}, t)\hat{H}\,|G_N\rangle - \langle G_{N-1}|\,\hat{H}\hat{\psi}_H(\mathbf{r}, t)\,|G_N\rangle \\ &= [E_0(N) - E_0(N-1)]\psi_N(\mathbf{r}, t) \end{aligned} \tag{11.13}$$

subject to the boundary condition $\psi_N(\mathbf{r}) \equiv \psi_N(\mathbf{r}, 0)$. Solving this equation we find

$$\psi_N(\mathbf{r}, t) = \psi_N(\mathbf{r})e^{-i\mu t/\hbar}, \tag{11.14}$$

where $\mu = E_0(N) - E_0(N-1)$ is the *chemical potential* of the system. Apparently, the time dependence of the Heisenberg field operator is governed by the chemical potential of the system,

$$\hat{\psi}_H(\mathbf{r},t) = \hat{\psi}(\mathbf{r})e^{-i\mu t/\hbar}, \tag{11.15}$$

or, in differential form,

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}_H(\mathbf{r},t) = \mu\hat{\psi}(\mathbf{r},t). \tag{11.16}$$

Alternatively, using the commutation relations (11.7) and (11.8) we can write the Heisenberg equation (11.10) in the form

$$i\hbar\frac{\partial}{\partial t}e^{i\hat{H}t/\hbar}\hat{\psi}(\mathbf{r})e^{-i\hat{H}t/\hbar} = e^{i\hat{H}t/\hbar}[\mathcal{H}_0 + g\hat{n}(\mathbf{r})]\hat{\psi}(\mathbf{r})e^{-i\hat{H}t/\hbar}. \tag{11.17}$$

After differentiating with respect to time we can eliminate the evolution operators and obtain

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r}) + [\hat{\psi}(\mathbf{r}),\hat{H}] = [\mathcal{H}_0 + g\hat{n}(\mathbf{r})]\hat{\psi}(\mathbf{r}). \tag{11.18}$$

Since $\hat{\psi}(\mathbf{r})$ is time independent this becomes

$$0 = i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r}) = [\hat{\psi}(\mathbf{r}),\hat{H}] = [\mathcal{H}_0 + g\hat{n}(\mathbf{r})]\hat{\psi}(\mathbf{r}). \tag{11.19}$$

Recalling the commutation relation (11.9) we can equally well write

$$0 = i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r}) = [\hat{\psi}(\mathbf{r}),\hat{H} - \mu\hat{N}] = [\mathcal{H}_0 + g\hat{n}(\mathbf{r}) - \mu]\hat{\psi}(\mathbf{r}). \tag{11.20}$$

Substituting Eq. (11.2) this operator identity takes the form of a nonlinear Schrödinger equation for the operators,

$$\left[-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) + g\,\hat{n}(\mathbf{r})\right]\hat{\psi}(\mathbf{r}) = \mu\hat{\psi}(\mathbf{r}). \tag{11.21}$$

Using Eq. (11.16) we obtain the time-dependent form,

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}_H(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) + g\,\hat{n}(\mathbf{r})\right]\hat{\psi}_H(\mathbf{r},t). \tag{11.22}$$

Equally well, we may start from the point of view that, *a priori*, the value of μ is not known. In this case we may define the field operator

$$\hat{\psi}(\mathbf{r},t) = \hat{\psi}_H(\mathbf{r},t)e^{i(\mu/\hbar)t}. \tag{11.23}$$

and search for the value of μ at which it becomes stationary, *i.e.* $\hat{\psi}(\mathbf{r},t) \to \hat{\psi}(\mathbf{r})$. In this case the equation of motion takes the form

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r},t) = [\hat{\psi}(\mathbf{r},t),\hat{H} - \mu\hat{N}], \tag{11.24}$$

which implies

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r},t)\left|G_N\right\rangle = [E_0(N) - E_0(N-1) - \mu]\hat{\psi}(\mathbf{r},t)\left|G_N\right\rangle. \tag{11.25}$$

Hence, the field operator $\hat{\psi}(\mathbf{r},t)$ is stationary if we choose μ equal to the chemical potential of the system.

11.2.2 Order parameter

Let us presume that within the many-body ground state $|G_N\rangle$ we have N_0 atoms occupying the single particle ground state $\varphi_0(\mathbf{r})$. These atoms are called the condensate atoms. In the occupation number representation a condensate of N_0 atoms is denoted by $|N_0\rangle$. In ideal Bose gases at $T = 0$ all atoms will be in the condensate ($N_0 = N$) but in general the interactions will give rise to depletion ($N_0 < N$). This is called *quantum depletion* and should be distinguished from *thermal depletion*, which is depletion by thermal excitation at non-zero temperatures. In dilute quantum gases the quantum depletion is small and can be calculated with a microscopic theory. In liquid ^{4}He the quantum depletion is severe and only a small fraction of the atoms can be attributed to the condensate. In this case one has to rely on numerical simulation for a small number of atoms or on a phenomenological description because an analytic microscopic theory is beyond reach.

In dilute gases the wavefunction $\varphi_0(\mathbf{r})$ exists but is yet to be determined. In search for $\varphi_0(\mathbf{r})$ we analyze the following off-diagonal matrix element of Eq. (11.21):

$$\langle N_0-1|\left[-\frac{\hbar^2}{2m}\Delta+\mathcal{U}(\mathbf{r})+g\,\hat{n}(\mathbf{r})\right]\hat{\psi}(\mathbf{r})\,|N_0\rangle=\mu\,\langle N_0-1|\,\hat{\psi}(\mathbf{r})\,|N_0\rangle\,, \tag{11.26}$$

On the r.h.s. we have a function of position,

$$\psi_{N_0}(\mathbf{r})\equiv\langle N_0-1|\,\hat{\psi}(\mathbf{r})\,|N_0\rangle\,. \tag{11.27}$$

What is the significance of this function? We recall the definition (7.108) for the field operators. Separating the term with construction operator $\hat{a}_0$ for the single particle ground state $\varphi_0(\mathbf{r})$ from the terms of construction operators $\hat{a}_{s\neq0}$ of the excited states $\varphi_{s\neq0}(\mathbf{r})$, the expression for the field operator $\hat{\psi}(\mathbf{r})$ becomes

$$\hat{\psi}(\mathbf{r})\equiv\varphi_0(\mathbf{r})\hat{a}_0+\sum_{s\neq0}\varphi_s(\mathbf{r})\hat{a}_s. \tag{11.28}$$

Substituting this expression into Eq. (11.27) we find a relation between the function $\psi_{N_0}(\mathbf{r},t)$ and the one-body ground state wavefunction $\varphi_0(\mathbf{r})$,

$$\psi_{N_0}(\mathbf{r})=\langle N_0-1|\,\sqrt{N_0}\varphi_0(\mathbf{r})\,|N_0-1\rangle=\sqrt{N_0}\varphi_0(\mathbf{r}). \tag{11.29}$$

Apparently, the probability amplitude $\varphi_0(\mathbf{r})$ to find a particle at position $\mathbf{r}$ can be expressed as the off-diagonal *average* (11.27) over the many-body states $|N_0\rangle$ and $|N_0-1\rangle$; *i.e.*, we have

$$\hat{\psi}(\mathbf{r})\,|N_0\rangle=\psi_{N_0}(\mathbf{r})\,|N_0-1\rangle\,. \tag{11.30}$$

As the kets for the number states are representation free these are position independent. Therefore, the l.h.s. of Eq. (11.21) evaluates to

$$\left[-\frac{\hbar^2}{2m}\Delta+\mathcal{U}(\mathbf{r})+g\,\langle N_0-1|\,\hat{n}(\mathbf{r})\,|N_0-1\rangle\right]\psi_{N_0}(\mathbf{r})=\mu\,\psi_{N_0}(\mathbf{r}). \tag{11.31}$$

Integrating over the matrix element of the number density operator and using the definition (7.110) of the total number operator $\hat{N}$, we find

$$N_0-1=\int d\mathbf{r}\,\langle N_0-1|\,\hat{n}(\mathbf{r})\,|N_0-1\rangle=\int d\mathbf{r}\,|\psi_{N_0-1}(\mathbf{r})|^2. \tag{11.32}$$

For $N_0 \ggg 1$ the *shape* of $\psi_{N_0}(\mathbf{r})$ can depend only very weakly (and in an infinite homogeneous system not at all) on the exact value of N_0. Hence, we may approximate to within an accuracy $1/N_0$

$$\langle N_0-1|\,\hat{n}(\mathbf{r})\,|N_0-1\rangle\simeq\langle N_0|\,\hat{n}(\mathbf{r})\,|N_0\rangle=|\psi_{N_0}(\mathbf{r})|^2. \tag{11.33}$$

The function $\psi_{N_0}(\mathbf{r})$ is called the *order parameter* or *condensate wavefunction* of the many-body system. It becomes independent of the particle number in the *thermodynamic limit*

$$\Psi_0(\mathbf{r}) \equiv \lim_{N_0\to\infty} \langle N_0 - 1|\, \hat{\psi}(\mathbf{r})\, |N_0\rangle \qquad \text{at constant } N_0/V. \tag{11.34}$$

Here we dropped the subscript N_0. Note that the approximation (11.33) amounts to replacing the construction operators for the condensate by real numbers,

$$\hat{a}_0\, |N_0\rangle = \sqrt{N_0}\, |N_0\rangle \Leftrightarrow \hat{a}_0^\dagger\, |N_0\rangle = \sqrt{N_0}\, |N_0\rangle\, . \tag{11.35}$$

This is known as the *Bogoliubov Ansatz.*

11.2.3 Gross-Pitaevskii equation

Expressing Eq.(11.31) in terms of the order parameter it takes the form of a non-linear Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) + g\, |\Psi_0(\mathbf{r})|^2\right) \Psi_0(\mathbf{r}) = \mu\Psi_0(\mathbf{r}). \tag{11.36}$$

This expression is called the *Gross-Pitaevskii* (GP) equation [28, 58]. Equivalently, in analogy with Eq. (11.15) we can introduce the time-dependent order parameter

$$\Psi_0(\mathbf{r},t) = \Psi_0(\mathbf{r})e^{-i\mu t/\hbar} \tag{11.37}$$

and write the GP equation in its time-dependent form

$$i\hbar\frac{\partial}{\partial t}\Psi_0(\mathbf{r},t) = \left(-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) + g|\Psi_0(\mathbf{r},t)|^2\right) \Psi_0(\mathbf{r},t). \tag{11.38}$$

The interaction term has the effect of modifying the external potential into an effective potential field,

$$\mathcal{U}_{\text{eff}}(\mathbf{r}) = \mathcal{U}(\mathbf{r}) + g|\Psi_0(\mathbf{r})|^2. \tag{11.39}$$

As this field depends on the solution of the GP equation it has to be determined self-consistently. The GP equation is an example of a Hartree mean field equation and the order parameter $\Psi_0(\mathbf{r})$ describes the mean field. The quantity

$$n_0(\mathbf{r}) = |\Psi_0(\mathbf{r})|^2 \tag{11.40}$$

represents the density of the mean field, usually called the *condensate density.* Importantly, the order parameter is not an ordinary wavefunction. Its time evolution is governed by the chemical potential and not by the energy as is the case for ordinary wavefunctions. In this sense the name *condensate wavefunction* is a bit unfortunate. It should certainly not be confused with the many-body wavefunction of the condensate. Even with as little as 10 particles the density of the order parameter is already defined to an accuracy of 1%. Importantly, because the GP equation is non-linear its solutions are in general not orthogonal. This reflects the mean field origin of the order parameter and further underlines the difference with the many-body wavefunction of the condensate.

The simplest example of a solution of the GP equation is obtained for the ground state of a homogeneous quantum fluid. In this case the order parameter follows by setting $\mathcal{U}(\mathbf{r}) = 0$ and $\Delta\Psi_0(\mathbf{r}) = 0$ in Eq. (11.36); the density is constant across the fluid, $|\Psi_0(\mathbf{r})|^2 = n_0$, and the chemical potential is given by

$$\mu = gn_0. \tag{11.41}$$

With the concept of the order parameter we discovered a powerful tool to describe the collective properties of a many-body system *while properly accounting for the quantum correlations between the atoms.* This concept is regarded among the most profound achievements of condensed matter physics.

11.2.4 Example: Gross-Pitaevskii equation for harmonically trapped Bose gas

As an important example we consider the properties of a Bose-Einstein condensate in an isotropic harmonic trap $\mathcal{U}(\mathbf{r}) = \frac{1}{2}m\omega^2 r^2$. In the absence of interactions ($g = 0$) the Gross-Pitaevskii equation reduces to the Schrödinger equation for the harmonic oscillator and the order parameter has the gaussian shape of harmonic-oscillator ground state

$$\Psi_0(\mathbf{r}) = \sqrt{N_0}\varphi_0(\mathbf{r}) = \frac{\sqrt{N_0}}{\pi^{3/4}l_0^{3/2}}e^{-r^2/2l_0^2}, \tag{11.42}$$

where the quantity l_0 is the *harmonic oscillator length*, defined by

$$\tfrac{1}{2}m\omega^2 l_0^2 = \tfrac{1}{2}\hbar\omega \Leftrightarrow l_0 = \sqrt{\hbar/m\omega}. \tag{11.43}$$

The harmonic-oscillator solution fails once the energy of interaction dominates over the kinetic energy, which is the case for (see Problem 11.3)

$$l_0 \ll N_0|a|. \tag{11.44}$$

Problem 11.3. Show that for $l_0 \ll N_0|a|$ the interaction energy dominates over the kinetic energy.

Solution. The kinetic energy is largest for the harmonic-oscillator ground state,

$$\left\langle \left(\hbar^2/2m\right)\Delta\Psi_0(\mathbf{r})\right\rangle \simeq \frac{\hbar^2}{2m}\frac{1}{l_0^2}.$$

The interaction energy in the ground state scales proportionally to the density $\left(N_0/l_0^3\right)$

$$|g\, n_0(\mathbf{r})| \simeq \frac{4\pi\hbar^2}{m}|a|\frac{N_0}{l_0^3}.$$

Hence, the kinetic energy dominates over the interaction energy for

$$l_0 \ll N_0|a|. \qquad \square$$

11.2.4.1 Thomas-Fermi approximation

The Gross-Pitaevskii equation can also be solved analytically for conditions where the interactions are repulsive and dominate over the kinetic energy,

$$N_0 a \gg l_0 \gg a > 0. \tag{11.45}$$

By the additional requirement $l_0 \gg a$ we exclude tightly confining traps in which the binary collisions are affected by the trap confinement. Under the condition (11.45) the kinetic energy term can be neglected and the Gross-Pitaevskii equation reduces to

$$\mu = gn_0(\mathbf{r}) + \mathcal{U}(\mathbf{r}) = gn_0(0). \tag{11.46}$$

This amounts to a local density approximation in which the chemical potential is set to be constant across the inhomogeneous gas. This approximation is known as the *Thomas-Fermi approximation* because Thomas and Fermi used a similar local density approximation to obtain the distribution of a degenerate electron cloud around the nucleus of a many-electron atom [67, 22]. Solving Eq. (11.46) for the density from we obtain the famous *Thomas-Fermi density profile* observed in the very first experiments with Bose-Einstein condensed gases [1, 14],

$$n_0(\mathbf{r}) = \left[\mu - \mathcal{U}(\mathbf{r})\right]/g \quad \text{with } N_0 = \int n_0(\mathbf{r})d\mathbf{r}. \tag{11.47}$$

Note that near the edge of the Thomas-Fermi profile the approximation must break down because the density (and thus the interaction energy) vanishes and the kinetic energy takes over. This results in a softening of the condensate surface over a distance ξ that may be estimated by equating the kinetic and interaction energies, $gn_0 \simeq \hbar^2/2m\xi^2$,

$$\xi = \frac{\hbar}{\sqrt{2mg\,n_0}}.$$

This characteristic length ξ is known as the *healing length.* For condensates with many atoms the presence of the healing layer is of little consequence because only a small fraction of the atoms occupy this region.

Let us calculate the *Thomas-Fermi radius* R_0 of a Bose-Einstein condensate in an isotropic harmonic trap $\mathcal{U}(\mathbf{r}) = \frac{1}{2}m\omega^2 r^2$. As the density is zero at the edge of the condensate we find with Eq. (11.46)

$$\tfrac{1}{2}m\omega^2 R_0^2 = \mu \Leftrightarrow R_0 = \sqrt{2\mu/m\omega^2}. \tag{11.48}$$

It is instructive to compare R_0 with, on the one hand, the *thermal radius* of a harmonically trapped cloud at the critical temperature for BEC,

$$\tfrac{1}{2}m\omega^2 R_{cr}^2 = k_B T_c \Leftrightarrow R_{cr} = \sqrt{2k_B T_c/m\omega^2}, \tag{11.49}$$

and, on the other hand, the harmonic oscillator length $l_0 = \sqrt{\hbar/m\omega}$. One may show that aside from exceptional experimental cases the following inequalities are satisfied:

$$\tfrac{1}{2}\hbar\omega \ll \mu \ll k_B T_c \Leftrightarrow l_0 \ll R_0 \ll R_{cr}. \tag{11.50}$$

This means that down to $T = T_c$ the interactions may be neglected ($g\,n_0(0) \ll k_B T_c$). In other words, above T_c the gas behaves as an ideal gas. However, as soon as the condensate becomes macroscopically occupied, its properties are strongly affected by the interactions ($g\,n_0(0) \gg \hbar\omega$). Apparently, since $R_0 \gg l_0$, the repulsive interactions give rise to a substantial broadening of the ground state wavefunction, from the size of the harmonic oscillator length in the case of the ideal gas to the Thomas-Fermi radius in the case of an interacting boson gas with positive scattering length. Note that the Thomas-Fermi approximation is valid because

$$\frac{\hbar^2}{2mR_0^2} = \frac{\hbar^2\omega^2}{4\mu} \ll \hbar\omega \ll \mu, \tag{11.51}$$

i.e. the kinetic energy contribution is small as compared to the chemical potential.

A relation between R_0 and the total number of atoms $N_0 = \int n_0(\mathbf{r})d\mathbf{r}$ is obtained by integrating over the density distribution (11.47),

$$g\,N_0 = \int \left[\mu - \tfrac{1}{2}m\omega^2 r^2\right] d\mathbf{r} = \mu\frac{4\pi}{3}R_0^3 - \frac{2\pi}{5}m\omega^2 R_0^5. \tag{11.52}$$

With the aid of Eq. (11.48) we can eliminate μ from Eq. (11.52) and obtain

$$R_0 = \left(\frac{15}{4\pi}\frac{g\,N_0}{m\omega^2}\right)^{1/5} = l_0\left(15\frac{a}{l_0}N_0\right)^{1/5} \tag{11.53}$$

where a is the scattering length and l_0 is the harmonic oscillator length. Hence, the Thomas-Fermi radius grows only slowly with increasing N_0, reflecting a compromise between growth of the central density $n_0(0)$ and growth of the condensate volume.

12

Weakly interacting bosons at finite temperature

12.1 Hartree-Fock approximation

In this chapter we weakly-interacting bosons at finite temperature. We consider the hamiltonian (11.4),

$$\hat{H} = \int d\mathbf{r} \left[\hat{H}_1(\mathbf{r}) + \hat{H}_2(\mathbf{r}) \right]. \tag{12.1}$$

This hamiltonian consists of two contributions, the one-body term

$$\hat{H}_1(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) \right] \hat{\psi}^\dagger(\mathbf{r}) \tag{12.2}$$

and the two-body interaction

$$\hat{H}_2(\mathbf{r}) = \tfrac{1}{2} g \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}). \tag{12.3}$$

To manipulate this hamiltonian we decompose the field operators $\hat{\psi}(\mathbf{r})$ with respect to a set of *normalized* single-particle states, $\{\varphi_s(\mathbf{r})\}$. Separating the ground state, $\varphi_0(\mathbf{r})$, from the excited states, $\varphi_{s\neq 0}(\mathbf{r})$, the expression for $\hat{\psi}(\mathbf{r})$ becomes

$$\hat{\psi}(\mathbf{r}) \equiv \varphi_0(\mathbf{r})\hat{a}_0 + \sum_{s\neq 0} \varphi_s(\mathbf{r})\hat{a}_s. \tag{12.4}$$

At this point the states are unknown and it is our task to determine the $\varphi_s(\mathbf{r})$ by applying a variational principle. Unless we impose additional constraints the optimized states will, in general, not be mutually orthogonal. However, for the time being we will simply neglect this. Applying the Hartee-Fock approximation, we assume that the energy of the system can be approximated by the expectation value of $\hat{H}$ for a *single* number state in which the occupations of the single-particle levels are statistically independent. In this approximation we retain only those terms from the hamiltonian that conserve the occupations of the individual states. The hamiltonian becomes (for the two-body part see Problem 12.1)

$$\begin{aligned} \hat{H} = \int d\mathbf{r} \left[\hat{H}_1(\mathbf{r}) + \hat{H}_2(\mathbf{r}) \right] = \int d\mathbf{r} \Bigg[& \sum_s \varphi_s^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + \mathcal{U}(\mathbf{r}) \right) \varphi_s(\mathbf{r})\hat{n}_s \\ & + \frac{1}{2} g \sum_s |\varphi_s(\mathbf{r})|^2 |\varphi_s(\mathbf{r})|^2 \hat{n}_s(\hat{n}_s - 1) + g \sum_{s,t}{}' |\varphi_s(\mathbf{r})|^2 |\varphi_t(\mathbf{r})|^2 \hat{n}_s \hat{n}_t, \Bigg] \end{aligned} \tag{12.5}$$

where the prime indicates the condition $s \neq t$.

It is now straightforward to calculate the energy,

$$E = \langle\langle \hat{H} \rangle\rangle = \mathrm{tr}\, \varrho \hat{H} = \int d\mathbf{r} \left[\sum_s \left[\frac{\hbar^2}{2m} \varphi_s^*(\mathbf{r}) \nabla^2 \varphi_s(\mathbf{r}) + \mathcal{U}(\mathbf{r}) |\varphi_s(\mathbf{r})|^2 \right] \langle\langle \hat{n}_s \rangle\rangle \right.$$
$$\left. + \frac{1}{2} g \sum_s |\varphi_s(\mathbf{r})|^2 |\varphi_s(\mathbf{r})|^2 \langle\langle \hat{n}_s(\hat{n}_s - 1) \rangle\rangle + g \sum_{s,t}{}' |\varphi_s(\mathbf{r})|^2 |\varphi_t(\mathbf{r})|^2 \langle\langle \hat{n}_s \hat{n}_t \rangle\rangle \right]. \tag{12.6}$$

Applying the Bogoliubov Ansatz (11.35) we set $\hat{n}_0 \to N_0 \gg 1$. The thermal occupation of the exited states (according to Bose-Einstein distribution) is given by $\bar{n}_{s \neq 0} = \langle\langle \hat{n}_s \rangle\rangle$. Furthermore, we approximate $N_0(N_0 + 1) \simeq N_0^2$ and define

$$\Psi_0(\mathbf{r}) = \sqrt{N_0} \varphi_0(\mathbf{r}), \;\; n_0(\mathbf{r}) = N_0 |\varphi_0(\mathbf{r})|^2 \;\text{ and }\; n_T(\mathbf{r}) = \sum_{s \neq 0} \bar{n}_s |\varphi_s(\mathbf{r})|^2. \tag{12.7}$$

Using integration by parts,

$$\int d\mathbf{r} \varphi_s^*(\mathbf{r}) \nabla^2 \varphi_s(\mathbf{r}) = - \int d\mathbf{r} |\nabla \varphi_s(\mathbf{r})|^2, \tag{12.8}$$

the total energy takes the compact form

$$E = \int d\mathbf{r} \left[\frac{\hbar^2}{2m} |\nabla \Psi_0(\mathbf{r})|^2 + \frac{\hbar^2}{2m} \sum_{s \neq 0} \bar{n}_s |\nabla \varphi_s(\mathbf{r})|^2 + \mathcal{U}(\mathbf{r}) [n_0(\mathbf{r}) + n_T(\mathbf{r})] \right.$$
$$\left. + \frac{1}{2} g\, n_0(\mathbf{r})^2 + 2g\, n_0(\mathbf{r})\, n_T(\mathbf{r}) + g\, n_T\,(\mathbf{r})^2 \right]. \tag{12.9}$$

At this point the actual wavefunctions (i.e., the set $\{\varphi_s(\mathbf{r})\}$) are still unknown. So, what remains to be done is to determine the optimal set of wavefunctions consistent with the above set of equations. For this purpose we consider Eq. (12.6) as a functional of the set $\{\varphi_s(\mathbf{r})\}$, $E = E[\varphi_{0,}, \varphi_{1,} \cdots]$, and construct the lagrangians $L_s[\varphi_{0,}, \varphi_{1,} \cdots; \lambda_0, \lambda_1, \cdots]$ for this functional under the constraint that the wavefunctions be normalized, $\langle \varphi_s | \varphi_s \rangle = 1$,

$$L_s[\varphi_{0,}, \varphi_{1,} \cdots; \lambda_0, \lambda_1, \cdots] = E[\varphi_{0,}, \varphi_{1,} \cdots] + \lambda_s \bar{n}_s (\langle \varphi_s | \varphi_s \rangle - 1). \tag{12.10}$$

Each of these lagrangians is minimized under variation of the corresponding wavefunction,

$$\frac{\delta}{\delta \varphi_s^*} L_s[\varphi_{0,}, \varphi_{1,} \cdots; \lambda_0, \lambda_1, \cdots] = 0. \tag{12.11}$$

As is conveniently seen from Eqs. (12.6) and (12.9), this leads to a set of coupled differential equations. For the ground state we find

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \mathcal{U}(\mathbf{r}) + g n_0(\mathbf{r}) + 2g\, n_T(\mathbf{r}) \right] \Psi_0(\mathbf{r}) = -\lambda_0 \Psi_0(\mathbf{r}), \tag{12.12}$$

and for the single-particle excited states this becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \mathcal{U}(\mathbf{r}) + 2g\, n(\mathbf{r}) \right] \varphi_s(\mathbf{r}) = -\lambda_s \varphi_s(\mathbf{r}), \tag{12.13}$$

where $n(\mathbf{r}) = n_0(\mathbf{r}) + n_T(\mathbf{r})$. Note that the interaction term for particles in the same state (here the condensate) differes by a factor 2 from when the are particles in different states. This can be traced back to the presence of the exchange terms in the latter case (see also Problem 12.1).

The grand potential of the system is given by

$$\Omega = -k_BT \ln \mathcal{Z}_{gr},$$

where

$$\mathcal{Z}_{gr} = \operatorname{tr} e^{-(\hat{H}-\mu\hat{N})/k_BT} = e^{-\langle\!\langle(\hat{H}-\mu\hat{N})\rangle\!\rangle/k_BT} \tag{12.14}$$

is the grand-canonical partition function. Let us suppose that $\hat{H}_0$ is the true hamiltonian of the system and $\hat{H}$ is a good opproximation of it en

$$\begin{aligned}\Omega &= -k_BT \ln \operatorname{tr} e^{-(\hat{H}-\mu\hat{N})/k_BT} \\ &= -k_BT \ln \operatorname{tr} e^{-(\hat{H}_0-\mu\hat{N})/k_BT} e^{-(\hat{H}-\hat{H}_0)/k_BT} \\ &= \Omega_0 + \langle\!\langle(\hat{H}-\hat{H}_0)\rangle\!\rangle.\end{aligned}$$

Turning to the occupation number representation of ...

$$\mathcal{Z}_{gr} = \sum_{\gamma} \langle \tilde{n}_\gamma | \, e^{-(\hat{H}-\mu\hat{N})/k_BT} \, | \tilde{n}_\gamma \rangle . \tag{12.15}$$

To calculate $\mathcal{Z}_{gr}$ we choose the representation of $\hat{H}$, where (in the absence of interactions) the hamiltonian is given by Eq. (7.105). Thus we have

$$\hat{H} - \mu\hat{N} = \sum_s \hat{n}_s(\varepsilon_s - \mu) \tag{12.16}$$

$$e^{-(\hat{H}-\mu\hat{N})/k_BT} = \prod_s e^{-\hat{n}_s(\varepsilon_s-\mu)/k_BT}.$$

$$\mathcal{Z}_{gr} = \sum_{n_1,n_2,\cdots} \langle n_1, \cdots, n_s, \cdots | \prod_s e^{-\hat{n}_s(\varepsilon_s-\mu)/k_BT} | n_1, \cdots, n_s, \cdots \rangle, \tag{12.17}$$

written as

$$\mathcal{Z}_{gr} = \sum_{n_1,n_2,\cdots} e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_BT}. \tag{12.18}$$

we note that we can sequentially factor-out the contributions of all single-particle states,

$$\mathcal{Z}_{gr} = \prod_s \sum_{n_s} e^{-n_s(\varepsilon_s-\mu)/k_BT}. \tag{12.19}$$

This is only possible since, in the grand Hilbert space, we are dealing with unrestricted sums. Introducing the quantity $r_s = e^{-(\varepsilon_s-\mu)/k_BT}$, Eq. (12.19) can be further simplified to the form

$$\mathcal{Z}_{gr} = \prod_s \sum_{n_s} r_s^{n_s}. \tag{12.20}$$

For identical bosons there is no restriction on the occupation n_s of a given state s and we recognize in r_s the ratio of a geometrical series. After summation we obtain,

$$\mathcal{Z}_{gr} = \prod_s \frac{1}{1-r_s}. \tag{12.21}$$

and the expression for the grand potential becomes

$$\Omega = -k_BT \ln \mathcal{Z}_{gr} = k_BT \sum_s \ln(1-r_s).$$

To evaluate the energy of the many-body system at finite temperature, we ask for the trace $E = \mathrm{tr}\hat{\varrho}\hat{H}$, where $\hat{\varrho}$ is the statistical operator.

$$E = \langle\langle \hat{H} \rangle\rangle = \mathrm{tr}\,\varrho\hat{H} = \mathcal{Z}_{gr}^{-1} \sum_{\gamma} \langle \tilde{n}_\gamma |\, e^{-(\hat{H}-\mu\hat{N})/k_BT} \hat{H}\, | \tilde{n}_\gamma \rangle$$

is the grand-canonical partition function.

$$E = \langle\langle \hat{H} \rangle\rangle = \mathrm{tr}\,\varrho\hat{H} = \mathcal{Z}_{gr}^{-1} \sum_{\gamma} \langle \tilde{n}_\gamma |\, e^{-(\hat{H}-\mu\hat{N})/k_BT} \hat{H}(\mathbf{r})\, | \tilde{n}_\gamma \rangle$$

$$E = \mathcal{Z}_{gr}^{-1} \sum_{n_1,n_2,\cdots} \int d\mathbf{r}\, \langle n_1, \cdots, n_s, \cdots |\, \prod_s e^{-\hat{n}_s(\varepsilon_s-\mu)/k_BT} \hat{H}(\mathbf{r})\, | n_1, \cdots, n_s, \cdots \rangle\,, \tag{12.22}$$

Problem 12.1. Derive the two-body contribution to Eq. (12.5)

Solution. The two-body hamiltonian can be written in the form

$$\hat{H}_2(\mathbf{r}) = \tfrac{1}{2} g \sum_{q,r,s,t} \varphi_q^\dagger(\mathbf{r})\varphi_r^\dagger(\mathbf{r})\varphi_s(\mathbf{r})\varphi_t(\mathbf{r})\hat{a}_q^\dagger\hat{a}_r^\dagger\hat{a}_s\hat{a}_t.$$

In the operator $\hat{a}_q^\dagger\hat{a}_r^\dagger\hat{a}_s\hat{a}_t$ we distinguish three different ways to obtain number operators by pairing creation operators with annihilation operators into a number operators:

$$\begin{aligned} &\hat{a}_q^\dagger\hat{a}_q^\dagger\hat{a}_q\hat{a}_q = \hat{a}_q^\dagger\hat{n}_q\hat{a}_q = \hat{n}_q(\hat{n}_q-1) && (q=r=s=t) \\ &\hat{a}_q^\dagger\hat{a}_r^\dagger\hat{a}_r\hat{a}_q = \hat{n}_q\hat{n}_r && (r=s\neq q=t) \\ &\hat{a}_q^\dagger\hat{a}_r^\dagger\hat{a}_q\hat{a}_r = \hat{n}_q\hat{n}_r && (r=t\neq q=s) \end{aligned}$$

Substituting these options into the hamiltonian results in the desired expression (12.5).

is statisticaalyunder equilibrium conditions the average occupation of the single-particle states are statistically independent and given by

$$\bar{n}_s = \langle \hat{a}_s^\dagger \hat{a}_s \rangle.$$

Furthermore, we only retain the terms that conserve the particle number

$$\langle \hat{a}_q^\dagger \hat{a}_r \rangle = \bar{n}_q \delta_{qr}$$

asd$[\hat{n}_q, \hat{a}_s] = -\hat{a}_s\delta_{qs}$

$$\langle \hat{a}_i^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_j \rangle = \langle \hat{a}_i^\dagger\hat{n}_q\hat{a}_s\delta_{qr} \rangle =$$

$=$

13

Weakly interacting Bose gas - elementary excitations

13.1 Amplitude-phase decomposition of the order parameter

To investigate the dynamical properties of a condensate it has to be excited in some way. So let us suppose that the distribution of the condensate density $n_0(\mathbf{r},t) = |\Psi(\mathbf{r},t)|^2$ has somehow been driven out of its stationary shape and ask for the time dependence of the deformation,

$$\frac{\partial}{\partial t}n_0(\mathbf{r},t) = \Psi^*(\mathbf{r},t)\frac{\partial}{\partial t}\Psi(\mathbf{r},t) + \Psi(\mathbf{r},t)\frac{\partial}{\partial t}\Psi^*(\mathbf{r},t). \tag{13.1}$$

To relate this expression to the hamiltonian we use the time-dependent GP equation and its complex conjugate,

$$\Psi^*\frac{\partial}{\partial t}\Psi = -\frac{i}{\hbar}\Psi^*\left(-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) + g\,n_0(\mathbf{r},t)\right)\Psi \tag{13.2a}$$

$$\Psi\frac{\partial}{\partial t}\Psi^* = +\frac{i}{\hbar}\Psi\left(-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) + g\,n_0(\mathbf{r},t)\right)\Psi^*. \tag{13.2b}$$

By *adding* these conjugates we obtain the *real part* of $\Psi^*\partial_t\Psi$,

$$\frac{\partial}{\partial t}n_0(\mathbf{r},t) = \frac{i\hbar}{2m}\left(\Psi^*\Delta\Psi - \Psi\Delta\Psi^*\right) = \frac{i\hbar}{2m}\boldsymbol{\nabla}\cdot\left(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*\right). \tag{13.3}$$

Interpreting the quantity

$$\mathbf{j}(\mathbf{r},t) = -\frac{i\hbar}{2m}\left(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*\right). \tag{13.4}$$

as the neutral current density we obtain the *continuity equation*

$$\frac{\partial}{\partial t}n_0(\mathbf{r},t) + \boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r},t) = 0. \tag{13.5}$$

This equation expresses the conservation of normalization and can be regarded as the quantum mechanical counterpart of the continuity equation of classical fluid dynamics, which expresses the conservation of mass.

To analyze deviations from the stationary state we write the order parameter in a form separating the fluctuations of the amplitude from those of the phase,

$$\Psi(\mathbf{r},t) = |\Psi(\mathbf{r},t)|e^{i\phi(\mathbf{r},t)}, \tag{13.6}$$

where the amplitude is given by

$$|\Psi(\mathbf{r},t)| = \sqrt{n_0(\mathbf{r},t)} \tag{13.7}$$

and the overall phase $\phi(\mathbf{r},t)$ is a real quantity defined as

$$\phi(\mathbf{r},t) \equiv -\mu t/\hbar + \Phi(\mathbf{r},t). \tag{13.8}$$

Here the phase $\Phi(\mathbf{r},t)$ is called the *fluctuating phase* and represents the *deviation* from the dynamical phase evolution $(-\mu t/\hbar)$ of the stationary state $\Psi_0(\mathbf{r})$ - see Eq. (11.37). Substituting the order parameter (13.6) into the current density (13.4) we relate current fluctuations to those of the density and phase. Since $|\Psi(\mathbf{r},t)|$ is real, the terms depending on $\nabla|\Psi|$ cancel when calculating $\mathbf{j}(\mathbf{r},t)$. Furthermore, since μ is constant across the order parameter we have

$$\boldsymbol{\nabla}\phi = \boldsymbol{\nabla}\Phi \tag{13.9}$$

and the terms depending on $\boldsymbol{\nabla}\mu$ vanish. Thus only the terms depending on $\boldsymbol{\nabla}\Phi$ survive and we obtain

$$\mathbf{j}(\mathbf{r},t) = -\frac{i\hbar}{2m}|\Psi|^2(2i\boldsymbol{\nabla}\Phi) = \frac{\hbar}{m}n_0(\mathbf{r},t)\boldsymbol{\nabla}\Phi(\mathbf{r},t). \tag{13.10}$$

This expression shows that the current density $\mathbf{j}(\mathbf{r},t)$ depends only on the number density $n_0(\mathbf{r},t)$ and the *gradient* of the fluctuating phase, $\nabla\Phi(\mathbf{r},t)$. Since the local current density in a fluid, $\mathbf{j}$, is related to the local flow velocity, $\mathbf{v}$, through the flux relation $\mathbf{j} = n\mathbf{v}$, the flow velocity in the condensate follows from the current density (13.10) and is given by

$$\mathbf{v} = \frac{\hbar}{m}\boldsymbol{\nabla}\Phi. \tag{13.11}$$

With this expression we have obtained a major result. Deviations from stationary shape $\Psi_0(\mathbf{r})$ not only affect the density of the order parameter but also give rise to gradients in its phase, which manifest themselves as currents in the quantum fluid. The form (13.11) demonstrates that the phase $\Phi(\mathbf{r},t)$ acts as a potential for the velocity field. Moreover, as the rotation of any gradient is zero (outside singularities), the velocity field is *rotation free*,

$$\boldsymbol{\nabla}\times\mathbf{v} = 0. \tag{13.12}$$

This means that (outside singularities) the fluid flows without circulation, which is called *irrotational* flow. Irrotational flow is the *pure potential flow* on which the classical hydrodynamics of *inviscid fluids* (i.e., fluids without viscosity) is based. We return to circulation in the presence of singularities when discussing vortices in Section 13.7.2.

To further explore the dynamical properties of a condensate we now *subtract* the equations (13.2) and obtain on the l.h.s. (twice) the *imaginary part* of $\Psi^*\partial_t\Psi$ by substituting the order parameter (13.6)

$$\Psi^*(\mathbf{r},t)\frac{\partial}{\partial t}\Psi(\mathbf{r},t) - \Psi(\mathbf{r},t)\frac{\partial}{\partial t}\Psi^*(\mathbf{r},t) = 2i|\Psi|^2\frac{\partial\phi}{\partial t} \tag{13.13}$$

Note that the terms depending on $\partial_t|\Psi|$ canceled because $|\Psi(\mathbf{r},t)|$ is real, so only the terms depending on $\partial_t\phi$ survive. Here $\phi(\mathbf{r},t)$ is the overall phase defined above. Subtracting also the r.h.s. we obtain

$$2i|\Psi|^2\frac{\partial\phi}{\partial t} = -\frac{i}{\hbar}\left[-\frac{\hbar^2}{2m}\left(\Psi^*\Delta\Psi + \Psi\Delta\Psi^*\right) + 2\mathcal{U}(\mathbf{r})|\Psi|^2 + 2g|\Psi|^4\right]. \tag{13.14}$$

Dividing both sides by $-2i|\Psi|^2/\hbar$ and evaluating the laplacians we find the following expression for the time dependence of the phase of the order parameter,

$$-\hbar\frac{\partial\phi}{\partial t} = \frac{\hbar^2}{2m}(\boldsymbol{\nabla}\phi)^2 + \mathcal{U}(\mathbf{r}) + g|\Psi|^2 - \frac{\hbar^2}{2m}\frac{1}{|\Psi|}\Delta|\Psi|. \tag{13.15}$$

Using Eqs. (13.11) and (13.9) we arrive at

$$m\frac{\partial \mathbf{v}}{\partial t} + \boldsymbol{\nabla}\left(\tfrac{1}{2}mv^2 + \mathcal{U}(\mathbf{r}) + gn_0 - \frac{\hbar^2}{2m}\frac{1}{|\Psi|}\Delta|\Psi|\right) = 0. \tag{13.16}$$

Importantly, as the equation of motion (13.15) and the continuity equation (13.5) correspond to the real and imaginary parts of the time-dependent GP equation, they constitute a set of coupled equations which are completely equivalent to Eqs. (13.2).

13.2 Fluctuations of the order parameter about the stationary value

At this point we have established the equations for the dynamical evolution of the density and phase of the order parameter and proceed to solve these equations. First we write the order parameter in the form

$$\Psi(\mathbf{r},t) = [\Psi_0(\mathbf{r}) + \delta\Psi(\mathbf{r},t)]e^{-i\mu t/\hbar}, \tag{13.17}$$

where

$$\Psi_0(\mathbf{r}) = \sqrt{n_0(\mathbf{r})} \tag{13.18}$$

is the stationary solution, $n_0(\mathbf{r})$ being the density distribution of the condensate at rest. The quantity $\delta\Psi(\mathbf{r},t)$ represents a deviation from the stationary shape and can be expressed in the form

$$\delta\Psi(\mathbf{r},t) = |\Psi(\mathbf{r},t)|e^{i\Phi(\mathbf{r},t)} - \Psi_0(\mathbf{r}). \tag{13.19}$$

Here $\Phi(\mathbf{r},t)$ is the deviation from the *dynamical phase* of the stationary state as introduced in Section 13.1. Substituting Eq. (13.17) into the time-dependent GP equation and neglecting the terms which depend nonlinearly on $\delta\Psi$ we obtain the *linearized* GP equation for the time dependence of *small* fluctuations of the order parameter Ψ about its stationary value (see Problem 13.1),

$$i\hbar\frac{\partial}{\partial t}\delta\Psi = -\frac{\hbar^2}{2m}\Delta\delta\Psi + gn_0(\mathbf{r})\left[\delta\Psi^* + 2\delta\Psi\right] - \mu\delta\Psi. \tag{13.20}$$

The above equation enables us to determine the *dispersion relation* for the *elementary excitations* of the condensate; i.e., the relation between the frequency and wavevector of the normal modes of oscillation of the condensate. We demonstrate this for the homogeneous case, in which the stationary solution of the order parameter reduces to a constant, $\Psi_0(\mathbf{r}) \to \Psi_0 = \sqrt{n_0}$, and the chemical potential is given by $\mu = gn_0$ (see Section 11.2.3). In this case Eq. (13.20) becomes

$$i\hbar\frac{\partial}{\partial t}\delta\Psi = -\frac{\hbar^2}{2m}\Delta\delta\Psi + gn_0[\delta\Psi + \delta\Psi^*]. \tag{13.21}$$

As this is a wave equation for a system with translational symmetry the normal modes can be written in the form

$$\delta\Psi(\mathbf{r},t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - B^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}. \tag{13.22}$$

To determine the relation between ω and k we substitute the solution (13.22) into the linearized GP equation (13.21),

$$\begin{aligned}\hbar\omega Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \hbar\omega B^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = [(\hbar^2k^2/2m + gn_0)A - gn_0B]e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} +& \\ + [-(\hbar^2k^2/2m + gn_0)B^* + gn_0A^*]e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}.&\end{aligned} \tag{13.23}$$

Equating the terms with the same phase evolution from both sides of the equation we find two conditions that should be simultaneously satisfied,

$$\hbar\omega A = (\hbar^2k^2/2m + gn_0)A - gn_0B \tag{13.24a}$$

$$\hbar\omega B = -(\hbar^2k^2/2m + gn_0)B + gn_0A. \tag{13.24b}$$

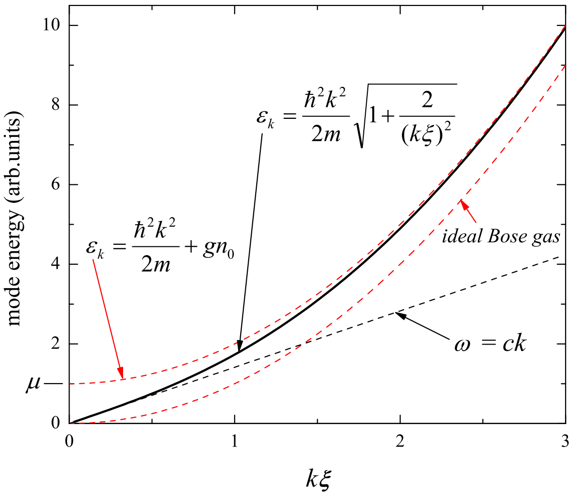

Figure 13.1: Bogoliubov excitation spectrum. For $k\xi \ll 1$ the excitations are hydrodynamic (sound); for $k\xi \gg 1$ the excitations are particle like.

Writing the set of equations in the form of an eigenvalue equation,

$$\begin{pmatrix} \hbar^2k^2/2m + gn_0 & -gn_0 \\ gn_0 & -(\hbar^2k^2/2m + gn_0) \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = \hbar\omega \begin{pmatrix} A \\ B \end{pmatrix}, \tag{13.25}$$

the eigenvalues are obtained by solving the characteristic equation

$$\begin{vmatrix} \hbar^2k^2/2m + gn_0 - \hbar\omega & -gn_0 \\ gn_0 & -(\hbar^2k^2/2m + gn_0 + \hbar\omega) \end{vmatrix} = 0. \tag{13.26}$$

This leads to two solutions, differing only in the sign. Retaining only the solution of positive energy we find

$$\varepsilon_k = \hbar\omega_k = \sqrt{\left(\hbar^2k^2/2m\right)^2 + 2gn_0\left(\hbar^2k^2/2m\right)} = \frac{\hbar^2k^2}{2m}\sqrt{1 + 2/\left(k\xi\right)^2}. \tag{13.27}$$

This is the famous *Bogoliubov excitation spectrum* [8]. As illustrated in Fig. 13.1 this spectrum has the following limiting behavior:

$$\varepsilon_k \simeq \begin{cases} \sqrt{gn_0/m}\,\hbar k & \text{for } k\xi \ll 1 \\ \hbar^2k^2/2m + gn_0 & \text{for } k\xi \gg 1. \end{cases} \tag{13.28}$$

Apparently, for large values of k the excitations show *quadratic* dispersion, whereas for small k the dispersion is *linear.*

As wave-like excitations of the density represent sound, the low-lying excitations of the bosonic ground state are sound waves, with

$$c = \sqrt{gn_0/m} = \sqrt{\tfrac{1}{2}}\frac{\hbar}{m\xi} \tag{13.29}$$

being the *speed of sound.* In terms of the speed of sound the crossover point is given by

$$k\xi = 1 \Leftrightarrow \hbar^2k^2/2m = mc^2. \tag{13.30}$$

Problem 13.1. Derive the linearized GP equation for the time dependence of a small fluctuation of the order parameter Ψ about its stationary shape,

$$i\hbar\partial_t\delta\Psi = -(\hbar^2/2m)\Delta\delta\Psi + gn_0(\mathbf{r})\left[\delta\Psi^* + 2\delta\Psi\right] - \mu\delta\Psi,$$

where $\delta\Psi(\mathbf{r},t)$ represents the fluctuation and $n_0(\mathbf{r})$ the stationary shape of a condensate of chemical potential μ.

Solution. Substituting the dynamically fluctuating order parameter (13.17) into the time-dependent GP equation (11.38) we obtain on the one left-hand side

$$i\hbar\partial_t\Psi = \mu\Psi_0 e^{-i\mu t/\hbar} + \mu\delta\Psi e^{-i\mu t/\hbar} + i\hbar\partial_t\delta\Psi e^{-i\mu t/\hbar}$$

and, noting that

$$|\Psi|^2\Psi = |\Psi_0|^2\Psi_0 + 2|\Psi_0|^2\delta\Psi + \Psi_0^2\delta\Psi^* + \Psi_0^*\delta^2\Psi + 2\Psi_0\delta\Psi\delta\Psi^* + \delta^2\Psi\delta\Psi^*$$

and neglecting the three nonlinear terms, we obtain on the right-hind side of the GP equation

$$\begin{aligned}-(\hbar^2/2m)\Delta\Psi + g|\Psi|^2\Psi = &-(\hbar^2/2m)\left(\Delta\Psi_0 + \delta\Psi\right)e^{-i\mu t/\hbar}\\ &+ g(|\Psi_0|^2\Psi_0 + 2|\Psi_0|^2\delta\Psi + \Psi_0^2\delta\Psi^*)e^{-i\mu t/\hbar}.\end{aligned}$$

Since $-(\hbar^2/2m)\Delta\Psi_0 + gn_0\Psi_0 = \mu\Psi_0$ and the phase of Ψ_0 may be chosen to be *real* we obtain the linearized expression. ☐

13.3 The order parameter in the limit $\omega, k \to 0$

Let us now focus on the elementary excitations of lowest energy; i.e., those with $\omega, k \to 0$. As Eq. (13.24a) represents a relation between the A and B coefficients we find for $\omega, k \to 0$,

$$B = \frac{\hbar^2k^2/2m + gn_0 - \hbar\omega}{gn_0}A \underset{\omega,k\to 0}{\simeq} A. \tag{13.31}$$

Substituting this result into Eq. (13.22) we obtain for the fluctuation

$$\delta\Psi(\mathbf{r},t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - A^*e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \text{ for } \omega, k \to 0. \tag{13.32}$$

Separating the coefficient A into its modulus and phase, $A = \sqrt{n_0}A_0e^{-i\phi}$, the fluctuation is found to be purely imaginary,

$$\delta\Psi(\mathbf{r},t) = i\sqrt{n_0}\,2A_0\sin(\mathbf{k}\cdot\mathbf{r} - \omega t - \phi). \tag{13.33}$$

Hence, we can write the order parameter in the form

$$\Psi(\mathbf{r},t) = \sqrt{n_0}(1 + i\Phi), \tag{13.34}$$

where

$$\Phi(\mathbf{r},t) \equiv 2A_0\sin(\mathbf{k}\cdot\mathbf{r} - \omega t - \phi) \tag{13.35}$$

is a dimensionless quantity. In view of Eq. (13.34), for $A_0 \ll 1$ this quantity can be interpreted as the phase of the order parameter

$$\Psi(\mathbf{r},t) \simeq \Psi_0e^{i\Phi(\mathbf{r},t)}. \tag{13.36}$$

Thus we found that the low-frequency elementary excitations manifest themselves as fluctuations of the phase whereas the effect on the amplitude (i.e., the density) may be neglected.

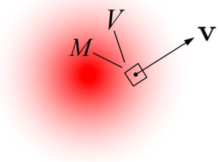

Figure 13.2: Fluid element of fixed volume V and mass $M = Mn$ moving at velocity $\mathbf{v}$ as part of an inhomogeneous fluid confined by an external potential.

13.4 Relation with classical hydrodynamics

At this point it is important to recall the basics of *inviscid flow* from classical hydrodynamics. For this purpose we consider a small volume element V, containing N atoms of mass m in an inhomogeneous fluid confined by an external potential $\mathcal{U}(\mathbf{r})$. The configuration is illustrated in Fig. 13.2. The number density of the fluid at position $\mathbf{r}$ and time t is given by $n = n(\mathbf{r}, t)$ and its flow velocity by $\mathbf{v}(\mathbf{r}, t)$. The conservation of mass when the fluid flows into and out of the (fixed-size) volume element V is expressed by the *continuity equation*

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) + \boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}, t) = 0 \tag{13.37}$$

as follows simply with the Gauss divergence theorem. In the Section 13.1 we found that the continuity equation is satisfied by the order parameter.

Also the linear momentum of the fluid inside the volume element V is a conserved quantity. As $m\mathbf{v}$ is the momentum of the individual atoms within V the total momentum is $Nm\dot{\mathbf{v}}$. This momentum is conserved if the net force on the fluid element is zero,

$$Nm\dot{\mathbf{v}} = \mathbf{F} - \boldsymbol{\nabla} p V. \tag{13.38}$$

Here $Nm\dot{\mathbf{v}}$ is the inertial force of the mass contained within V. This quantity is balanced by sum of the external force $\mathbf{F}$ and the gradient force $-\boldsymbol{\nabla} p V$, where $p = p(\mathbf{r}, t)$ is the local pressure. In the microscopic picture the total force is given by the sum of N equal forces, $\mathbf{F} = -N\boldsymbol{\nabla}\mathcal{U}$. Note that in the absence of flow Eq. (13.38) represents hydrostatic equilibrium between the external force and the pressure gradient. The quantity

$$\dot{\mathbf{v}}(\mathbf{r}, t) = \frac{d}{dt}\mathbf{v}(\mathbf{r}, t) = \frac{\partial \mathbf{v}}{\partial x} v_x + \frac{\partial \mathbf{v}}{\partial y} v_y + \frac{\partial \mathbf{v}}{\partial z} v_z + \frac{\partial \mathbf{v}}{\partial t} = (\mathbf{v} \cdot \boldsymbol{\nabla})\,\mathbf{v} + \frac{\partial \mathbf{v}}{\partial t} \tag{13.39}$$

is the total derivative with respect to time, which represents the rate at which the velocity changes in the coordinate system moving along with the fluid. Substituting this expression into Eq. (13.38) and dividing by N we obtain the *Euler equation* for inviscid flow

$$m\frac{\partial \mathbf{v}}{\partial t} = -m\,(\mathbf{v} \cdot \boldsymbol{\nabla})\,\mathbf{v} - \boldsymbol{\nabla}\mathcal{U} - \frac{1}{n}\boldsymbol{\nabla} p. \tag{13.40}$$

Imposing the condition that the flow be irrotational we have $2\,(\mathbf{v} \cdot \boldsymbol{\nabla})\,\mathbf{v} = \boldsymbol{\nabla} v^2$ as follows with Eq. (E.10) and the Euler equation takes the form

$$m\frac{\partial \mathbf{v}}{\partial t} + \boldsymbol{\nabla}\left(\tfrac{1}{2} m v^2 + \mathcal{U}(\mathbf{r})\right) + \frac{1}{n}\boldsymbol{\nabla} p = 0. \tag{13.41}$$

Comparing Eq. (13.41) with (13.16) we notice that the flow field of the condensate resembles that of irrotational inviscid flow of classical hydrodynamics but there is a quantum correction

$$\frac{1}{n}\boldsymbol{\nabla}p \to \boldsymbol{\nabla}\left(gn_0 - \frac{\hbar^2}{2m}\frac{1}{|\Psi|}\Delta|\Psi|\right). \tag{13.42}$$

Indeed, recalling Eq. (8.88) we have $\boldsymbol{\nabla}p = n\boldsymbol{\nabla}\mu$. Thus, integrating over the elementary volume, $\int_V \boldsymbol{\nabla}p\cdot d\mathbf{r} = \int dp = p$, we find for the pressure

$$p = \int_V gn_0\boldsymbol{\nabla}n_0\cdot d\mathbf{r} + p_{\mathrm{QM}} = \tfrac{1}{2}gn_0^2 + p_{\mathrm{QM}}. \tag{13.43}$$

Here, the first term,

$$\int_V gn_0\boldsymbol{\nabla}n_0\cdot d\mathbf{r} = \int gn_0dn_0 = \tfrac{1}{2}gn_0^2, \tag{13.44}$$

can be written as an integral over the *bulk modulus* of the fluid

$$\int gn_0dn_0 = \int gK(p)dp.$$

The bulk modulus, $K(p) = n_0\,(\partial n_0/\partial p)$, is the inverse of the *compressibility*, well-known from classical hydrodynamics. The second term

$$p_{\mathrm{QM}} = -\int_V n_0\boldsymbol{\nabla}\left(\frac{\hbar^2}{2m}\frac{1}{|\Psi|}\Delta|\Psi|\right)\cdot d\mathbf{r} \tag{13.45}$$

is called the quantum pressure and has no classical analogue. It accounts for (non-hydrodynamic) phenomena involving changes in the order parameter over small distances as they occur in the core of a vortex and in elementary excitations at larger values of k.

13.5 Bogoliubov spectrum from the hydrodynamic formalism

At the end of the previous section we established that the equations of motion for the amplitude and phase of the order parameter show a strong similarity with those of the classical hydrodynamics of an irrotational fluid. We now proceed and search for the limitations on this analogy. In particular we shall analyze how the presence of the quantum pressure affects the dispersion curve of the elementary excitations. In classical hydrodynamics the time evolution of the density distribution of a fluid, $n(\mathbf{r},t)$, is related to that of its velocity field $v(\mathbf{r},t)$. To obtain the excitation spectrum we consider a linear deviation from the stationary values (n_0 and $\mathbf{v}_0$) of the fields,

$$n = n_0 + \delta n \quad \text{and} \quad \mathbf{v} = \mathbf{v}_0 + \delta\mathbf{v}. \tag{13.46}$$

For a condensate at rest ($\mathbf{v}_0 = 0$) the second equation simplifies to

$$\mathbf{v} = \delta\mathbf{v}. \tag{13.47}$$

To include the quantum pressure we use Eq. (13.42) and write the Euler equation in the form

$$m\frac{\partial}{\partial t}\mathbf{v} + \boldsymbol{\nabla}\left(\tfrac{1}{2}mv^2 + \mathcal{U}(\mathbf{r}) + gn - \frac{\hbar^2}{2m}\frac{1}{|\Psi|}\Delta|\Psi|\right) = 0. \tag{13.48}$$

To leading order in δn the contribution of the quantum pressure becomes

$$-\frac{\hbar^2}{2m}\frac{1}{|\Psi|}\Delta|\Psi| = \frac{\hbar^2}{8m}\frac{1}{n^2}\left(\nabla n\right)^2 - \frac{\hbar^2}{4m}\frac{1}{n}\nabla^2 n \simeq -\frac{\hbar^2}{4m}\frac{1}{n}\nabla^2\delta n, \tag{13.49}$$

where we used the relation $|\Psi| = \sqrt{n}$. Expressing all terms of the Euler equation in this way we obtain (after division by m and multiplication by n_0) to leading order in δn and $\delta\mathbf{v}$

$$\frac{\partial}{\partial t} n_0 \delta\mathbf{v} + \boldsymbol{\nabla}\left(\frac{g n_0}{m}\delta n - \frac{\hbar^2}{4m^2}\boldsymbol{\nabla}^2 \delta n\right) = 0. \tag{13.50}$$

Similarly, to leading order in δn and $\delta\mathbf{v}$ the continuity equation becomes

$$\frac{\partial}{\partial t}\delta n + \boldsymbol{\nabla}\cdot n_0\,\delta\mathbf{v} = 0. \tag{13.51}$$

Since δn and $\delta\mathbf{v}$ must be real they can be written in the form

$$\delta n = A e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + A^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \tag{13.52}$$

$$\delta\mathbf{v} = i\mathbf{k}\left[B e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - B^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right]. \tag{13.53}$$

Substituting these expressions into Eqs. (13.51) and (13.50) we find, respectively,

$$\omega A + k^2 n_0 B = 0 \tag{13.54}$$

$$\omega n_0 B + \frac{g n_0}{m} A + \frac{\hbar^2 k^2}{4m^2} A = 0. \tag{13.55}$$

Solving the corresponding eigenvalue equation,

$$\begin{pmatrix} \omega & k^2 \\ \dfrac{\hbar^2 k^2}{4m^2} + \dfrac{g n_0}{m} & \omega \end{pmatrix}\begin{pmatrix} A \\ n_0 B \end{pmatrix} = 0, \tag{13.56}$$

we regain the Bogoliubov excitation spectrum

$$\varepsilon_k = \hbar\omega = \sqrt{\left(\hbar^2 k^2/2m\right)^2 + 2 g n_0 \left(\hbar^2 k^2/2m\right)}. \tag{13.57}$$

If, on the other hand, we leave out the quantum pressure contribution $\hbar^2 k^2/4m^2$ we find only the linear dispersion

$$\omega = \sqrt{g n_0/m}\, k. \tag{13.58}$$

This shows that the appearance of the particle-like dispersion in the Bogoliubov spectrum can be traced back to the quantum pressure term, which is *not* present in the classical hydrodynamic equations; hence it is a non-hydrodynamic effect.

13.5.1 Hydrodynamics in the Thomas-Fermi limit

In the Thomas-Fermi approximation we neglect the quantum pressure and the hydrodynamics of the condensate is described by a system of two coupled equations, the Euler equation

$$m\frac{\partial}{\partial t}\mathbf{v} + \boldsymbol{\nabla}\left(\tfrac{1}{2} m v^2 + \mathcal{U}(\mathbf{r}) + g n\right) = 0. \tag{13.59}$$

and the continuity equation

$$\frac{\partial}{\partial t} n + \boldsymbol{\nabla}\cdot n\,\mathbf{v} = 0. \tag{13.60}$$

To obtain the hydrodynamic response we consider a linear deviation from the stationary values (n and $\mathbf{v}$) of the fields,

$$n = n_0 + \delta n \quad \text{and} \quad \mathbf{v} = \mathbf{v}_0 + \delta\mathbf{v}. \tag{13.61}$$

For a condensate at rest ($\mathbf{v}_0 = 0$) we have $\mathbf{v} = \delta\mathbf{v}$ and the continuity equation takes the linearized form

$$\frac{\partial}{\partial t}\delta n + \boldsymbol{\nabla}\cdot n_0\,\delta\mathbf{v} = 0. \tag{13.62}$$

$$m\frac{\partial}{\partial t}\delta\mathbf{v} + \boldsymbol{\nabla}\left(\mathcal{U}(\mathbf{r}) + gn_0 + g\delta n\right) = 0. \tag{13.63}$$

These two first-order partial differential equations can be combined into a single second-order partial differential equation,

$$\frac{\partial^2}{\partial t^2}\delta n = \boldsymbol{\nabla}\cdot\frac{n_0}{m}\boldsymbol{\nabla}\left(\mathcal{U}(\mathbf{r}) + gn_0 + g\delta n\right). \tag{13.64}$$

The stationary solution satisfies the equation

$$\boldsymbol{\nabla}\cdot\frac{n_0}{m}\boldsymbol{\nabla}\left(\mathcal{U}(\mathbf{r}) + gn_0\right) = 0, \tag{13.65}$$

which is only valid for arbitrary $\mathcal{U}(\mathbf{r})$ provided the chemical potential is constant accross the condensate,

$$\mathcal{U}(\mathbf{r}) + gn_0 = \mu. \tag{13.66}$$

Hence, Eq. (13.64) reduces to

$$\frac{\partial^2}{\partial t^2}\delta n = \boldsymbol{\nabla}\cdot c^2\boldsymbol{\nabla}\delta n, \tag{13.67}$$

where in $c = \sqrt{gn_0/m}$ we recognize the local speed of sound.

For a spherical BEC of *homogeneously distributed density* for $r \le 1$ this becomes

$$\frac{\partial^2}{\partial t^2}\delta n = c^2\Delta\delta n. \tag{13.68}$$

Spherical symmetry

In a ball-shaped condensate of homogeneous density and radius ζ we have separation of variables and the deviation from equilibrium can be written in the form

$$\delta n(r,\theta,\phi,t) = \delta n_{kl}(r)Y_l^m(\theta,\phi)e^{i\omega t},$$

where the quantum number k appears in the equation to allow for more than one solution of given l. This leads to the following radial wave equation

$$\left[c^2\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right) + \omega^2\right]\delta n_{kl}(r) = 0.$$

This equation is valid for $\rho < \zeta$. Changing to the variable $\delta A_{kl} = r\delta n_{kl}$ this takes the form

$$\delta A_{kl}''(r) + \left[-l(l+1)/r^2 + k^2\right]\delta A_{kl}(r) = 0,$$

where $k = \omega/c$.

For pure breathing modes ($l = 0$) the differential equation reduces to

$$\left[\frac{d^2}{dr^2} + k^2\right]\delta A_{kl}(r) = 0.$$

The lowest breathing solution (free end boundary condition at $r = \zeta$) is

$$\delta A_{kl}(r) = A_0\mathrm{sin}kr + B_0\mathrm{cos}kr.$$

Hence, the regular solution for the deviation of the density at radial position r is

$$\delta n_{kl}(r) = \delta n_0 \frac{\sin kr}{kr}.$$

For the frequency we calculate with $k\zeta = 3.9$

$$\omega = \sqrt{gn_0/m}\pi/\zeta.$$

Using the equilibrium condition at the interface

$$\tfrac{1}{2}gn_0^2 = p_F$$

we arrive at

$$\omega = (2gp_F)^{1/4}3.9/\zeta$$

Cylindrical symmetry

In a cylindrical condensate of homogeneous density within a radius ζ we have separation of variables and the local density deviation from equilibrium can be written in the form

$$\delta n(\rho, \phi, z, t) = \delta n_{km}(\rho)\,\varphi_m(\phi)e^{ik_z z}e^{i\omega t}, \tag{13.69}$$

where k is the wavevector for motion along the z direction. For given k_z and m this leads to the following radial wave equation

$$\left[c^2\left(\frac{d^2}{d\rho^2} + \frac{1}{\rho}\frac{d}{d\rho} - \frac{m^2}{\rho^2} - k_z^2\right) + \omega^2\right]\delta n_{km}(\rho) = 0, \tag{13.70}$$

valid for $\rho < \zeta$. Restricting ourselves to $k_z = 0$ and changing to the variable $\delta A_{km} = \sqrt{\rho}\delta n_{km}$ the radial wave equation becomes

$$\left[\frac{d^2}{d\rho^2} + \frac{1/4 - m^2}{\rho^2} + k^2\right]\delta A_{km}(\rho) = 0. \tag{13.71}$$

where $k = \omega/c$.

For pure breathing modes ($m = 0$) the differential equation reduces to

$$\left[\frac{d^2}{d\rho^2} + \frac{1}{4\rho^2} + k^2\right]\delta A_{km}(\rho) = 0. \tag{13.72}$$

The lowest breathing solution (free end boundary condition at $\rho = \zeta$) is

$$\delta A_{kl}(r) = A_0\sqrt{\rho}J_0(k\rho).$$

Hence, the regular solution for the deviation of the density at radial position ρ is

$$\delta n_{kl}(r) = \delta n_0 J_0(k\rho).$$

For the frequency we calculate with $k\zeta = 4.5$

$$\omega = \sqrt{gn_0/m}4.5/\zeta.$$

Using the equilibrium condition at the interface

$$\tfrac{1}{2}gn_0^2 = p_F.$$

we arrive at

$$\omega = \left(\frac{2gp_F}{m^2}\right)^{1/4} 4.5/\zeta.$$

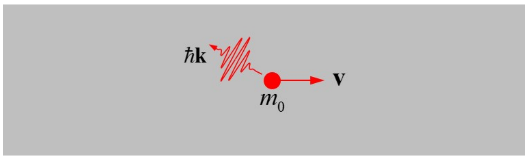

Figure 13.3: A body moving at velocity v through a Bose-Einstein condensate at rest.

13.6 Superfluidity - Landau criterion and critical velocity

Superfluidity is the name for a complex of phenomena in degenerate quantum fluids.[1] It was discovered in 1938 in liquid ^{4}He by Kapitza as well as by Allan and Misener, who found that, below a critical temperature $T_\lambda \simeq 2.17$ K, liquid ^{4}He flows without friction through narrow capillaries or slits. London (1938) conjectured a relation with the phenomenon of BEC and Landau (1941) suggested an explanation for the absence viscosity. Not surprisingly, the question arises 'is a dilute Bose-Einstein condensed gas a superfluid'? In this section we shall arrive at the conclusion that BEC is *not sufficient* to observe viscous-free flow.

As all experiments with quantum gases require surface-free confinement, a capillary arrangement like in liquid helium is out of the question from the experimental point of view. Therefore, we analyze an equivalent situation in which a body of mass m_0 moves at velocity $\mathbf{v}$ through a Bose-condensed atomic gas as sketched in Figure 13.3. The body may be an impurity atom or a spherical condensate of a different atomic species. For simplicity we presume the Bose-condensed gas to be a homogeneous Bose-Einstein condensate at rest at $T = 0$. In the absence of external forces the momentum of the body $\mathbf{p} = m_0\mathbf{v}$ is conserved unless the condensate gives rise to friction. At the microscopic level friction means the creation of excitations and this will only occur if this excitation process is energetically favorable.

Before excitation the energy of the moving body is $p^2/2m_0$ and the energy of the condensate is zero ($\varepsilon_0 \equiv 0$); i.e., the total energy of the system is

$$E_i = p^2/2m_0. \tag{13.73}$$

After creating in the condensate an excitation of energy ε_k and momentum $\hbar\mathbf{k}$ the energy of the body is known to be $(\mathbf{p} - \hbar\mathbf{k})^2/2m_0$ as follows by conservation of momentum. Thus, the total energy in the final state is

$$E_f = (\mathbf{p} - \hbar\mathbf{k})^2/2m_0 + \varepsilon_k = p^2/2m_0 + \hbar^2k^2/2m_0 - \hbar\mathbf{k}\cdot\mathbf{p}/m_0 + \varepsilon_k. \tag{13.74}$$

Energy conservation excludes excitation if $E_f - E_i > 0$, which is equivalent to $\varepsilon_k > \hbar\mathbf{k}\cdot\mathbf{v} - \hbar^2k^2/2m_0$. This condition is most difficult to satisfy for $\mathbf{v}$ parallel to $\mathbf{k}$, in which case we obtain after some rearranging

$$v < \varepsilon_k/\hbar k + \hbar k/2m_0 \equiv v_c. \tag{13.75}$$

Here v_c is the *critical velocity* for the creation of elementary excitations of momentum $\hbar k$. Thus we found that elementary excitations of momentum $\hbar k$ *cannot* be created if the speed of the body is less than v_c.

In the case of an *ideal* Bose gas the elementary excitations are free-particle-like; i.e., the dispersion is given by $\varepsilon_k = \hbar^2k^2/2m$, where m is the mass of the condensate atoms. Substituting this dispersion into Eq. (13.75) we find for the critical velocity in an ideal gas

$$v_c = \hbar k/2m_r, \tag{13.76}$$

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[1] A.J. Leggett, Rev. Mod. Phys. **73**, 307 (2001); also in *Bose-Einstein Condensation: from Atomic Physics to Quantum Fluids*, C.M. Savage and M. Das (Eds.), World Scientific, Singapore (2000).

where $m_r = mm_0/(m + m_0)$ is the reduced mass of the body with the excited atom. For heavy bodies $\mu \simeq m$ and v_c is simply half the speed of the excited atom. Importantly, in an ideal gas v_c is seen to scale with the momentum of the excitation. Hence, for any velocity of the body it is possible to create elementary excitations under conservation of energy and momentum. The efficiency of excitation is of course another matter. Here, this is left out of consideration because it only sets the time scale on which friction brings the body to rest.

In the case of the liquid ^{4}He at $T = 0$ the low-lying excitations are phonon-like $\varepsilon_k = \hbar ck$, with c the speed of sound. Substituting the linear dispersion into Eq. (13.75) the condition for excitation-free motion becomes

$$v < c + \hbar k/2m_0 \equiv v_c.$$

Apparently, below a critical velocity, the *Landau critical velocity* $v_c = c$, none of the phonon-like modes can be excited, which explains the absence of phonon-related friction. Note that the Landau critical velocity is independent of the mass of the moving body. In general the criterion $v < c$ is not sufficient to guarantee superfluidity, because any other cause of dissipation, like the excitation of vortices or of different elementary modes (like the so-called rotons in liquid helium), could destroy the effect. This being said we conclude from experiment that this is apparently not the case in liquid ^{4}He! Nevertheless, the existence of other types of excitations (vortices) should not be forgotten, if only because they make it extremely difficult to observe the theoretical value for the Landau critical velocity in liquid helium.

13.7 Gross-Pitaevskii equation for elongated condensates

13.7.1 Introduction

In many experiments with quantum fluids we are dealing with very long, axially symmetric configurations (ellipsoidal or cylindrical shapes), for instance a cylindrical column of liquid helium. To investigate such configurations the z direction is chosen along the longest symmetry axis and we search for (excited-state) solutions of the GP equation in cylindrical coordinates $\mathbf{r} = (\rho, \phi, z)$,[1]

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2}\right) + \mathcal{U}(\mathbf{r},t) + g|\Psi(\mathbf{r},t)|^2\right]\Psi(\mathbf{r},t), \tag{13.77}$$

where ρ is the radial distance to the z axis. In the third term of the laplacian we recognize the operator $L_z^2 = -\hbar^2\partial^2/\partial\phi^2$ representing the square of the orbital angular momentum $\mathbf{L}$ around the z axis, $\mathbf{L} = \mathbf{r}_\perp \times \mathbf{p} = -i\hbar(\mathbf{r}_\perp \times \boldsymbol{\nabla}) = \hat{\mathbf{z}}L_z$ with $\mathbf{r}_\perp = (\rho, \phi)$. In general, the effective potential

$$\mathcal{U}_{\text{eff}}(\mathbf{r},t) = \mathcal{U}(\mathbf{r},t) + g|\Psi(\mathbf{r},t)|^2 \tag{13.78}$$

will give rise to coupling between the cylindrical degrees of freedom. However, for very elongated configurations we can identify several important regular solutions that conserve the cylindrical symmetry (either completely or approximately) and in which the variables ρ, ϕ and z may be treated as separable at least up to first order in perturbation theory.

13.7.2 Condensate confined by a cylinder

Let us first consider confinement of a condensate by a infinitely long hard-walled cylinder of radius R_0. In this case the external potential depends only on the radial distance ρ to the symmetry axis, $\mathcal{U}(\mathbf{r}) = \mathcal{U}(\rho)$, with $\mathcal{U}(\rho) = 0$ for $\rho < R_0$ and $\mathcal{U}(\rho) \to \infty$ for $\rho \geq R_0$. This implies the boundary condition that the condensate wavefunction vanishes at the wall of the cylinder; *i.e.*, $\Psi(R_0, \phi, z) = 0$. As long as the interaction term $g|\Psi(\mathbf{r})|^2$ does not break the cylindrical symmetry (*e.g.* no phonons,

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[1] The corresponding expression for the classical kinetic energy is (aside from the common denominator $2m$) $\mathbf{p}^2 = (\hat{\boldsymbol{\rho}} \cdot \mathbf{p})^2 + (\hat{\mathbf{z}} \cdot \mathbf{p})^2 + (\hat{\boldsymbol{\rho}} \times \mathbf{p})^2$.

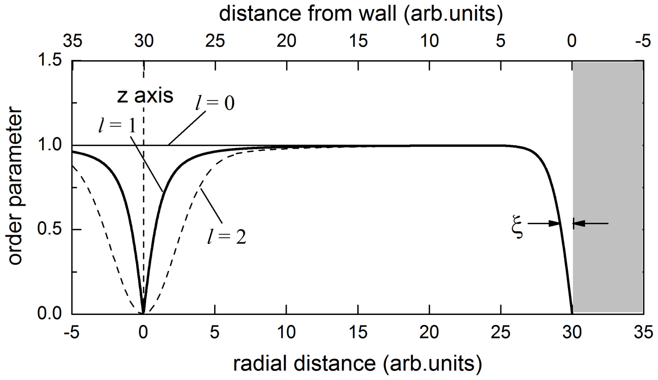

Figure 13.4: Boundary layer of the superfluid near a hard wall, where the order parameter drops to zero. The thickness of the layer is comparable to the healing length. Near the symmetry axis vortices with $l = 1$ and $l = 2$ are sketched.

no solitons) we can separate the cylindrical variables and write the order parameter as a product of the form

$$\Psi(\rho,\phi,z,t) = \psi_l\left(\rho\right)\varphi_l(\phi)e^{ikz}e^{-i\mu_l t/\hbar}, \tag{13.79}$$

where k is the wavevector for motion along the z direction and $\varphi_l(\phi)$ represents the eigenfunctions of the L_z operator,

$$L_z\varphi_l(\phi) = l\hbar\varphi_l(\phi) \text{ with } \varphi_l(\phi) = \frac{1}{\sqrt{2\pi}}e^{-il\phi}, \tag{13.80}$$

where l is called the quantum number of circulation. Recalling the relation (13.11) between the gradient of the phase and the flow velocity of the fluid the order parameter (13.79) represents stationary flow patterns of two types: *linear flow* along the symmetry axis and *circular flow* around the symmetry axis. The nonlinearity caused by the interaction term can also give rise to static and dynamic flow patterns along the z direction representing soliton modes but a discussion of these excitations of the order parameter is postponed until Section #. In particular the circular flow is interesting. Evaluating the angular momentum operator L_z we find that the circulation around the z direction is quantized in units of $\hbar$ and obtain for given value l the radial GP equation

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}-\frac{l^2}{\rho^2}-k^2\right)+g|\Psi_{k,l}(\mathbf{r})|^2\right]\Psi_{k,l}(\mathbf{r}) = \mu_{k,l}\Psi_{k,l}(\mathbf{r}). \tag{13.81}$$

This equation is valid for $\rho < R_0$ and can be made dimensionless by dividing by $n^{1/2}\mu_l$, where μ_l is the chemical potential for a condensate with l units of circulation and n the density far from the symmetry axis ($\rho \gg \xi$) and far from the wall ($R_0 - \rho \gg \xi$). Introducing the dimensionless variable $\varrho \equiv \rho/\xi$, where $\xi = \hbar/(2m\mu_l)^{1/2}$ is the healing length of a fluid at density $n = \mu_l/g$,

$$\left(-\frac{d^2}{d\varrho^2}-\frac{1}{\varrho}\frac{d}{d\varrho}+\frac{l^2}{\varrho^2}+(k\xi)^2+|f_{k,l}\left(\varrho\right)|^2\right)f_{k,l}\left(\varrho\right) = f_{k,l}\left(\varrho\right), \tag{13.82}$$

where $f_{k,l}\left(\varrho\right) \equiv n^{-1/2}\psi_{k,l}\left(\varrho\right)$ for $\varrho < R_0/\xi$.

13.7.3 Ground state - order parameter near hard wall

In the limit $R_0 \to \infty$ the Eq. (13.82) represents the GP equation for the homogeneous fluid. For $k = 0$ and $l = 0$ this equation reduces to the GP equation for the ground state, with solution $f_0 \equiv 1$. For a cylinder with a finite radius R_0 the order parameter must vanish at the wall, $f_0(R_0/\xi) = 0$.

In principle the confinement will affect the chemical potential but for large R_0 this effect mag be neglected. Hence, on the symmetry axis we may presume $f_0(0) = 1$. Further we note that the second term of Eq. (13.82) may be neglected since on the axis $f_0'(\varrho)/\varrho = 0$ for symmetry reasons and near the wall $f_0'(\varrho)/\varrho \ll 1$ when R_0 is sufficiently large. Thus, the radial GP equation reduces to

$$-f_0'' + f_0^3 - f_0 = 0. \tag{13.83}$$

As the variables f_0 and ϱ separate we can solve this equation by integration (see Problem 13.2). Restoring the dimensions we find

$$\psi_0(\rho) = \sqrt{n}\tanh\left[\sqrt{\tfrac{1}{2}}\,(R_0 - \rho)/\xi\right] \tag{13.84}$$

This shape is illustrated in Fig. 13.4. The order parameter is seen to decay smoothly to zero over a distance of the order of the healing length.

Problem 13.2. Show that the solution of the differential equation $-f_0'' + f_0^3 - f_0 = 0$ under the boundary conditions $f_0'(0) = 0$, $f_0(0) = 1$ and $f_0(b) = 0$ is given by

$$f_0(\varrho) = \tanh[2^{-1/2}(b - \varrho)].$$

Solution. First we multiply by f' and obtain after integration by parts

$$-\tfrac{1}{2}(df_0/d\varrho)^2 + \tfrac{1}{4}f_0^4 - \tfrac{1}{2}f_0^2 = a_1. \tag{a}$$

Recalling that $f_0'(0) = 0$ and $f_0(0) = 1$ the integration constant is found to be $a_1 = -1/4$. Taking the square root of Eq. (a) and integrating we obtain

$$2\varrho = \pm\int\frac{1}{f_0^2 - 1}df_0 = \pm\left(\tanh^{-1} f_0 + a_2\right).$$

Using the boundary condition $f_0(b) = 0$ the second integration constant is given by $a_2 = \pm 2b$. Taking the hyperbolic tangent on both sides we find the desired expression. Here we have chosen the minus sign because ϱ is a positive quantity. Note that the condition $f_0'(\varrho)/\varrho \ll 1$ for $\varrho \to b$ is satisfied. □

13.7.4 Order parameter with nonzero circulation

Let us now solve the radial GP equation (13.82) in the presence of circulation in the fluid ($l > 0$). Very close to the z axis ($\varrho \ll 1$) the circulation term dominates over the interaction and Eq. (13.82) reduces to

$$-\frac{d^2 f_l}{d\varrho^2} - \frac{1}{\varrho}\frac{df_l}{d\varrho} + \frac{l^2}{\varrho^2}f_l = f_l. \tag{13.85}$$

This is the Bessel differential equation. Therefore, close to the axis the solutions are give by Bessel functions $J_{\pm l}(\varrho)$. Searching for solutions with boundary condition $f_l(0) = 0$ the Bessel functions near the axis can be approximated by

$$f_l(\varrho) = \alpha\varrho^{|l|} \text{ for } \varrho \ll 1, \tag{13.86}$$

where α is a numerical coefficient.

For $\varrho \gg 1$ the interaction dominates over the circulation term. Hence, for $\xi \ll \rho \ll R_0$ Eq. (13.82) reduces to

$$\frac{l^2}{\varrho^2}f_l + f_l^3 = f_l. \tag{13.87}$$

Applying the boundary condition $f_l(\varrho) \to 1$ for $\varrho \gg 1$ we find

$$f_l(\varrho) = (1 - l^2/\varrho^2)^{1/2} \simeq 1 - l^2/2\varrho^2 \text{ for } \varrho \gg 1.$$

Unfortunately, the full radial dependence cannot be represented in analytical form. The result of numerical solutions for the cases $l = 1$ and $l = 2$ are shown in Fig. 13.4.

The azimuthal dependence of the order parameter is given by Eq. (13.80) and after restoring the dimensions the full order parameter is given by

$$\Psi(\rho, \phi, z) = \sqrt{n} f_l(\rho/\xi) e^{-i\Phi} \text{ with } \Phi_l = l\phi. \tag{13.88}$$

This expression is invariant under translation along the z direction and implies a velocity orthogonal to the radial vector $\mathbf{r}_\perp$,

$$\mathbf{v}_l = \frac{\hbar}{m} \boldsymbol{\nabla} \Phi_l = \frac{\hbar}{m} \frac{l}{\rho} \hat{\boldsymbol{\phi}} \tag{13.89}$$

Hence, the phase is independent of ρ.

$$\oint \mathbf{v}_l \cdot ds = \frac{h}{m} l. \tag{13.90}$$

13.8 Solitons

A special class of solutions of the GP equation are solitary wave solutions known as *solitons*. The soliton is a dispersion-free wave. This means that it is stationary in the coordinate system moving along with the wave. Hence, a soliton moving at speed v along the z axis can be described by the expression

$$\Psi(\mathbf{r}, t) = \Psi_0(\mathbf{r}_\perp, z - vt) e^{-i\mu t/\hbar}, \tag{13.91}$$

where $\mathbf{r}_\perp = (\rho, \phi)$. Substituting this expression in the time-dependent GP equation we obtain in cylindrical coordinates

$$ih \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2} \right) + \mathcal{U}(\mathbf{r}) + g |\Psi(\mathbf{r}, t)|^2 \right] \Psi(\mathbf{r}, t). \tag{13.92}$$

In the absence of vorticity this becomes

$$\begin{aligned} \mu \Psi(\mathbf{r}, t) - iv\hbar e^{-i\mu t/\hbar} \frac{\partial}{\partial z(t)} \Psi_0(\mathbf{r}_\perp, z - vt) = \\ = \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{\partial^2}{\partial z^2} \right) + \mathcal{U}(\mathbf{r}) + g |\Psi_0(\mathbf{r}_\perp, z - vt)|^2 \right] \Psi(\mathbf{r}, t). \end{aligned} \tag{13.93}$$

This equation is made dimensionless by dividing by $\mu n^{1/2} e^{-i\mu t/\hbar}$, where n is the density at large distance from the center of the soliton

$$f(\mathbf{r}_\perp, \zeta) - iv \frac{\hbar}{\mu \xi} \frac{\partial}{\partial \zeta} f(\mathbf{r}_\perp, \zeta) = \left[-\left(\frac{\partial^2}{\partial \varrho^2} + \frac{1}{\varrho} \frac{\partial}{\partial \varrho} + \frac{\partial^2}{\partial \zeta^2} \right) + |f(\mathbf{r}_\perp, \zeta)|^2 \right] f(\mathbf{r}_\perp, \zeta). \tag{13.94}$$

where $\varrho \equiv \rho/\xi$, $\zeta \equiv z/\xi$ and $f(\mathbf{r}_\perp, \zeta) \equiv n^{-1/2} \Psi_0(\mathbf{r}_\perp, \zeta)$. Introducing the dimensionless quantity

$$2u \equiv v \frac{\hbar}{\mu \xi} \tag{13.95}$$

soliton speed

$$u \equiv mv\xi/\hbar = \frac{\hbar}{2\mu\xi} v \tag{13.96}$$

Eq. (13.94) reduces to the form

$$-i2u \frac{\partial f}{\partial \zeta} = -\frac{\partial^2 f}{\partial \zeta^2} + f^3 - f. \tag{13.97}$$

A

Classical Mechanics

A.1 Introduction

The goal of *classical mechanics* is to describe the time evolution of systems of point-like particles, called *classical particles*, subject to Newton's laws of motion. To introduce the subject we consider a mechanical *system* of N classical particles labeled by the *particle index* α. The *position* of particle α is denoted by the vector $\mathbf{r}_\alpha$. The first derivative with respect to time t, $\dot{\mathbf{r}}_\alpha \equiv d\mathbf{r}_\alpha/dt$, is called the *velocity* of the particle and the second derivative, $\ddot{\mathbf{r}}_\alpha \equiv d^2\mathbf{r}_\alpha/dt^2$, its *acceleration.*

We suppose that for a given state of the system the evolution does not depend on the instant that we choose to follow it in time; i.e., *time is homogeneous*. Space is taken to be both *homogeneous and isotropic*; i.e., it is possible to choose a frame of reference in which the evolution of the system is independent of position and orientation. Such a reference frame is called an *inertial* frame. In an inertial frame a *free* particle either stays at rest or moves at constant velocity. This is *Newton's first law*: the law of inertia.

A system of N classical particles has at most $3N$ *degrees of freedom*; i.e., $3N$ independent ways to change in time. For *free* particles this motion can be described by Newton's equations of motion using $3N$ coordinates, for instance the cartesian coordinates x_α, y_α and z_α, with $\alpha \in \{1, \cdots N\}$. However, in many cases the motion is not free (not decribed by) but subject to constraints. These can be time independent (*scleronomous*) or have an explicit time dependence (*rheonomous*). An example of a scleronomous constraint is the fixed distance between two particles in a rotating rigid body. A ball rolling on the deck of a ship is an example of a system (the ball) with a rheonomous constraint (confinement to the deck of the ship). The system is called *holonomic* if the constraining relations reduce the $3N$ degrees of freedom the system (which can greatly simplify calculations). This is the case for constraint *equalities*, for instance the above mentioned fixed distance between two particles in a rotating rigid body. If the constraints do *not* affect the $3N$ degrees of freedom the system is called *nonholonomic.* An example is a system of particles confined to a box, where the confinement is accounted for by constraint *inequalities.* Nonholonomic constraints can sometimes be avoided by idealizations of the theory.

The field of classical mechanics is subdivided into three subjects: (a) *statics*, which is the theory of mechanical equilibrium between forces; (b) *kinematics*, which is the theory of motion without entering in the origin of this motion; (c) *dynamics*, which is the theory of motion under the influence of forces. This appendix cannot be more than a summary. It is partially based on unplublished lecture notes by De Groot and Suttorp at the University of Amsterdam. For a comprehensive introduction the reader is referred to volume 1 of the Landau-Lifshitz series [40] and the book by Herbert Goldstein [27].

A.2 Dynamical evolution

A.2.1 Newton's equation of motion

The time development of a system of N particles under the influence of external forces is called the *dynamical evolution* of that system. In classical mechanics the dynamical evolution of a single particle is described by *Newton's second law*, which states that the total force $\mathbf{F}_\alpha$ acting on particle α is proportional to the acceleration of that particle, with the proportionality constant m_α being its *inertial mass*,

$$\mathbf{F}_\alpha = m_\alpha \ddot{\mathbf{r}}_\alpha. \tag{A.1}$$

For a system of N particles the force $\mathbf{F}_\alpha$ is given by the resultant of all external forces, $\mathbf{F}_\alpha^{\mathrm{ext}}$, and the sum of the interaction forces $\mathbf{F}_{\alpha\beta}$ of particle α with all other particles of the system,

$$\mathbf{F}_\alpha^{\mathrm{ext}} + {\sum_{\beta=1}^{N}}{}' \mathbf{F}_{\alpha\beta} = m_\alpha \ddot{\mathbf{r}}_\alpha, \tag{A.2}$$

where the prime indicates the condition $\beta \neq \alpha$. This expression represents a set of N coupled differential equations which is impossible to solve for a macroscopic number of particles. However, as we shall see below, in many cases excellent approximations can be obtained by replacing the interparticle forces by one or more relations acting as constraints on the motion of particle α.

A.2.2 Kinematic evolution of holonomous systems

For a *holonomic* system of N particles at positions $\mathbf{r}_\alpha$ with l constraints we can introduce $f = 3N - l$ *independent* coordinates $q_i(t)$ known as the *generalized coordinates*, with $i \in \{1, \cdots f\}$ being the *coordinate index.* Together these define the evolution of the system as a function of time in the f-dimensional *configuration space* of the system. The time derivatives $\dot{q}_i(t)$ are called the *generalized velocities.*[1]

- The *rheonomous* constraints of a N-particle system with $f = 3N - l$ degrees of freedom constitute a set of l *time-dependent* relations $f_k(\mathbf{r}_1, \cdots, \mathbf{r}_N, t) = 0$, where $k \in \{1, \cdots l\}$ is called the *constraint index.* In this case the position of particle α may be expressed as a function of the f coordinates q_i plus time,

  $$\mathbf{r}_\alpha = \mathbf{r}_\alpha(q_1, \cdots, q_f, t). \tag{A.3}$$

  The velocities follow with

  $$\dot{\mathbf{r}}_\alpha = \sum_{i=1}^{f} \frac{\partial \mathbf{r}_\alpha}{\partial q_i} \dot{q}_i + \frac{\partial \mathbf{r}_\alpha}{\partial t}, \tag{A.4}$$

  which shows that the velocity of particle α is (in general) a function of $q_i, \dot{q}_i$ and t,

  $$\dot{\mathbf{r}}_\alpha = \dot{\mathbf{r}}_\alpha(q_1, \cdots, q_f, \dot{q}_1, \cdots, \dot{q}_f, t). \tag{A.5}$$

  Hence, in *rheonomous* systems $\mathbf{r}_\alpha$ and $\dot{\mathbf{r}}_\alpha$ depend *explicitly* on time.

- For *scleronomous* constraints the l constraining relations do *not* contain an explicit time dependence: $f_k(\mathbf{r}_1, \cdots, \mathbf{r}_N) = 0$, with $k \in \{1, \cdots l\}$. This makes it possible to *choose* the f coordinates q_i in such a way that the position of the particles does not depend explicitly on time. For instance, a rigid body has $f = 6$ degrees of freedom, because the position of an arbitrary particle α is specified by $\mathbf{r}_\alpha = \mathbf{r}_\alpha(X, Y, Z, r, \theta, \phi)$, where $\mathbf{R} = (X, Y, Z)$ is the position of the center of mass and $\mathbf{r} = (r, \theta, \phi)$ to position relative to $\mathbf{R}$ inside the body. For a homogeneous rigid sphere on a static surface this reduces to $f = 4$ and $\mathbf{r}_\alpha = \mathbf{r}_\alpha(X, Y, \theta, \phi)$.

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[1] In this appendix we adopt the following index convention: $\alpha \in \{1, \cdots N\}$ for the *particle index*, $i \in \{1, \cdots f\}$ for the *coordinate index* and $k \in \{1, \cdots l\}$. for the *constraint index.*

A.2.3 Virtual displacements - principle of d'Alembert

The force $\mathbf{F}_\alpha$ acting on particle α is the superposition of all forces acting on that particle. These forces can be separated into *known* forces $\mathbf{F}_\alpha^{\mathrm{ext}}$, like gravity or externally applied forces, and *unknown* forces $\mathbf{K}_\alpha$,

$$\mathbf{F}_\alpha = \mathbf{F}_\alpha^{\mathrm{ext}} + \mathbf{K}_\alpha. \tag{A.6}$$

The unknown forces are called *forces of constraint.* These unknown forces are *reaction forces* that reduce the freedom of motion of the particles. Their actual value is unknown but always such that the constraints remain satisfied, for instance to assure that a train stays in the rails.

The explicit appearance of the reaction forces can be eliminated from the formalism. To demonstrate this we first consider *mechanical equilibrium.* This is the state in which all particles are at rest in their equilibrium position; i.e., $\mathbf{F}_\alpha = 0$ and $\mathbf{K}_\alpha = -\mathbf{F}_\alpha^{\mathrm{ext}}$ for all particles. By pulling on one of the particles we expect to perform work against the restoring force of the system but as long as the displacements $\delta\mathbf{r}_\alpha$ remain small (i.e., close to the equilibrium position) we find that this work vanishes because the forces $\mathbf{F}_\alpha$ remain vanishingly small,

$$\sum_\alpha \mathbf{F}_\alpha \cdot \delta\mathbf{r}_\alpha = \sum_\alpha (\mathbf{F}_\alpha^{\mathrm{ext}} + \mathbf{K}_\alpha) \cdot \delta\mathbf{r}_\alpha = 0. \tag{A.7}$$

In other words, in equilibrium the restoring force is zero. This implies that in the absence of external forces the reaction forces have to be zero, $\mathbf{F}_\alpha = \mathbf{K}_\alpha = 0$.

Now suppose that the system is pulled *out of equilibrium.* In this case we have forces acting on (in general) all the particles; i.e., $\mathbf{F}_\alpha = m_\alpha \ddot{\mathbf{r}}_\alpha \neq 0$ and $\mathbf{K}_\alpha = -\mathbf{F}_\alpha^{\mathrm{ext}} + \mathbf{F}_\alpha \neq 0$. Shifting the external forces to the l.h.s. of (A.7) this equation takes the form

$$\sum_\alpha (m_\alpha \ddot{\mathbf{r}}_\alpha - \mathbf{F}_\alpha^{\mathrm{ext}}) \cdot \delta\mathbf{r}_\alpha = \sum_\alpha \mathbf{K}_\alpha \cdot \delta\mathbf{r}_\alpha. \tag{A.8}$$

The dot product leads us to distinguish between the component of $\delta\mathbf{r}_\alpha$ along $\mathbf{K}_\alpha$ and the component perpendicular to $\mathbf{K}_\alpha$. A parallel displacement would require work but is not in accordance with the constraints; a perpendicular displacement is in accordance with the constraints but does not result in work (as long as the displacements remain sufficiently small). This insight brings us to the *principle of d'Alembert*: under *virtual displacements* $\delta\mathbf{r}_\alpha$ (in accordance with the constraints) no work is done by the reaction forces,

$$\delta W = \sum_\alpha \mathbf{K}_\alpha \cdot \delta\mathbf{r}_\alpha = 0. \tag{A.9}$$

By analyzing virtual displacement we can eliminate the reaction forces from (A.8) and the principle of d'Alembert takes the form

$$\delta W = \sum_\alpha (m_\alpha \ddot{\mathbf{r}}_\alpha - \mathbf{F}_\alpha^{\mathrm{ext}}) \cdot \delta\mathbf{r}_\alpha = 0. \tag{A.10}$$

As this expression also holds outside equilibrium, we have obtained a condition for the *dynamical* evolution of a mechanical system in which the constraints are satisfied implicitly. In Section A.3 the d'Alembert principle will be used to derive the central equations of classical mechanics: the equations of Lagrange.

Let us have a closer look at the virtual displacements. These can be thought of as instantly being present at any desired point in time just to analyze how they would affect the system; i.e., unlike real displacements, which are based on (A.3), virtual displacements have *no* (explicit) time dependence. To be relevant, they have to be in accordance with the constraints; i.e., $\delta\mathbf{r}_\alpha$ has to be perpendicular to $\mathbf{K}_\alpha$. This leads to the practical difficulty that (in principle) the virtual displacement of one particle affects the virtual reaction forces of all other particles; i.e., the $\delta\mathbf{r}_\alpha$ cannot be chosen independently. This difficulty can be eliminated by decomposing the virtual displacements in terms of the generalized coordinates defined by the constraints,

$$\delta \mathbf{r}_\alpha = \sum_{i=1}^{f} \frac{\partial \mathbf{r}_\alpha}{\partial q_i} \delta q_i. \tag{A.11}$$

Note the absence of the time variable. Substituting this expression into (A.10) we obtain

$$\delta W = \sum_{i=1}^{f} \left[\sum_{\alpha=1}^{N} (m_\alpha \ddot{\mathbf{r}}_\alpha - \mathbf{F}_\alpha^{\text{ext}}) \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i} \right] \delta q_i = 0 \tag{A.12}$$

and since the q_i are independent variables the principle of d'Alembert takes the form of a set of f coupled differential equations

$$\sum_\alpha (m_\alpha \ddot{\mathbf{r}}_\alpha - \mathbf{F}_\alpha^{\text{ext}}) \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i} = 0, \quad \text{with } i \in \{1, \cdots, f\}. \tag{A.13}$$

Inversely, it is easily verified that (A.10) is always valid provided the equations (A.13) are simultaneously satisfied.

Bernoulli's principle

In the absence of dynamical evolution (the *static* case - $\ddot{\mathbf{r}}_\alpha = 0$) the principle of d'Alembert reduces to the *Bernoulli principle* of virtual displacements :

$$\delta W = \sum_\alpha \mathbf{F}_\alpha^{\text{ext}} \cdot \delta \mathbf{r}_\alpha = 0. \tag{A.14}$$

As an example of *Bernoulli's principle* without constraints we consider a system of $N = 2$ identical particles subject to a force $\mathbf{F}_\alpha^{\text{ext}} = -\boldsymbol{\nabla}_\alpha U(\mathbf{r}_1, \mathbf{r}_2)$, where $U(\mathbf{r}_1, \mathbf{r}_2)$ is a potential function which depends on the position of both particles. This is an example of a conservative force (see Section A.5.2). The expression for the virtual work is $\delta W = \mathbf{F}_1^{\text{ext}} \cdot \delta \mathbf{r}_1 + \mathbf{F}_2^{\text{ext}} \cdot \delta \mathbf{r}_2 = 0$. For two free particles confined by a harmonic potential the condition $\delta W = 0$ is satisfied at the minimum of the potential. For two repulsive particles we have $\mathbf{F}_1^{\text{ext}} = -\mathbf{F}_2^{\text{ext}}$ and the condition $\delta W = 0$ is satisfied for $\delta \mathbf{r}_1 = -\delta \mathbf{r}_2$ perpendicular to $\mathbf{F}_1^{\text{ext}}$. Note the correlation between $\delta \mathbf{r}_1$ and $\delta \mathbf{r}_2$ (these are *not* independent). The virtual displacements correspond to a rotation of the pair about the potential center. The latter case shows that the virtual variation does not automatically correspond to minimum of δW but can also represent a degenerate case.

Kinetic energy relations

Introducing the *kinetic energy*,

$$T \equiv \tfrac{1}{2} \sum_\alpha m_\alpha \dot{\mathbf{r}}_\alpha^2, \tag{A.15}$$

we note that, in view of (A.5), the kinetic energy of particle α is in the most general case a function of $q_i(t), \dot{q}_i(t)$ and t,

$$T = T(q_1, \cdots, q_f, \dot{q}_1, \cdots, \dot{q}_f, t). \tag{A.16}$$

For future convenience of use we derive the partial derivatives with respect to q_i and $\dot{q}_i$,

$$\frac{\partial T}{\partial q_i} = \sum_\alpha m_\alpha \dot{\mathbf{r}}_\alpha \cdot \frac{\partial \dot{\mathbf{r}}_\alpha}{\partial q_i} \tag{A.17a}$$

$$\frac{\partial T}{\partial \dot{q}_i} = \sum_\alpha m_\alpha \dot{\mathbf{r}}_\alpha \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i}. \tag{A.17b}$$

Here we used the relation $\partial \dot{\mathbf{r}}_\alpha / \partial \dot{q}_i = \partial \mathbf{r}_\alpha / \partial q_i$, which follows immediately from (A.4) and (A.3).

Problem A.1. Consider the kinematics of a single particle moving in a stationary circular orbit of radius $R = 1$. Derive the equations of motion and show that motion is in accordance with the principle of d'Alembert.

Solution. To describe the orbit we choose a two-dimensional cartesian coordinate system with the position vector $\mathbf{r}$ given by

$$x = r\cos\phi \qquad y = r\sin\phi,$$

where (x, y) are the cartesian coordinates and (r, ϕ) the polar coordinates of $\mathbf{r}$. In this problem we have one (skeronomic) constraint: the radius of the orbit is constant. Choosing the origin of the coordinate system at the center of the circle the constraint takes the form $r = 1$ and the motion can be described using ϕ as the only generalized coordinate, $\mathbf{r} = \mathbf{r}(\phi)$. The time evolution is given by

$$\begin{aligned} x(t) &= \cos\omega t, & \dot{x}(t) &= -\omega\sin\omega t, & \ddot{x}(t) &= -\omega^2\cos\omega t \\ y(t) &= \sin\omega t, & \dot{y}(t) &= \omega\cos\omega t, & \ddot{y}(t) &= -\omega^2\sin\omega t, \end{aligned}$$

where $\phi(t) \equiv \omega t$, with $\omega = \dot{\phi}$ the angular velocity about the origin. These expressions show that the velocity is always tangential to the circle with the acceleration pointing to the center. Note that the velocity is proportional to ω and the acceleration scales with ω^2. As there are no "known" forces acting on the particle, the d'Alembert principle tells us that the force must a reaction force, $\mathbf{K} = m\ddot{\mathbf{r}}$, which constrains the orbit of the particle to the circle. Furthermore, as no work is done by reaction forces under virtual displacements,

$$\delta W = m\ddot{\mathbf{r}} \cdot \delta\mathbf{r} = 0,$$

the virtual displacements have to be orthogonal to the force; i.e., tangential to the circle (in accordance with the constraint $r = 1$). Note that the x and y motion only differ by a constant phase shift. Hence, the circular motion maps on that of a one-dimentional harmonic oscillator, which also is a mechanical system with one degree of freedom ($f = 1$). □

A.3 Lagrange equations

In this section we derive the equations of Lagrange, which are the equations of motion of classical mechanics. The Lagrange equations offer important advantages over Newton's equations of motion because forces of constraint are eliminated from the formalism. In this way the *state* of a classical system of f degrees of freedom can be uniquely specified by a set of $2f$ generalized coordinates,

$$(\mathbf{q}, \dot{\mathbf{q}}) \equiv (q_1, \cdots, q_f; \dot{q}_1, \cdots, \dot{q}_f). \tag{A.18}$$

This set is known as the *classical phase* of the system. As the generalized coordinates are linearly independent, the classical phase corresponds to a point in a $2f$-dimensional vector space, called the (generalized) *phase space* of the system. Each point in the phase space corresponds to a different *classical state.* In the Lagrange equations the vectors $\mathbf{q} \equiv (q_1, \cdots, q_f)$ and $\dot{\mathbf{q}} \equiv (\dot{q}_1, \cdots, \dot{q}_f)$ serve as *dynamical variables* because the evolution of the classical phase in time represents the dynamical evolution of the system. Separately, $\mathbf{q}$ and $\dot{\mathbf{q}}$ evolve as vectors in the (generalized) *configuration space* and (generalized) *velocity space*, respectively. The Lagrange equations are equally valid for conservative and non-conservative forces. Examples of conservative forces are the *gravitational* force and the *Lorentz* force. The friction force is an example of a non-conservative force. In the present section the Lagrange equations are obtained from the principle of d'Alembert. In Section A.4 they will be derived from the principle of least action of Hamilton.

A.3.1 Absence of constraining forces

First we show how the Lagrange equations are obtained form Newton's second law. In the absence of constraining forces the particles are called *free* and the equations of motion (A.1) suffice to describe the motion of the particles. Using Eq. (A.15) for the kinetic energy, we find that a force acting on particle α can be written in the form

$$\mathbf{F}_\alpha = \frac{d}{dt}\frac{\partial T}{\partial \dot{\mathbf{r}}_\alpha}. \tag{A.19}$$

Now we restrict ourselves to forces that can be expressed as the negative gradient of a *potential function* $U = U(\mathbf{r}_1, \cdots, \mathbf{r}_N, t)$,

$$\mathbf{F}_\alpha^{\mathrm{ext}} = -\frac{\partial U}{\partial \mathbf{r}_\alpha}. \tag{A.20}$$

In the special case of a *time-independent* potential function the force field is called *conservative* and potential function can be interpreted as the *potential energy* $U = V(\mathbf{r}_1, \cdots, \mathbf{r}_N)$. We return to the concept of potential energy in the context of the conservation laws (see Section A.5.2). Combining (A.19) and (A.20) we find

$$-\frac{\partial U}{\partial \mathbf{r}_\alpha} = \frac{d}{dt}\frac{\partial T}{\partial \dot{\mathbf{r}}_\alpha}. \tag{A.21}$$

At this point we introduce the *Lagrangian* $\mathcal{L}(\mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, t)$ as the difference between the kinetic energy and the potential function,

$$\mathcal{L}(\mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, t) \equiv T(\dot{\mathbf{r}}_\alpha) - U(\mathbf{r}_\alpha, t). \tag{A.22}$$

Because the potential function $U(\mathbf{r}_1, \cdots, \mathbf{r}_N, t)$ does not depend explicitly on $\dot{\mathbf{r}}_\alpha$, and $T(\dot{\mathbf{r}}_1, \cdots, \dot{\mathbf{r}}_N)$ not explicitly on $\mathbf{r}_\alpha$, (A.21) we arrive at the so-called *Lagrange equations* for particle α,

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_\alpha} = 0, \quad \text{with } \alpha \in \{1, \cdots, N\}. \tag{A.23}$$

A.3.2 Presence of constraining forces

Lagrange equations can also be derived for systems with *holonomic* constraints. So let us turn to a system of N particles in which *holonomic* constraints add up to the reaction forces $\mathbf{K}_\alpha$. How do these constraints affect the evolution of the system? To answer this question we apply the principle of d'Alembert. Rewriting (A.13) in the form

$$\sum_\alpha \mathbf{F}_\alpha^{\mathrm{ext}} \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i} = \sum_\alpha m_\alpha \ddot{\mathbf{r}}_\alpha \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i}, \quad \text{with } i \in \{1, \cdots, f\}, \tag{A.24}$$

we can introduce a *generalized force* defined by f components, one for every degree of freedom of the system,

$$Q_i \equiv \sum_\alpha \mathbf{F}_\alpha^{\mathrm{ext}} \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i}, \quad \text{with } i \in \{1, \cdots, f\}. \tag{A.25}$$

Using the r.h.s. of (A.24) the Q_i can be expressed as

$$Q_i = \frac{d}{dt}\left(\sum_\alpha m_\alpha \dot{\mathbf{r}}_\alpha \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i}\right) - \sum_\alpha m_\alpha \dot{\mathbf{r}}_\alpha \cdot \frac{\partial \dot{\mathbf{r}}_\alpha}{\partial q_i}, \tag{A.26}$$

and after substitution of (A.17) this becomes

$$Q_i = \frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_i}\right) - \frac{\partial T}{\partial q_i}, \quad \text{with } i \in \{1, \cdots, f\}. \tag{A.27}$$

This expression holds for any holonomic system. It has the structure of a Lagrange equation but the forces remain to be specified. Below we derive the Lagrange equation for three types of forces: (a) conservative or non-conservative potential forces; (b) generalized potential forces; (c) non-potential forces.

(a) If the components of the generalized force can be expressed as the gradients of the potential function $U = U(\mathbf{r}_1, \cdots, \mathbf{r}_N, t)$ we can substitute (A.20) into (A.25) and obtain

$$Q_i \equiv -\sum_\alpha \frac{\partial U}{\partial \mathbf{r}_\alpha} \cdot \frac{\partial \mathbf{r}_\alpha}{\partial q_i} = -\frac{\partial U}{\partial q_i}. \tag{A.28}$$

Substituting this equation into (A.27) and taking into account $\partial U/\partial \dot{q}_i = 0$ (because U does not depend explicitly on the $\dot{q}_i$), the equations of motion takes the form

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}}{\partial q_i} = 0, \quad \text{with } i \in \{1, \cdots, f\}, \tag{A.29}$$

where

$$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t) \equiv T(\mathbf{q}, \dot{\mathbf{q}}, t) - U(\mathbf{q}, t). \tag{A.30}$$

The set of equations (A.29) will be referred to as the *Lagrange equations*. Note that in the non-holonomic case we have $f = 3N$ and the set of generalized coordinates $\{q_i\}$ coincides with the full set of cartesian coordinates $\{\mathbf{r}_\alpha\}$; i.e., (A.29) coincides with (A.23).

(b) The derivation of Eq. (A.29) breaks down in cases where $\partial U/\partial \dot{q}_i \neq 0$; i.e., for velocity-dependent forces. However, by construction, the Lagrange equations will still be obtained if the generalized forces can be written the form

$$Q_i = -\frac{\partial U}{\partial q_i} + \frac{d}{dt}\left(\frac{\partial U}{\partial \dot{q}_i}\right), \quad \text{with } i \in \{1, \cdots, f\}. \tag{A.31}$$

Substituting this expression into (A.27) we find

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}}{\partial q_i} = 0, \quad \text{with } i \in \{1, \cdots, f\}. \tag{A.32}$$

Here the Lagrangian is defined as.

$$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t) \equiv T(\mathbf{q}, \dot{\mathbf{q}}, t) - U(\mathbf{q}, \dot{\mathbf{q}}, t). \tag{A.33}$$

In the presence of a velocity dependence the function $U = U(\mathbf{q}, \dot{\mathbf{q}}, t)$ is called a *generalized potential function.*

(c) Not all forces can be derived from a potential function. However, also for non-potential forces (for instance friction forces) the equation (A.27) is valid. In the most general case, when both potential and non-potential forces are present, the Lagrange equations can be written in the form

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}}{\partial q_i} = Q_i, \quad \text{with } i \in \{1, \cdots, f\}. \tag{A.34}$$

Here Q_i are the components of the non-potential force. Forces that can be derived from a potential function are presumed to be contained in the Lagrangian.

A.3.2.1 Motion in a central potential field

As a first example we consider the motion of a particle of mass m freely moving in a *central* potential, $\mathcal{U}(r)$. This is a *conservative* potential which only depends on the distance of the particle to the center of the potential. As the force is central, the orbit will be confined to the plane defined by the position and velocity of the particle at $t = 0$. The Lagrangian is given by

$$\mathcal{L} = \tfrac{1}{2} m\, \dot{\mathbf{r}}^2 - \mathcal{U}(r). \tag{A.35}$$

Choosing the xy plane of a cartesian coordinate system with its origin at the potential center, the position vector given by

$$\mathbf{r} = \hat{\mathbf{x}}\, r\cos\phi + \hat{\mathbf{y}}\, r\sin\phi \tag{A.36}$$

where $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are the unit vectors along the x and y direction, and (r, ϕ) are the polar coordinates of $\mathbf{r}$. Differentiating Eq. (A.36) with respect to time find for the velocity

$$\dot{\mathbf{r}} = \hat{\mathbf{x}}\,(\dot{r}\cos\phi - r\sin\phi\,\dot{\phi}) + \hat{\mathbf{y}}\,(\dot{r}\sin\phi + r\cos\phi\,\dot{\phi}). \tag{A.37}$$

Then, using the orthogonality of the unit vectors $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ we obtain

$$\dot{\mathbf{r}}^2 = (\dot{r}\cos\phi - r\sin\phi\,\dot{\phi})^2 + (\dot{r}\sin\phi + r\cos\phi\,\dot{\phi})^2 = \dot{r}^2 + r^2\dot{\phi}^2 \tag{A.38}$$

and the Lagrangian becomes

$$\mathcal{L} = \tfrac{1}{2} m\,(\dot{r}^2 + r^2\dot{\phi}^2) - \mathcal{U}(r). \tag{A.39}$$

Since the polar coordinates are obtained from the cartesian coordinates by an orthogonal transformation, both sets of coordinates can serve as a complete set of generalized coordinates on which the action principle is based. In other words, the Lagrange equations also apply to the case of polar coordinates.

For the ϕ motion the Lagrange equation becomes

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\phi}} = \frac{\partial \mathcal{L}}{\partial \phi} \quad \Leftrightarrow \quad \frac{d}{dt}\left(mr^2\dot{\phi}\right) = 0. \tag{A.40}$$

This shows that the quantity $mr^2\dot{\phi}$ is *conserved.* In this quantity we recognize the angular momentum about the potential center, $m\,(\mathbf{r}\times\mathbf{v}) = mr^2\dot{\phi}$. Note that this conservation law implies that the area enclosed by the orbit in a given time is conserved in time

$$dA = \tfrac{1}{2} r^2 d\phi = c dt. \tag{A.41}$$

This Keppler's second law. In particular, for a *circular* orbit the angular velocity is conserved: $\dot{\phi} \equiv \omega$ and $\phi = \omega t$ (with the initial phase of the circular motion chosen to be zero at $t = 0$).

For the r motion the Lagrange equation becomes

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{r}} = \frac{\partial \mathcal{L}}{\partial r} \quad \Leftrightarrow \quad F = \frac{d}{dt}\,(m\dot{r}) = mr\dot{\phi}^2 - \frac{\partial \mathcal{U}(r)}{\partial r}. \tag{A.42}$$

For a *circular* orbit this reduces to the well-known condition for *stationary* motion,

$$m\omega^2 r - \partial\mathcal{U}(r)/\partial r = 0 \tag{A.43}$$

A.3.2.2 Friction force

In this example we ask for the steady-state velocity of particle falling in a gravitational field in the presence of friction. For a gravitational field along the z axis the potential is $V = \alpha z$. This is a conservative potential field. The friction force is a velocity dependent force,

$$F = -\beta\dot{z}. \tag{A.44}$$

This is a *non-conservative* and therefore *non-Newtonian* force. The Lagrangian is determined only by the kinetic energy and the potential fields (in this case only the gravitational potential),

$$\mathcal{L} = \tfrac{1}{2}\dot{z}^2 - \alpha z. \tag{A.45}$$

Substituting the friction force into the r.h.s. of the Lagrange equation (A.29) we obtain

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{z}} - \frac{\partial \mathcal{L}}{\partial z} = -\beta \dot{z}. \tag{A.46}$$

Substituting the Lagrangian (A.45) we obtain

$$\ddot{z} + \beta \dot{z} - \alpha = 0. \tag{A.47}$$

The steady-state condition is $\ddot{z} = 0$; hence, we find for the steady-state velocity

$$\dot{z} = -\alpha/\beta. \tag{A.48}$$

A.3.2.3 Lorentz force

The celebrated example of a velocity-dependent force for which a generalized potential can be defined is the *Lorentz* force. This force governs the motion of a charged particle moving through an electromagnetic field in vacuum. The *Lorentz* force is given by

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}), \tag{A.49}$$

where q is the electric charge and $\mathbf{v} = \dot{\mathbf{r}}$ the velocity of the particle. The *generalized electromagnetic potential* from which the Lorentz force may be derived has the form,

$$U(\mathbf{r}, \mathbf{v}, t) = q(\varphi - \mathbf{v} \cdot \mathbf{A}), \tag{A.50}$$

where $\varphi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ are the scalar and vector potentials of the electromagnetic field. To demonstrate this assertion we start from (A.31) and find in the vector notation [1]

$$\mathbf{F}(\mathbf{r}, \dot{\mathbf{r}}, t) = -\partial_{\mathbf{r}} U + \frac{d}{dt}\partial_{\dot{\mathbf{r}}} U = -q[\partial_{\mathbf{r}}\varphi - \partial_{\mathbf{r}}(\dot{\mathbf{r}} \cdot \mathbf{A}) + \frac{d}{dt}\partial_{\dot{\mathbf{r}}}(\dot{\mathbf{r}} \cdot \mathbf{A})]. \tag{A.51}$$

Because $\mathbf{A}(\mathbf{r}, t)$ does not depend explicitly on $\dot{\mathbf{r}}$ and in view of the vector rule (E.17) the last term of (A.51) can be rewritten as

$$\frac{d}{dt}\partial_{\dot{\mathbf{r}}}(\dot{\mathbf{r}} \cdot \mathbf{A}) = \frac{d\mathbf{A}}{dt} = \partial_t \mathbf{A} + (\dot{\mathbf{r}} \cdot \partial_{\mathbf{r}})\mathbf{A}. \tag{A.52}$$

Substitution of this expression into (A.51) we obtain

$$\mathbf{F} = -q[\partial_{\mathbf{r}}\varphi + \partial_t \mathbf{A} + (\dot{\mathbf{r}} \cdot \partial_{\mathbf{r}})\mathbf{A} - \partial_{\mathbf{r}}(\dot{\mathbf{r}} \cdot \mathbf{A})], \tag{A.53}$$

which yields with (E.16) the expression for the Lorentz force

$$\mathbf{F} = -q(\partial_{\mathbf{r}}\varphi + \partial_t \mathbf{A} - \dot{\mathbf{r}} \times \partial_{\mathbf{r}} \times \mathbf{A}) = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \tag{A.54}$$

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[1] In this example we use the short-hand notation $\partial_{\mathbf{q}} \equiv \partial/\partial \mathbf{q} \equiv (\partial/\partial q_x, \partial/\partial q_y, \partial/\partial q_z)$ and $\partial_t \equiv \partial/\partial t$.

A.4 The Lagrange formalism

In Section A.3 the Lagrange equations were derived from the Newton equations of motion together with the principle of d'Alembert. An alternative approach is to derive the Lagrange equations from the *principle of Hamilton.* In this approach we start by noting that the time evolution of the system corresponds to a unique *path* of the vector $\mathbf{q} \equiv (q_1, \cdots, q_f)$ in the f-dimensional configuration space of the generalized coordinates. As these coordinates are mutually independent, this path can be predicted over an infinitesimal time interval from t to $t + \delta t$ by the relation

$$\mathbf{q}(t+\delta t) = \mathbf{q}(t) + \dot{\mathbf{q}}(t)\delta t. \tag{A.55}$$

Hence, to predict the continuation of the path at time t, *both* $\mathbf{q}(t)$ and $\dot{\mathbf{q}}(t)$ have to be known. In other words, together $\mathbf{q}$ and $\dot{\mathbf{q}}$ fully determine the *classical state* of the system (often represented by a point in the so-called *phase space* of position and momentum).

A.4.1 Principle of Hamilton

Let us consider the case where the *actual* path $\mathbf{q}(t)$ runs from the starting point $\mathbf{q}(t_0)$ to the end point $\mathbf{q}(t_1)$ during the time interval (t_0, t_1), and let $\mathbf{q}'(t)$ be some *adjacent* path, slightly differing from the actual path but with the same starting point and end point. The key idea behind the principle of Hamilton is that any continuous deviation from the actual path,

$$\delta\mathbf{q}(t) = \mathbf{q}'(t) - \mathbf{q}(t), \tag{A.56}$$

with boundary conditions

$$\delta\mathbf{q}(t_0) = 0 \quad \text{and} \quad \delta\mathbf{q}(t_1) = 0, \tag{A.57}$$

has to be unfavorable in some respect. Thus we search for a functional of $\mathbf{q}$ and $\dot{\mathbf{q}}$ (the *cost functional* of the variational problem) which is minimal for the actual path from $\mathbf{q}(t_0)$ to $\mathbf{q}(t_1)$. Minimizing this functional with respect to the path provides us with criteria that have to be satisfied along the actual path (for instance conservation laws). This cost functional is called the *action* and is given by the integral of a lagrangian function $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$ over the time interval (t_0, t_1),

$$S = \int_{t_0}^{t_1} \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)dt. \tag{A.58}$$

Whatever this "Lagrangian" may turn out to be, the expression for the action is plausible; at each point in time t within the interval (t_0, t_1), knowledge of $\mathbf{q}$ and $\dot{\mathbf{q}}$ suffice to determine the actual path from $\mathbf{q}(t_0)$ to $\mathbf{q}(t_1)$. So if the Lagrangian is to be deterministic for the actual path, it can only be a function of the variables $\mathbf{q}$, $\dot{\mathbf{q}}$ and t. This minimization procedure is called the *action principle*[1]or the *principle of Hamilton.*

The principle of Hamilton is a variational principle that enables us to derive properties of the Lagrangian for systems in which the function $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$ is at least twice differentiable; i.e., *smooth* with respect to the variables $\mathbf{q}$, $\dot{\mathbf{q}}$ and t. Fortunately, many systems fall in this class and we shall study some examples. Let us consider the change in action of such a system over the time interval (t_0, t_1) when deforming the path defined by $\mathbf{q}(t)$ and $\dot{\mathbf{q}}(t)$ into an adjacent smooth continuous path $\mathbf{q}'(t)$ and $\dot{\mathbf{q}}'(t)$ given by $\mathbf{q}' = \mathbf{q} + \delta\mathbf{q}$ and $\dot{\mathbf{q}}' = \dot{\mathbf{q}} + \delta\dot{\mathbf{q}}$,

$$\delta S = \int_{t_0}^{t_1} [\mathcal{L}(\mathbf{q} + \delta\mathbf{q}, \dot{\mathbf{q}} + \delta\dot{\mathbf{q}}, t) - \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)]dt. \tag{A.59}$$

---

[1] Traditionally the action principle is called the *priciple of least action.* This is an unfortunate name because the variational method provides stationary points rather than minima.

As the Lagrangian is smooth we can use a Taylor expansion with respect to $\delta\mathbf{q}$ and $\delta\dot{\mathbf{q}}$,[1]

$$\mathcal{L}(\mathbf{q}+\delta\mathbf{q},\dot{\mathbf{q}}+\delta\dot{\mathbf{q}},t)=\mathcal{L}(\mathbf{q},\dot{\mathbf{q}},t)+\frac{\partial\mathcal{L}}{\partial\mathbf{q}}\cdot\delta\mathbf{q}+\frac{\partial\mathcal{L}}{\partial\dot{\mathbf{q}}}\cdot\delta\dot{\mathbf{q}}+\cdots, \tag{A.60}$$

and the change of action takes the form

$$\delta S=\int_{t_0}^{t_1}\sum_i\left(\frac{\partial\mathcal{L}}{\partial q_i}\delta q_i+\frac{\partial\mathcal{L}}{\partial\dot{q}_i}\delta\dot{q}_i\right)dt. \tag{A.61}$$

By partial integration of the second term this integral becomes

$$\delta S=\sum_i\left[\frac{\partial\mathcal{L}}{\partial\dot{q}_i}\delta q_i\right]_{t_0}^{t_1}+\int_{t_0}^{t_1}\sum_i\left(\frac{\partial\mathcal{L}}{\partial q_i}-\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{q}_i}\right)\delta q_i dt. \tag{A.62}$$

Since the variation is zero at the boundaries of the path, see (A.57), this expression reduces to

$$\delta S=\int_{t_0}^{t_1}\sum_i\left(\frac{\partial\mathcal{L}}{\partial q_i}-\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{q}_i}\right)\delta q_i dt. \tag{A.63}$$

At this point we can formulate a necessary condition for minimal action: the functional must be stationary ($\delta S=0$) under *arbitrary* variations of the path,[2]

$$\int_{t_0}^{t_1}\sum_i\left(\frac{\partial\mathcal{L}}{\partial q_i}-\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{q}_i}\right)\delta q_i dt=0. \tag{A.64}$$

Since the variations δq_i are independent this condition is only satisfied if all terms of the summation vanish simultaneously,

$$\frac{\partial\mathcal{L}}{\partial q_i}-\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{q}_i}=0,\quad\text{with } i\in\{1,\cdots,f\}. \tag{A.65}$$

These equations constitute the *Euler-Lagrange equations* of the action variational principle in which we recognize the *Lagrange equations* of classical mechanics. In Section A.3 these were obtained starting from the principle of d'Alembert.

The action principle has revealed the Lagrangian as the optimal functional from which the laws of physics of a mechanical of the system can be derived. As the Lagrangian is optimized by variation of the path in phase space it is independent of the choice of coordinates. The latter also holds for the form of the Lagrange equations.

Properties of the Lagrangian

Above the Lagrangian $\mathcal{L}(\mathbf{q},\dot{\mathbf{q}},t)$ is introduced as a smooth (at least twice differentiable) function of the variables, $\mathbf{q}$, $\dot{\mathbf{q}}$ and t for which the action is stationary under the condition that the Lagrange equations (A.65) are satisfied. Lagrangians have the following properties:

(a) *Additive property*: The Lagrangian $\mathcal{L}$ of a system consisting of two non-interacting subsystems can be written as the sum of the Lagrangians $\mathcal{L}_1$ and $\mathcal{L}_2$ of the two subsystems,

$$\mathcal{L}=\mathcal{L}_1+\mathcal{L}_2. \tag{A.66}$$

This has to be the case because the paths of the subsystems in configuration space can be varied independently. Hence, the least action of the total system must coincide with the sum of the least actions of the two subsystems.

---

[1] Note the following equivalent notations for the gradient operator, $\partial_{\mathbf{q}}\equiv\partial/\partial\mathbf{q}\equiv(\partial/\partial q_1,\cdots,\partial/\partial q_f)$.

[2] Note that the inverse is not generally true: being stationary does not mean that the action is minimal.

(b) *Definition up to a multiplicative factor*: The path of least action is invariant under multiplication of the Lagrangian by an arbitrary constant. For $\mathcal{L}' = \alpha\mathcal{L}$ we find

$$S' = \alpha \int_{t_0}^{t_1} \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)dt = \alpha S. \tag{A.67}$$

Hence, $\delta S' = \alpha\delta S$, which implies that the condition $\delta S' = 0$ is equivalent to $\delta S = 0$. This means that the multiplication by α does not affect the stationarity condition and leads to the same Euler-Lagrange equation.

(c) *Definition up to a total time derivative*: The path of least action is invariant under addition of a total time derivative to the Lagrangian. For $\mathcal{L}' = \mathcal{L} + d\mathrm{f}/dt$ we find

$$S' = \int_{t_0}^{t_1} \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)dt + \int_{t_0}^{t_1} \frac{d\mathrm{f}}{dt}dt = S + \mathrm{f}(t_1) - \mathrm{f}(t_0). \tag{A.68}$$

Hence, S' and S differ by a constant and this does not affect the variation, $\delta S' = \delta S$. Thus, the addition of $d\alpha/dt$ does not change the stationarity condition and leads to the same Euler-Lagrange equation.

A.4.2 Lagrangian of a free particle

To gain insight in the functional form of the Lagrangian we consider a free particle. In classical mechanics space and time are postulated to be homogeneous, so the Lagrangian of the particle (which determines the time evolution of the system) must be independent of position $\mathbf{r}$ and time t. This leaves the velocity $\mathbf{v} = \dot{\mathbf{r}}$ as the only variable, $\mathcal{L} = \mathcal{L}(\mathbf{v})$. Since $\mathcal{L}$ is independent of $\mathbf{r}$ we have $\partial\mathcal{L}/\partial\mathbf{r} = 0$ and the Lagrange equation (A.65) becomes

$$\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\mathbf{v}} = 0. \tag{A.69}$$

Hence, $\partial\mathcal{L}/\partial\mathbf{v}$ must be a constant and since $\mathbf{v}$ is the only variable of $\mathcal{L}$ the velocity must be constant, $\mathbf{v}(t) = \mathbf{v}_0$. Thus we found *Newton's law of inertia.*

Space is postulated to be isotropic. Thus, the Lagrangian may only depend on the absolute value of the velocity, v; i.e., it has to be some function of the velocity squared,

$$\mathcal{L} = \mathcal{L}(v^2). \tag{A.70}$$

This observation immediately implies that the Lagrangian is invariant under time reversal; i.e., time is isotropic in newtonian mechanics. To get more precise information about the functional dependence of $\mathcal{L}$ on v^2 we turn to *Galileo's principle of relativity*, which is also based on the homogeneity and isotropy of space and time. According to this principle the equations of motion (hence also the Lagrangian) must be *invariant under a Galilean transformation*, which is a transformation of one inertial frame to another (from the inertial frame $\mathcal{S}$ to the frame $\mathcal{S}'$)

$$\mathbf{r}' = \mathbf{r} + \mathbf{V}t; \qquad t' = t, \tag{A.71}$$

where $\mathbf{V}$ is the relative velocity of the frame $\mathcal{S}'$ with respect to the frame $\mathcal{S}$. Thus we are led to compare two Lagrangians, $\mathcal{L}(v'^2)$ and $\mathcal{L}(v^2)$, defined with respect to two inertial frames which move with an infinitesimally small but *constant* velocity $\mathbf{w} = \mathbf{v}' - \mathbf{v}$ with respect to each other. Using the relation $v'^2 = v^2 + 2\mathbf{v}\cdot\mathbf{w} + w^2$ we find

$$\mathcal{L}(v'^2) = \mathcal{L}(v^2) + \frac{\partial\mathcal{L}}{\partial v^2}(2\mathbf{v} + \mathbf{w})\cdot\mathbf{w} + \frac{\partial^2\mathcal{L}}{\partial(v^2)^2}\left[(2\mathbf{v} + \mathbf{w})\cdot\mathbf{w}\right]^2 + \cdots . \tag{A.72}$$

As the time evolution of the system must be independent of the choice of inertial frame, the two Lagrangians must be equivalent. In view of property (A.68) this means that they cannot differ by more than a total time derivative. Since $\mathbf{v}$ is by definition a total time derivative and $\mathbf{w}$ a constant, $\partial\mathcal{L}/\partial v^2$ has to be a constant; i.e., the function $\mathcal{L}$ has to be a linear function of v^2,

$$\mathcal{L} = \mathcal{L}_0 + \alpha v^2. \tag{A.73}$$

For any other functional dependence on v^2 the Lagrangian is either trivially zero or differs from $\mathcal{L}$ by more than a total time derivative. Once we accept that $\mathcal{L}$ has to be a linear function of v^2 we find that all higher order terms of the expansion vanish. As the constant $\mathcal{L}_0$ can also be regarded as a total time derivative we may write the Lagrangian as simply proportional to v^2,

$$\mathcal{L} = \tfrac{1}{2}mv^2 = T. \tag{A.74}$$

The proportionality constant m is called the *mass* of the particle and serves to calibrate the Lagrangian. This calibration is possible in view of property (A.67). The chosen calibration yields the *kinetic energy* of the particle, $T = \tfrac{1}{2}mv^2$.

For a free particle the principle of least action is very intuitive. The particle has to follow a straight path in configuration space (which coincides in this case with real space) because for a constant Lagrangian any deviation from a straight path leads to an increase of the action integral. The example also shows that the mass must be positive ($m > 0$) because otherwise the action could be reduced by deviating from the straight path, which contradicts experimental observation.

A.4.3 Lagrangian of a single particle in a potential field

Let us now add to the kinetic energy of the particle a (smooth) function of position and time (i.e., a time-dependent field),

$$\mathcal{L}(\mathbf{r}, \dot{\mathbf{r}}, t) = \tfrac{1}{2}mv^2 - U(\mathbf{r}, t). \tag{A.75}$$

Being a function of $\mathbf{r}$, $\dot{\mathbf{r}}$ and t, the new expression is again a Lagrangian if the Lagrange equations are satisfied:

$$\frac{\partial\mathcal{L}}{\partial\mathbf{r}} = \frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\mathbf{v}}. \tag{A.76}$$

When will this be the case? Since $U(\mathbf{r}, t)$ is independent of $\mathbf{v}$ and $T = \tfrac{1}{2}m\mathbf{v}^2$ is independent of $\mathbf{r}$ and t, substitution of (A.75) into the Lagrange equations (A.76) leads to the following condition

$$-\frac{\partial U}{\partial\mathbf{r}} = \frac{d}{dt}\frac{\partial T}{\partial\mathbf{v}} = m\frac{d\mathbf{v}}{dt}. \tag{A.77}$$

Interpreting the negative gradient of $U(\mathbf{r}, t)$ as a force,

$$\mathbf{F} = -\frac{\partial U}{\partial\mathbf{r}} \tag{A.78}$$

we recognize in (A.77) *Newton's second law*, $\mathbf{F} = m\ddot{\mathbf{r}}$. Hence, the Lagrange equations are satisfied if the particle moves in accordance with the Newton equations of motion; i.e., under non-relativistic conditions. The function $U(\mathbf{r}, t)$ is called the *potential field* of the system. If this field does not depend on position, $U(\mathbf{r}, t) = U(t)$, it is called *uniform.* If it does not depend on time, $U(\mathbf{r}, t) = U(\mathbf{r})$, the field is called *conservative.*

A.4.3.1 Generalized potential functions

The above discussion can be generalized to include velocity-dependent potentials, called *generalized potential functions.* For this purpose we add to the kinetic energy a (smooth) function of $\mathbf{r}$, $\dot{\mathbf{r}}$ and t,

$$\mathcal{L}(\mathbf{r}, \dot{\mathbf{r}}, t) = \tfrac{1}{2}mv^2 - U(\mathbf{r}, \dot{\mathbf{r}}, t). \tag{A.79}$$

This function is a Lagrangian if it satisfies the Lagrange equations. Substituting $\mathcal{L}(\mathbf{r}, \dot{\mathbf{r}}, t)$ into (A.76), we find that the condition (A.77) is replaced by

$$-\frac{\partial U}{\partial \mathbf{r}} + \frac{d}{dt}\frac{\partial U}{\partial \mathbf{v}} = \frac{d}{dt}\frac{\partial T}{\partial \mathbf{v}}. \tag{A.80}$$

In other words, the Lagrange equations are satisfied for *generalized forces* of the type

$$\mathbf{Q} = -\frac{\partial U}{\partial \mathbf{r}} + \frac{d}{dt}\frac{\partial U}{\partial \mathbf{v}}. \tag{A.81}$$

Note that (A.81) reduces to (A.78) for velocity-independent potentials; hence, the class of generalized forces includes gradient forces as a subclass. Although any generalized potential function gives rise to a generalized force, the inverse is *not* true. For instance, friction forces, $\mathbf{F} = -\alpha \mathbf{v}$, cannot be expressed in the form (A.81). On the other hand, the Lorentz force is an example of a generalized force because we can define a generalized potential function for which (A.81) is satisfied (see Problem A.2).

Problem A.2. Show, using the Einstein notation, that the Lorentz force, $F_i = q[E_i + (\mathbf{v} \times \mathbf{B})_i]$, is the generalized force resulting from the generalized potential function $U = q(\varphi - v_j \cdot A_j)$, where $\varphi(\mathbf{r}, t)$ is the scalar and $\mathbf{A}(\mathbf{r}, t)$ the vector potential. Further, $E_i = -\partial_i \varphi - \partial_t A_i$ and $B_i = \varepsilon_{ijk} \partial_j A_k$ are the cartesian components of the (generally time dependent) $\mathbf{E}$ and $\mathbf{B}$ fields, respectively. Use the short-hand notation $\partial_i \equiv \partial / \partial r_i$ and $\partial_t \equiv \partial / \partial t$.

Solution. The first term of (A.81) yields

$$-\partial_i U = q\left[-\partial_i \varphi - v_j \partial_i A_j(\mathbf{r}, t)\right] \tag{a}$$

and the second term can be written as

$$\frac{d}{dt}\frac{\partial U}{\partial v_i} = q\frac{d}{dt}\left(\frac{\partial \varphi(\mathbf{r}, t)}{\partial v_i} - \frac{\partial v_j A_j(\mathbf{r}, t)}{\partial v_i}\right) = -q\frac{d}{dt}A_i(\mathbf{r}, t) = q\left[-\partial_j A_i(\mathbf{r}, t)\, \dot{r}_j - \partial_t A_i(\mathbf{r}, t)\right]. \tag{b}$$

Combining (a) and (b) we obtain for the generalized force

$$Q_i = q\left[-\partial_i \varphi - \partial_t A_i + v_j \partial_i A_j - v_j \partial_j A_i\right]. \tag{c}$$

In the first two terms within the brackets we recognize the E_i-component of the $\mathbf{E}$ field. Likewise, recalling $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$, we recognize in the last two terms the component $(\mathbf{v} \times \mathbf{B})_i$ of the $\mathbf{v} \times \mathbf{B}$ field[1]

$$(\mathbf{v} \times \mathbf{B})_i = \varepsilon_{ijk} v_j (\boldsymbol{\nabla} \times \mathbf{A})_k = \varepsilon_{ijk} \varepsilon_{klm} v_j \partial_l A_m = v_j \partial_i A_j - v_j \partial_j A_i.$$

Hence, Eq. (c) can be rewritten as $Q_i = q\left[E_i + (\mathbf{v} \times \mathbf{B})_i\right]$, which is indeed the expression for the Lorentz force. □

A.5 Many-particle systems

A.5.1 Lagrangian

At this point we return to many-particle systems. In view of property (A.66) we know that the Lagrangian of a system of N *non*-interacting particles is given by

$$\mathcal{L} = \tfrac{1}{2} \sum_\alpha m_\alpha v_\alpha^2, \tag{A.82}$$

---

[1] In the Einstein notation the contraction of the Levi-Civita tensor is given by $\varepsilon_{ijk}\varepsilon_{klm} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}$.

where $\alpha \in \{1, \cdots N\}$. In search for the Lagrangian in the presence of interactions between the particles as well as interactions with the environment we use a procedure similar to the one introduced for the single particle: we add to the Lagrangian (A.82) a generalized potential function

$$\mathcal{L}(\cdots, \mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, \cdots, t) = \tfrac{1}{2} \sum_\alpha m_\alpha \dot{\mathbf{r}}_\alpha^2 - U(\cdots, \mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, \cdots, t). \tag{A.83}$$

The potential function depends in principle on the position and velocities of *all* the particles as well as on time

$$U(\cdots, \mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, \cdots, t) = U^{int}(\cdots, \mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, \cdots) + U^{ext}(\cdots, \mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, \cdots, t). \tag{A.84}$$

The function U^{int} is called the *internal* generalized potential function and represents the interaction between all particles of the system; *e.g.*, the Van der Waals interaction between the atoms in a classical gas. The function U^{ext} is called the *external* generalized potential function and represents externally applied fields; *e.g.*, the electromagnetic potential of a light field.

The function (A.83) is a Lagrangian if it satisfies the Lagrange equations,

$$\frac{\partial \mathcal{L}}{\partial \mathbf{r}_\alpha} = \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \mathbf{v}_\alpha}, \quad \text{with } \alpha \in \{1, \cdots N\}. \tag{A.85}$$

Since the first term on the r.h.s. of (A.83) is independent of $\mathbf{r}_\alpha$ we find that the condition (A.85) can be written in the form

$$-\frac{\partial U}{\partial \mathbf{r}_\alpha} + \frac{d}{dt} \frac{\partial U}{\partial \mathbf{v}_\alpha} = \frac{d}{dt} \frac{\partial T}{\partial \mathbf{v}_\alpha} = m_\alpha \ddot{\mathbf{r}}_\alpha, \quad \text{with } \alpha \in \{1, \cdots N\}. \tag{A.86}$$

Hence, the quantity

$$\mathbf{Q}_\alpha = -\frac{\partial U}{\partial \mathbf{r}_\alpha} + \frac{d}{dt} \frac{\partial U}{\partial \mathbf{v}_\alpha}, \quad \text{with } \alpha \in \{1, \cdots N\}, \tag{A.87}$$

can be interpreted as the generalized force acting on particle α as the result of its interaction with all other particles in the system.

Generalization to the presence of scleronomous constraints

It is straightforward to generalize the formalism to holonomic systems with *scleronomous* constraints. In this case the positions $\mathbf{r}_\alpha$ and velocities $\dot{\mathbf{r}}_\alpha$ of the particles can be expressed in terms of $f = 3N - l$ generalized coordinates $q_1, \cdots, q_f$ and velocities $\dot{q}_1, \cdots, \dot{q}_f$,

$$\mathbf{r}_\alpha = \mathbf{r}_\alpha(q_1, \cdots, q_f) \tag{A.88a}$$

$$\dot{\mathbf{r}}_\alpha = \sum_{i=1}^{f} \frac{\partial \mathbf{r}_\alpha}{\partial q_i} \dot{q}_i. \tag{A.88b}$$

Substituting these expressions into (A.83) we obtain

$$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}) = \tfrac{1}{2} \sum_{i,j=1}^{f} a_{ij}(\mathbf{q}) \dot{q}_i \dot{q}_j - U(\mathbf{q}, \dot{\mathbf{q}}). \tag{A.89}$$

Here we use the vector notation (A.18); the coefficient $a_{ij}(\mathbf{q})$ is given by

$$a_{ij}(\mathbf{q}) = \sum_\alpha m_\alpha \frac{\partial \mathbf{r}_\alpha}{\partial q_i} \frac{\partial \mathbf{r}_\alpha}{\partial q_j}. \tag{A.90}$$

In terms of the generalized coordinates and velocities the Lagrange equation take the form

$$\frac{\partial \mathcal{L}}{\partial q_i} = \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i}, \quad \text{with } i \in \{1, \cdots f\}, \tag{A.91}$$

and the components of the generalized force become

$$Q_i = -\frac{\partial U}{\partial q_i} + \frac{d}{dt}\frac{\partial U}{\partial \dot{q}_i}, \quad \text{with } i \in \{1, \cdots f\}. \tag{A.92}$$

Note that in the absence of constraints we have $f = 3N$ and the generalized coordinates turn into the cartesian coordinates of the particles, $(q_1, \cdots, q_f) \to (x_1, y_1, z_1, \cdots, x_N, y_N, z_N)$, and we regain (A.85) and (A.87).

Open and closed systems

A mechanical system is called *closed* if it does not interact with its environment; i.e., the potential function can be written as $U = U^{int}(\cdots, \mathbf{r}_\alpha, \dot{\mathbf{r}}_\alpha, \cdots)$. Hence, for closed systems both the potential function and the Lagrangian are time independent. An example of a closed mechanical system is an atom in field-free space. If the system is not closed it is called open. An example of an *open* system is a cloud of interacting particles confined by an external potential.

A.5.2 Energy conservation

In the absence of *time-dependent* external forces the evolution of a mechanical system only depends on the state of that system and not on the instant that this state is created in time. In view of this *homogeneity of time* the Lagrangian of such a system cannot depend explicitly on time; i.e., the total time derivative of (A.83) can be written in the form

$$\frac{d\mathcal{L}}{dt} = \sum_\alpha \frac{\partial \mathcal{L}}{\partial \mathbf{r}_\alpha} \cdot \dot{\mathbf{r}}_\alpha + \sum_\alpha \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} \cdot \ddot{\mathbf{r}}_\alpha. \tag{A.93}$$

With the aid of the Lagrange equation (A.85) this becomes

$$\frac{d\mathcal{L}}{dt} = \sum_\alpha \dot{\mathbf{r}}_\alpha \cdot \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} + \sum_\alpha \ddot{\mathbf{r}}_\alpha \cdot \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} = \sum_\alpha \frac{d}{dt}\left(\dot{\mathbf{r}}_\alpha \cdot \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha}\right). \tag{A.94}$$

Rewriting this expression in the form

$$\frac{d}{dt}\left(\sum_\alpha \dot{\mathbf{r}}_\alpha \cdot \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} - \mathcal{L}\right) = 0 \tag{A.95}$$

we find that the quantity

$$E = \sum_\alpha \dot{\mathbf{r}}_\alpha \cdot \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} - \mathcal{L} \tag{A.96}$$

is a *constant of the motion*; i.e., it is *conserved* along the path from t_0 to t_1. This quantity is called the *energy* of the system. Mechanical systems for which the energy is conserved are called *conservative* systems. It is straightforward to generalize (A.96) to holonomic systems with *scleronomous* constraints,

$$E(\mathbf{q}, \dot{\mathbf{q}}) = \sum_i \dot{q}_i \frac{\partial \mathcal{L}}{\partial \dot{r}_i} - \mathcal{L}. \tag{A.97}$$

A.5.2.1 Potential energy

The energy of a *conservative* system can always be written as the sum of a *kinetic energy* and a *potential energy* contribution. This can be seen as follows. The kinetic energy is uniquely determined by the velocities of the particles,

$$T(\dot{\mathbf{r}}_1, \cdots, \dot{\mathbf{r}}_N) = \tfrac{1}{2} \sum_\alpha m_\alpha v_\alpha^2.$$

In general this quantity will change in time under the influence of inter-particle forces but (since the system is conservative) the (total) energy has to remain constant, $E(\mathbf{r}_1, \cdots, \mathbf{r}_N, \dot{\mathbf{r}}_1, \cdots, \dot{\mathbf{r}}_N) = E$. Since the same kinetic energy can be obtained for different distributions of velocity over the particles the difference of E and T has to be a function of the positions *only.* This difference is called the *potential energy* $V(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ of the system,

$$V(\mathbf{r}_1, \cdots, \mathbf{r}_N) = E(\mathbf{r}_1, \cdots, \mathbf{r}_N, \dot{\mathbf{r}}_1, \cdots, \dot{\mathbf{r}}_N) - T(\dot{\mathbf{r}}_1, \cdots, \dot{\mathbf{r}}_N). \tag{A.98}$$

Beware of the difference between the potential energy $V(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ and the generalized potential function $U(\mathbf{r}_1, \cdots, \mathbf{r}_N, \dot{\mathbf{r}}_1, \cdots, \dot{\mathbf{r}}_N)$; the former determines the kinetic energy of a conservative system (also in the presence of generalized forces between the particles); the latter determines the force on all particles, both for conservative and non-conservative systems.

An *open* mechanical system is conservative if the external potential is constant in time.

A.5.3 Momentum conservation in closed systems

The evolution of a *closed* mechanical system only depends on the internal state of that system and not on the absolute position where this state is created in space. In view of this *homogeneity of space* the Lagrangian of a closed system must be independent of the absolute position of that system; i.e., (A.83) must be invariant under a translation of the system over a distance $\mathbf{R}$,

$$\mathbf{r}'_\alpha = \mathbf{r}_\alpha + \mathbf{R}. \tag{A.99}$$

Thus we are led to compare two Lagrangians, defined with respect to two inertial frames shifted with respect to each other over an infinitesimally small distance $\delta\mathbf{r}_\alpha = \mathbf{r}'_\alpha - \mathbf{r}_\alpha = \delta\mathbf{R}$. For this displagrangianlacement the change change in Lagrangian is given by

$$\delta\mathcal{L} = \sum_\alpha \frac{\partial\mathcal{L}}{\partial\mathbf{r}_\alpha} \cdot \delta\mathbf{R} + \cdots . \tag{A.100}$$

Hence, a necessary condition that the Lagrangian be invariant under an *arbitrary* small shift $\delta\mathbf{R}$ is

$$\sum_\alpha \frac{\partial\mathcal{L}}{\partial\mathbf{r}_\alpha} = 0. \tag{A.101}$$

Note that also the sum over all higher order terms has to vanish but this has no relevance in the present context. Using the Lagrange equation (A.85) the condition (A.101) becomes

$$\sum_\alpha \frac{\partial\mathcal{L}}{\partial\mathbf{r}_\alpha} = \frac{d}{dt} \sum_\alpha \frac{\partial\mathcal{L}}{\partial\mathbf{v}_\alpha} = 0. \tag{A.102}$$

Apparently, in a closed system the quantity

$$\mathbf{P} = \sum_\alpha \mathbf{p}_\alpha \tag{A.103}$$

with

$$\mathbf{p}_\alpha = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} \tag{A.104}$$

is a *constant of the motion.* The quantity $\mathbf{P}$ is called the *canonical momentum* of the system and $\mathbf{p}_\alpha$ is the canonical momentum of particle α. Hence, for closed systems the canonical momenta of the individual particles always add up to the total momentum of the system, irrespective of the absence or presence of generalized forces between the particles. With (A.85) it immediately follows that

$$\dot{\mathbf{p}}_\alpha = \frac{\partial \mathcal{L}}{\partial \mathbf{r}_\alpha}. \tag{A.105}$$

Example: velocity-independent potential functions

In the special case of systems with only *velocity-independent* interactions between the particles (e.g., gravitational forces) the canonical momentum only depends on the kinetic energy and we find the well-known expression

$$\mathbf{p}_\alpha = m_\alpha \mathbf{v}_\alpha. \tag{A.106}$$

The Hamiltonian is given by

$$E = \sum_\alpha m_\alpha \mathbf{v}_\alpha^2 - \mathcal{L}, \tag{A.107}$$

which becomes after substitution of the Lagrangian (A.83)

$$E = T + V. \tag{A.108}$$

A.5.3.1 Generalization to holonomic systems with scleronomous constraints - symmetry

It is straightforward to generalize (A.104) and (A.105) to *holonomic* systems with *scleronomous* constraints,

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i} \tag{A.109a}$$

$$\dot{p}_i = \frac{\partial \mathcal{L}}{\partial q_i} \tag{A.109b}$$

with $i \in \{1, \cdots f\}$.

A.5.4 Conservation of angular momentum in closed systems

In view of the *isotropy of space* the Lagrangian of a *closed* system must be independent of the absolute orientation of that system; i.e., (A.83) must be invariant under rotation of the system over an angle $\boldsymbol{\Omega}$ about an axis in direction $\hat{\boldsymbol{\Omega}}$ through the origin of the inertial frame of observation,

$$\mathbf{r}'_\alpha = \mathbf{r}_\alpha + \boldsymbol{\Omega} \times \mathbf{r}_\alpha. \tag{A.110}$$

Under such a rotation also the velocity vector changes direction

$$\mathbf{v}'_\alpha = \mathbf{v}_\alpha + \boldsymbol{\Omega} \times \mathbf{v}_\alpha. \tag{A.111}$$

Thus we are led to compare two Lagrangians, defined with respect to two inertial frames rotated with respect to each other over an infinitesimally small angle $\delta\boldsymbol{\Omega}$ so that $\delta\mathbf{r}_\alpha = \mathbf{r}'_\alpha - \mathbf{r}_\alpha = \delta\boldsymbol{\Omega} \times \mathbf{r}_\alpha$ and $\delta\mathbf{v}_\alpha = \mathbf{v}'_\alpha - \mathbf{v}_\alpha = \delta\boldsymbol{\Omega} \times \mathbf{v}_\alpha$. For this rotation we have

$$\delta\mathcal{L} = \sum_\alpha \frac{\partial \mathcal{L}}{\partial \mathbf{r}_\alpha} \cdot \delta\boldsymbol{\Omega} \times \mathbf{r}_\alpha + \sum_\alpha \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} \cdot \delta\boldsymbol{\Omega} \times \dot{\mathbf{r}}_\alpha + \cdots . \tag{A.112}$$

Hence, a necessary condition that the Lagrangian be invariant under an *arbitrary* rotation (about an axis through the origin) is

$$\sum_\alpha \left(\mathbf{r}_\alpha \times \frac{\partial \mathcal{L}}{\partial \mathbf{r}_\alpha} + \dot{\mathbf{r}}_\alpha \times \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_\alpha} \right) = 0. \tag{A.113}$$

Here we used the permutation rules for the vector products (see Appendix E). Turning to canonical variables the condition becomes

$$\sum_\alpha (\mathbf{r}_\alpha \times \dot{\mathbf{p}}_\alpha + \dot{\mathbf{r}}_\alpha \times \mathbf{p}_\alpha) = \frac{d}{dt} \sum_\alpha (\mathbf{r}_\alpha \times \mathbf{p}_\alpha) = 0. \tag{A.114}$$

Apparently, in a closed system the quantity

$$\mathbf{L} = \sum_\alpha (\mathbf{r}_\alpha \times \mathbf{p}_\alpha), \tag{A.115}$$

with

$$\mathbf{L}_\alpha \equiv \mathbf{r}_\alpha \times \mathbf{p}_\alpha, \tag{A.116}$$

is a constant of the motion. The quantity $\mathbf{L}$ is called the *angular momentum* of the system and $\mathbf{L}_\alpha$ is the angular momentum of particle α, both with respect to the origin of the inertial system. Although the value of $\mathbf{L}$ depends on the choice of origin, the conservation holds irrespective of this choice.

A.6 The Hamilton formalism

In the Lagrange formalism the dynamical evolution of mechanical systems is expressed in terms of the dynamical variables $\mathbf{q} \equiv (q_1, \cdots, q_f)$ and $\dot{\mathbf{q}} \equiv (\dot{q}_1, \cdots, \dot{q}_f)$ with the aid of the Lagrangian $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$ and the Lagrange equations. With this approach we identified the sum over the canonical momenta $\mathbf{p} \equiv (p_1, \cdots, p_f)$ as a conserved quantity of a closed mechanical system. In the Hamilton formalism the dynamical evolution is described in terms of the dynamical variables $\mathbf{q}$ and $\mathbf{p}$; i.e., the dependence on $\dot{\mathbf{q}}$ is eliminated from the formalism and replaced by a dependence on $\mathbf{p}$.

A.6.1 Legendre transformation of Lagrangian - Hamiltonian

To replace the dependence on $\dot{\mathbf{q}}$ by a dependence on $\mathbf{p}$ we use a Legendre transformation of the function $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$ into the function

$$H(\mathbf{q}, \mathbf{p}, t) = \mathbf{p} \cdot \dot{\mathbf{q}} - \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t). \tag{A.117}$$

The function $H(\mathbf{q}, \mathbf{p}, t)$ is called the *function of Hamilton* or *Hamiltonian* of the system. Note that with the sign convention of (A.117) the Hamiltonian represents the energy of the system

$$E = H(\mathbf{q}, \mathbf{p}, t). \tag{A.118}$$

To convince ourselves that the Hamiltonian has the desired properties we consider the total differential

$$dH = -d\mathcal{L} + d(\sum_i p_i \dot{q}_i). \tag{A.119}$$

For the total differential of the Lagrangian $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$ we have with the aid of (A.109a) and (A.109b)

$$d\mathcal{L} = \sum_i \frac{\partial \mathcal{L}}{\partial q_i} dq_i + \sum_i \frac{\partial \mathcal{L}}{\partial \dot{q}_i} d\dot{q}_i + \frac{\partial \mathcal{L}}{\partial t} dt = \sum_i \dot{p}_i dq_i + \sum_i p_i d\dot{q}_i + \frac{\partial \mathcal{L}}{\partial t} dt. \tag{A.120}$$

The total differential of the transformation term is

$$d(\sum_i p_i \dot{q}_i) = \sum_i \dot{q}_i dp_i + \sum_i p_i d\dot{q}_i. \tag{A.121}$$

Substituting (A.120) and (A.121) into (A.119) we obtain

$$dH = -\sum_i \dot{p}_i dq_i + \sum_i \dot{q}_i dp_i + \frac{\partial \mathcal{L}}{\partial t} dt. \tag{A.122}$$

Thus we have verified that H is indeed a function of $\mathbf{q}$ and $\mathbf{p}$. From the total differential we obtain

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{A.123a}$$

$$\dot{q}_i = +\frac{\partial H}{\partial p_i} \tag{A.123b}$$

with $i \in \{1, \cdots f\}$. These equations are called the *Hamilton equations* of motion. In view of their symmetrical form they are called the *canonical equations* of motion.

A.6.1.1 Energy conservation

From (A.122) we further infer

$$\frac{\partial H}{\partial t} = \frac{\partial \mathcal{L}}{\partial t}. \tag{A.124}$$

Together with (A.118) this shows that the energy is conserved if the Lagrangian (hence, also the Hamiltonian) do not depend explicitly on time; i.e., for $\partial H/\partial t = 0$.

A.6.1.2 Example: charged particle in an electromagnetic field

As an example of a system with a *time-independent* generalized potential function $U(\mathbf{r}, \dot{\mathbf{r}})$ we consider the motion of a charged particle in a static electromagnetic field. As we showed in Example A.3.2.3 the force on a charged particle can be written as the gradient of a generalized potential function

$$U(\mathbf{r}, \dot{\mathbf{r}}) = q[\varphi(\mathbf{r}) - \mathbf{v} \cdot \mathbf{A}(\mathbf{r})] \tag{A.125}$$

and the Lagrangian is of the form (A.33). As the kinetic energy is given by

$$T(\dot{\mathbf{r}}) = \tfrac{1}{2} m \mathbf{v}^2, \tag{A.126}$$

the Lagrangian becomes

$$\mathcal{L}(\mathbf{r}, \dot{\mathbf{r}}) \equiv \tfrac{1}{2} m \mathbf{v}^2 - q[\varphi - \mathbf{v} \cdot \mathbf{A}]. \tag{A.127}$$

From this we calculate the canonical momentum

$$\mathbf{p} \equiv \frac{\partial \mathcal{L}}{\partial \mathbf{v}} = m\mathbf{v} + q\mathbf{A}. \tag{A.128}$$

Thus we found that the canonical momentum consists in this case of two contributions; the first term is called the *kinetic momentum* and the second term the *electromagnetic momentum.* The Hamiltonian is given by

$$H = \mathbf{v} \cdot \mathbf{p} - \mathcal{L} = m\mathbf{v}^2 + q\mathbf{A} \cdot \mathbf{v} - \tfrac{1}{2} m \mathbf{v}^2 + q(\varphi - \mathbf{v} \cdot \mathbf{A}) = \tfrac{1}{2} m \mathbf{v}^2 + q\varphi. \tag{A.129}$$

The potential energy is given by

$$V(\mathbf{r}) = H - T = q\varphi(\mathbf{r}). \tag{A.130}$$

Expressing (A.129) in terms of the canonical variables $\mathbf{r}$ and $\mathbf{p}$ we obtain with the aid of (A.128) the Hamiltonian of the system,

$$H = \frac{1}{2m} (\mathbf{p} - q\mathbf{A})^2 + q\varphi. \tag{A.131}$$

A.7 Center of mass and relative coordinates

A.7.1 Center of mass motion of a closed system

In Section A.5.3 we found that the momentum of a *closed* mechanical system with *velocity-independent* interparticle forces,

$$\mathbf{P} = \sum_\alpha m_\alpha \dot{\mathbf{r}}_\alpha, \tag{A.132}$$

is conserved in time. However, this quantity is not conserved when changing from one inertial frame to another. Obviously, the velocity of the particles depends on the inertial system in which the velocity is measured. Hence, also the kinetic momentum depends on the inertial system. To analyze this dependence we change from the inertial frame $\mathcal{S}$ to a new inertial frame $\mathcal{S}'$ in which the origin of old frame is moving at velocity $\mathbf{V}$. This change of inertial system is described by a *galilean transformation*,

$$\mathbf{r}'_\alpha = \mathbf{r}_\alpha - \mathbf{V}t \tag{A.133a}$$

$$\dot{\mathbf{r}}'_\alpha = \dot{\mathbf{r}}_\alpha - \mathbf{V}. \tag{A.133b}$$

The observed difference in momentum between both inertial systems is given by

$$\mathbf{P}' = \mathbf{P} - \sum_\alpha m_\alpha \mathbf{V}. \tag{A.134}$$

This expression reveals the existence of an inertial frame in which the momentum is zero, $\mathbf{P}' = 0$. Thus we find for the momentum in an inertial system moving with velocity $\mathbf{V}$ with respect to the zero-momentum frame,

$$\mathbf{P} = \sum_\alpha m_\alpha \mathbf{V}. \tag{A.135}$$

In other words, the momentum of the entire system behaves like that of a single particle with mass

$$M = \sum_\alpha m_\alpha. \tag{A.136}$$

This quantity is called the *total mass* of the system. Introducing the position vector

$$\mathbf{R} = \sum_\alpha m_\alpha \mathbf{r}_\alpha / \sum_\alpha m_\alpha \tag{A.137}$$

we find the relation

$$\mathbf{P} = M\dot{\mathbf{R}} = M\mathbf{V}. \tag{A.138}$$

The vector $\mathbf{R}$ is called the *center of mass* of the system. Hence, in the zero-momentum frame the center of mass is at rest.

It is also instructive to compare the total angular momentum in the frame $\mathcal{S}'$ with that in the frame $\mathcal{S}$. Using Eq. (A.133a) the total angular momentum in the frame $\mathcal{S}'$ can be expressed as

$$\mathbf{L}' = \sum_\alpha (\mathbf{r}_\alpha \times \mathbf{p}'_\alpha) - \mathbf{V}t \times \sum_\alpha \mathbf{p}'_\alpha, \tag{A.139}$$

where $\mathbf{V}t$ is the position of the origin of $\mathcal{S}$ as observed in $\mathcal{S}'$. The second term vanishes if we choose for $\mathcal{S}'$ the zero-momentum frame. To proceed we multiply both sides of Eq. (A.133b) by the particles mass,

$$\mathbf{p}'_\alpha = \mathbf{p}_\alpha - m_\alpha \mathbf{V}. \tag{A.140}$$

Substituting this expression into Eq. (A.139) we find

$$\mathbf{L}' = \mathbf{L} - \sum_{\alpha} (m_\alpha \mathbf{r}_\alpha \times \mathbf{V}) . \tag{A.141}$$

In terms of the position and momentum of the center of mass this becomes

$$\mathbf{L} = \mathbf{L}' + \mathbf{R} \times \mathbf{P}. \tag{A.142}$$

Thus we recognize two contributions to the angular momentum of the system: $\mathbf{L}'$ is called the *intrinsic* angular momentum, which is the angular momentum with the center of mass at rest, and $\mathbf{R} \times \mathbf{P}$ is the angular momentum resulting from the center of mass motion in the inertial frame of reference.

A.7.2 Relative motion in a closed system of two atoms

To deal with interatomic interactions and collisions between particles one introduces *relative coordinates*. The position of particle 1 relative to particle 2 is given by

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{A.143}$$

Taking the derivative with respect to time we find for the relative velocity of particle 1 with respect to particle 2

$$\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2. \tag{A.144}$$

Let us analyze in some detail the case of a system of two particles. The total momentum of the pair (the center of mass momentum) is a conserved quantity and given by

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 = m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = m_1 \dot{\mathbf{r}}_1 + m_2 \dot{\mathbf{r}}_2. \tag{A.145}$$

The total mass is given by the sum of the two particles masses, $M = m_1 + m_2$. With the relation $\mathbf{P} = M\mathbf{V}$, where $\mathbf{V} = \dot{\mathbf{R}}$ is the center of mass velocity, we find for the position of the center of mass

$$\mathbf{R} = (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2)/(m_1 + m_2). \tag{A.146}$$

Adding and subtracting (A.145) and (A.144) allows us to express $\mathbf{v}_1$ and $\mathbf{v}_2$ in terms of $\mathbf{P}$ and $\mathbf{v}$,

$$\mathbf{P} + m_2 \mathbf{v} = (m_1 + m_2)\, \mathbf{v}_1 \tag{A.147a}$$

$$\mathbf{P} - m_1 \mathbf{v} = (m_1 + m_2)\, \mathbf{v}_2. \tag{A.147b}$$

With these expressions the total kinetic energy of the pair, $E = \epsilon_1 + \epsilon_2$, can be split in a contribution of the *center of mass* and a contribution of the relative motion

$$E = \frac{1}{2} m_1 \mathbf{v}_1^2 + \frac{1}{2} m_2 \mathbf{v}_2^2 = \frac{1}{2} m_1 \frac{(\mathbf{P} + m_2 \mathbf{v})^2}{(m_1 + m_2)^2} + \frac{1}{2} m_2 \frac{(\mathbf{P} - m_1 \mathbf{v})^2}{(m_1 + m_2)^2} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2m_r}, \tag{A.148}$$

where

$$\mathbf{p} = m_r \mathbf{v} = m_r \dot{\mathbf{r}} = \frac{m_r}{m_1} \mathbf{p}_1 - \frac{m_r}{m_2} \mathbf{p}_2 \tag{A.149}$$

is the relative momentum with

$$m_r = m_1 m_2/(m_1 + m_2) \tag{A.150}$$

representing the *reduced mass* of the pair. Because both $\mathbf{P}$ and E are conserved quantities in elastic collisions also $\mathbf{p}^2$ must be conserved. This implies that in elastic collisions the relative momentum

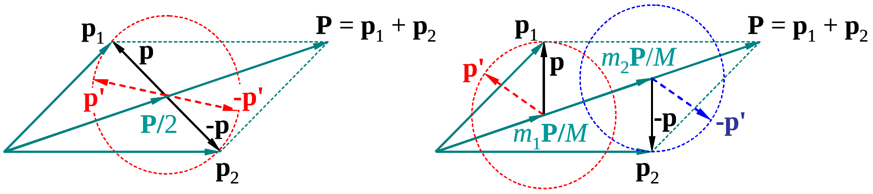

Figure A.1: Center of mass and relative momenta for two colliding atoms: *left*: equal mass; *right*: unequal mass with $m_1/m_2 = 1/3$.

$p = |\mathbf{p}|$ is conserved, but *not* its direction. Adding and subtracting (A.143) and (A.146) we can express $\mathbf{r}_1$ and $\mathbf{r}_2$ in terms of $\mathbf{R}$ and $\mathbf{r}$,

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r} \text{ and } \mathbf{r}_2 = \mathbf{R} - \frac{m_1}{M}\mathbf{r}. \tag{A.151}$$

Likewise combining (A.145) and (A.149) we can express $\mathbf{p}_1$ and $\mathbf{p}_2$ in terms of $\mathbf{P}$ and $\mathbf{p}$,

$$\mathbf{p}_1 = \frac{m_1}{M}\mathbf{P} + \mathbf{p} \text{ and } \mathbf{p}_2 = \frac{m_2}{M}\mathbf{P} - \mathbf{p}. \tag{A.152}$$

The vector diagram is shown in Fig. A.1.

Problem A.3. Show that the Jacobian of the transformation $d\mathbf{r}_1 d\mathbf{r}_2 = \left|\frac{\partial(\mathbf{r}_1,\mathbf{r}_2)}{\partial(\mathbf{R},\mathbf{r})}\right| d\mathbf{R}d\mathbf{r}$ is -1.

Solution. Because the x, y and z directions separate we can write the Jacobian as the product of three 1D Jacobians.

$$\left|\frac{\partial(\mathbf{r}_1,\mathbf{r}_2)}{\partial(\mathbf{R},\mathbf{r})}\right| = \prod_{i=x,y,z}\left|\frac{\partial(r_{1i},r_{2i})}{\partial(R_i,r_i)}\right| = \prod_{i=x,y,z}\begin{vmatrix} 1 & m_1/M \\ 1 & -m_2/M \end{vmatrix} = -1. \qquad \square$$

Problem A.4. Show that the Jacobian of the transformation $d\mathbf{p}_1 d\mathbf{p}_2 = \left|\frac{\partial(\mathbf{p}_1,\mathbf{p}_2)}{\partial(\mathbf{P},\mathbf{p})}\right| d\mathbf{P}d\mathbf{p}$ is -1.

Solution. Because the x, y and z directions separate we can write the Jacobian as the product of three 1D Jacobians.

$$\left|\frac{\partial(\mathbf{p}_1,\mathbf{p}_2)}{\partial(\mathbf{P},\mathbf{p})}\right| = \prod_{i=x,y,z}\left|\frac{\partial(p_{1i},p_{2i})}{\partial(P_i,p_i)}\right| = \prod_{i=x,y,z}\begin{vmatrix} m_1/M & 1 \\ m_2/M & -1 \end{vmatrix} = -1. \qquad \square$$

A.7.3 Kinematics of scattering

In any collision the momentum $\mathbf{P}$ is conserved. Thus, also the center of mass energy $\mathbf{P}^2/2M$ is conserved and since also the total energy must be conserved also the relative kinetic energy $\mathbf{p}^2/2m_r$ is conserved in *elastic* collisions, be it in general not *during* the collision. In this section we consider the consequence of the conservation laws for the momentum transfer between particles in elastic collisions in which the relative momentum changes from $\mathbf{p}$ to $\mathbf{p}'$, with $\mathbf{q} = \mathbf{p}' - \mathbf{p}$. Because the relative energy is conserved, also the modulus of the relative momentum will be conserved, $|\mathbf{p}| = |\mathbf{p}'|$, and the only effect of the collision is to change the direction of the relative momentum over an angle ϑ. Hence, the *scattering angle* ϑ fully determines the energy and momentum transfer in the collision. Using (A.147) the momenta of the particles before and after the collision (see Fig. A.1) are given by

$$\mathbf{p}_1 = m_1\mathbf{P}/M + \mathbf{p} \longrightarrow \mathbf{p}_1' = m_1\mathbf{P}/M + \mathbf{p}' \tag{A.153a}$$

$$\mathbf{p}_2 = m_2\mathbf{P}/M - \mathbf{p} \longrightarrow \mathbf{p}_2' = m_2\mathbf{P}/M - \mathbf{p}'. \tag{A.153b}$$

Hence, the momentum transfer is

$$\Delta\mathbf{p}_1 = \mathbf{p}_1' - \mathbf{p}_1 = \mathbf{p}' - \mathbf{p} = \mathbf{q} \tag{A.154a}$$

$$\Delta\mathbf{p}_2 = \mathbf{p}_2' - \mathbf{p}_2 = \mathbf{p} - \mathbf{p}' = -\mathbf{q}. \tag{A.154b}$$

The energy transfer is

$$\Delta E_1 = \frac{\mathbf{p}_1'^2}{2m_1} - \frac{\mathbf{p}_1^2}{2m_1} = \frac{(m_1\mathbf{P}/M + \mathbf{p}')^2}{2m_1} - \frac{(m_1\mathbf{P}/M + \mathbf{p})^2}{2m_1} = \frac{\mathbf{P}\cdot\mathbf{q}}{M} \tag{A.155a}$$

$$\Delta E_2 = \frac{\mathbf{p}_2'^2}{2m_2} - \frac{\mathbf{p}_2^2}{2m_2} = \frac{(m_2\mathbf{P}/M - \mathbf{p}')^2}{2m_2} - \frac{(m_2\mathbf{P}/M - \mathbf{p})^2}{2m_2} = -\frac{\mathbf{P}\cdot\mathbf{q}}{M}. \tag{A.155b}$$

In the special case $\mathbf{p}_1 = 0$ we have

$$\mathbf{P} = \mathbf{p}_2 = \frac{-\mathbf{p}}{1 - m_2/M} = -\frac{M}{m_1}\mathbf{p} \tag{A.156}$$

or

$$\mathbf{p} = -m_r\mathbf{v}_2. \tag{A.157}$$

The momentum transfer becomes

$$q = \sqrt{\mathbf{q}^2} = \sqrt{(\mathbf{p}' - \mathbf{p})^2} = \sqrt{2\mathbf{p}^2 - 2\mathbf{p}'\cdot\mathbf{p}} = p\sqrt{2 - 2\cos\vartheta}. \tag{A.158}$$

For small angles this implies

$$\vartheta = q/p. \tag{A.159}$$

The energy transfer becomes

$$\Delta E_1 = \frac{\mathbf{P}\cdot\mathbf{q}}{M} = -\frac{\mathbf{p}\cdot(\mathbf{p}' - \mathbf{p})}{m_1} = \frac{\mathbf{p}^2}{m_1}(1 - \cos\vartheta) = \frac{m_r^2}{m_1}\mathbf{v}_2^2(1 - \cos\vartheta), \tag{A.160}$$

where ϑ is the scattering angle. This can be written in the form

$$\Delta E_1 = \tfrac{1}{4}\xi m_2\mathbf{v}_2^2(1 - \cos\vartheta), \tag{A.161}$$

where

$$\xi = \frac{4m_r^2}{m_1 m_2} = \frac{4m_1 m_2}{(m_1 + m_2)^2} = 4\frac{m_r}{M}. \tag{A.162}$$

is the thermalization efficiency parameter. For $m_1 = m_2$ this parameter reaches its maximum value ($\xi = 1$) and we obtain

$$\Delta E_1 = \tfrac{1}{2}E_2(1 - \cos\vartheta). \tag{A.163}$$

For $m_1 \ll m_2$ the efficiency parameter is given by $\xi \simeq 4m_1/m_2$.

B

Various concepts from Quantum Mechanics

In this appendix we give a summary of formal quantum mechanics for purposes of internal reference. For a proper introduction the reader is referred to one of the major textbooks on quantum mechanics, such as those by Paul Dirac [19], Albert Messiah [49, 50], Gordon Baym [5], Claude Cohen Tannoudji, Bernard Diu and Franck Laloë [10], Eugen Merzbacher [48], and Jun John Sakurai [63].

B.1 Dirac formalism

B.1.1 Introduction

In the formulation of Dirac, the dynamical state of a physical system is established by observation of its *dynamical variables* (e.g., the position of a particle, its translational momentum, orbital angular momentum with respect to a point of reference, spin, energy, ...). Each dynamical variable $\mathcal{A}$ corresponds to a *hermitian operator* A which defines a *complete orthonormal set of eigenstates* $\{|a_i\rangle\}$ called *kets*, representing the *basis vectors* of a complex vector space, the *Hilbert space* of the dynamical system. A hermitian operator with the mentioned properties is called an *observable.* The set of eigenstates $\{|a_i\rangle\}$ is called a *representation* of the Hilbert space, often referred to as the representation $\{A\}$. The representation $\{A\}$ serves to describe measurements of the observable A. The measurement is expressed by the eigenvalue relation

$$A|a_i\rangle = a_i|a_i\rangle, \tag{B.1}$$

where a_i is the eigenvalue corresponding to the eigenstate $|a_i\rangle$. Observables are characterized by a spectrum of *real* eigenvalues. The kets are abstract state vectors which provide a *representation-free notation* for the *states.* In this introduction we focus on *discrete* representations (e.g., the standard representation $\{L^2, L_z\}$ of orbital angular momentum - cf. Appendix B.1.3). The discussion can be extended to *continuous* representations in which summations are replaced by integrations and in the orthonormality condition the Kronecker symbol becomes a Dirac delta function - cf. Appendix B.1.2.

By *completeness* we mean that an arbitrary state $|\psi\rangle$ of the system can be *represented* by the linear superposition,

$$|\psi\rangle = \sum_i |a_i\rangle\langle a_i|\psi\rangle, \tag{B.2}$$

where $\langle a_i|\psi\rangle$ is the *inner product* of the vectors $|\psi\rangle$ and $|a_i\rangle$; i.e., the *projection* of $|\psi\rangle$ onto $|a_i\rangle$. This is called the *superposition principle.* In matrix notation $\langle a_i|$ is written as a row vector and $|\psi\rangle$ as a column vector. In the Dirac formalism, the vectors $\langle a_i|$ are called *bras.* They are related to the *kets* by hermitian conjugation (antilinear transposition - in matrix notation the column vector is transformed into a row vector with the coordinates replaced by their complex conjugates; i.e., $\langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle$). The *orthonormality* of the basis is expressed by the property $\langle a_j|a_i\rangle = \delta_{ij}$.

The inner product $\langle a_i|\psi\rangle$ represents the *amplitude*, short for *probability amplitude*, to observe the eigenstate $|a_i\rangle$ when the system prepared in the state $|\psi\rangle$. The corresponding *density*, short for *probability density* or *occupation density*, is given by

$$\mathcal{P}_i = |\langle a_i|\psi\rangle|^2. \tag{B.3}$$

The completeness of the representation $\{A\}$ is expressed by the *Parseval relation* (which is a probability sum rule),

$$\sum_i \mathcal{P}_i = \sum_i |\langle a_i|\psi\rangle|^2 = 1 \tag{B.4}$$

and the *closure relation* (which is a decomposition sum rule),

$$\mathbb{1} = \sum_i |a_i\rangle\langle a_i|. \tag{B.5}$$

Here $\mathbb{1}$ is the *identity operator*.

Presuming $|\psi\rangle$ to be normalized, $\langle\psi|\psi\rangle = 1$, the quantity

$$\langle A\rangle = \langle\psi|A|\psi\rangle \tag{B.6}$$

is called the *expectation value* of the operator A. For $|\phi\rangle = A|\psi\rangle$ we write $\langle\psi|A^\dagger = \langle\phi|$, where $A^\dagger$ is called the hermitian conjugate of A. This implies the relation

$$\langle\psi|A|\psi\rangle^* = \langle\psi|A^\dagger|\psi\rangle, \tag{B.7}$$

which is real for hermitian operators ($A^\dagger = A$). If the matrix elements $\langle b_i|A|b_j\rangle$ of the operator A are known in some representation $\{B\}$, the expectation value is given by

$$\langle A\rangle = \sum_{i,j}\langle\psi|b_j\rangle\langle b_j|A|b_i\rangle\langle b_i|\psi\rangle. \tag{B.8}$$

For the representation $\{A\}$, defined above, the matrix is diagonal, $\langle a_i|A|a_j\rangle = a_i\delta_{i,j}$, and Eq. (B.8) reduces to

$$\langle A\rangle = \sum_i\langle\psi|a_i\rangle a_i\langle a_i|\psi\rangle = \sum_i a_i\mathcal{P}_i. \tag{B.9}$$

This result is also intuitively correct: the expectation value corresponds to the sum of the eigenvalues weighted by the probability to have that eigenvalue.

Two dynamical variables $\mathcal{A}$ and $\mathcal{B}$ are called *compatible* if they can be measured simultaneously to arbitrary precision; i.e., share a complete set of eigenstates. This is the case if and only if the corresponding operators A and B commute. Operators that do not commute are called *incompatible*. In general, the shared basis is not uniquely defined, because two eigenstates can have the same eigenvalues. This is called *degeneracy*. To obtain a unique basis a *complete set of commuting observables* $A, B, C, \cdots$ is required, together providing all quantum numbers of the dynamical system. This is called the representation $\{A, B, C, \cdots\}$.

Problem B.1. Show that two commuting observables A and B share a complete set of eigenstates.

Solution. Consider the eigenvalue equations for the operators A and B,

$$A\,|\alpha,k\rangle = \alpha\,|\alpha,k\rangle \text{ and } B\,|\beta,l\rangle = \beta\,|\beta,l\rangle\,,$$

where $\{|\alpha,k\rangle\}$ is a complete set of k_α-fold degenerate states corresponding to the operator A and $\{|\beta,l\rangle\}$ a complete set of l_β-fold degenerate states corresponding to the operator B. In search for a joint basis we know that the eigenstates of A can be expressed in the eigenstates of B

$$|\alpha,k\rangle = \sum_\beta\sum_{l=1}^{l_\beta}|\beta,l\rangle\,\langle\beta,l|\alpha,k\rangle = \sum_\beta|\beta\rangle\,,$$

where

$$|\beta\rangle \equiv \sum_{l=1}^{l_\beta} |\beta, l\rangle \langle \beta, l|\alpha, k\rangle .$$

Note that $|\beta\rangle$ is a linear combination of *degenerate* eigenstates of B, all with eigenvalue β. This implies that $|\beta\rangle$ itself is an eigenstate of B with eigenvalue β as follows from

$$B|\beta\rangle \equiv \sum_{l=1}^{l_\beta} B|\beta, l\rangle \langle \beta, l|\alpha, k\rangle = \sum_{l=1}^{l_\beta} \beta|\beta, l\rangle \langle \beta, l|\alpha, k\rangle = \beta|\beta\rangle .$$

Next we show that $|\beta\rangle$ is also an eigenstate of A. Since $[A, B] = 0$ we have

$$B(A|\beta\rangle) = AB|\beta\rangle = A\beta|\beta\rangle = \beta(A|\beta\rangle).$$

Hence $A|\beta\rangle$ is also an eigenstate of B with eigenvalue β. Having the eigenvalue β this eigenstate has to be of the form, $A|\beta\rangle = \lambda|\beta\rangle$. This shows that $|\beta\rangle$ is also an eigenstate of A. The corresponding eigenvalue λ has to be equal to α as follows from

$$\sum_\beta A|\beta\rangle = A|\alpha, k\rangle = \alpha|\alpha, k\rangle = \sum_\beta \alpha|\beta\rangle . \qquad \square$$

B.1.2 Continuous bases - position and momentum representation

For a particle in the *arbitrary* state $|\psi\rangle$ the wavefunction $\psi(\mathbf{r})$ represents the probability amplitude to observe the particle at position $\mathbf{r}$. The $\psi(\mathbf{r})$ defines the state $|\psi\rangle$ in the *position representation* and $\mathbf{r}$ stands for the *position coordinates*. In the Dirac formalism the same probability amplitude is obtained by projecting the state vector $|\psi\rangle$ onto the eigenstate $|\mathbf{r}\rangle$ of the position operator $\underline{\mathbf{r}}$,

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle. \tag{B.10}$$

The set $\{|\mathbf{r}\rangle\}$ forms a basis of the Hilbert space of the particle because $|\psi\rangle$ is completely defined by specifying the probability amplitude $\psi(\mathbf{r})$ for all values of $\mathbf{r}$,

$$|\psi\rangle = \int d\mathbf{r}\, |\mathbf{r}\rangle\langle \mathbf{r}|\psi\rangle. \tag{B.11}$$

This shows that the closure relation is given by

$$\mathbb{1} = \int d\mathbf{r}\, |\mathbf{r}\rangle\langle \mathbf{r}| \tag{B.12}$$

and the Parseval relation takes the form of the normalization integral,

$$1 = \int d\mathbf{r} |\langle \mathbf{r}|\psi\rangle|^2 = \int |\psi(\mathbf{r})|^2 d\mathbf{r}. \tag{B.13}$$

To find the orthogonality relation for the position representation we note that the probability amplitude to observe the particle at position $\mathbf{r}'$ is given by

$$\psi(\mathbf{r}') = \int d\mathbf{r}\, \langle \mathbf{r}'|\mathbf{r}\rangle \psi(\mathbf{r}). \tag{B.14}$$

Since $|\psi\rangle$ was chosen arbitrary this implies

$$\langle \mathbf{r}'|\mathbf{r}\rangle = \delta(\mathbf{r} - \mathbf{r}'), \tag{B.15}$$

which is the Dirac deltafunction in three dimensions.

In search for the *momentum representation* we consider the Fourier transform

$$\psi(\mathbf{p}) = \int d\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\psi(\mathbf{r}). \tag{B.16}$$

The inverse transform is given by

$$\psi(\mathbf{r}) = (2\pi\hbar)^{-3}\int d\mathbf{p}\, e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\psi(\mathbf{p}). \tag{B.17}$$

In the plane wave $e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$ we recognize the wavefunction of a free particle in state $|\mathbf{p}\rangle$,

$$\langle\mathbf{r}|\mathbf{p}\rangle = e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{B.18}$$

Substituting this expression into the Fourier transform (B.16) we find with the aid of the closure relation (B.12)

$$\psi(\mathbf{p}) = \int d\mathbf{r}\, \langle\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle = \langle\mathbf{p}|\psi\rangle. \tag{B.19}$$

Substituting this expression into the inverse transform we obtain

$$|\psi\rangle = (2\pi\hbar)^{-3}\int d\mathbf{p}\, |\mathbf{p}\rangle\langle\mathbf{p}|\psi\rangle. \tag{B.20}$$

Since $|\psi\rangle$ was chosen arbitrarily, this shows that the set $\{|\mathbf{p}\rangle\}$ forms the basis of the momentum representation for the Hilbert of the particle. The wavefunction $\psi(\mathbf{p}) = \langle\mathbf{p}|\psi\rangle$ represents the probability amplitude that the particle is measured with momentum $\mathbf{p}$. The closure relation is given by

$$\mathbb{1} = (2\pi\hbar)^{-3}\int d\mathbf{p}\, |\mathbf{p}\rangle\langle\mathbf{p}| \tag{B.21}$$

and the Parseval relation becomes,

$$1 = (2\pi\hbar)^{-3}\int d\mathbf{p}|\langle\mathbf{p}|\psi\rangle|^2 = (2\pi\hbar)^{-3}\int |\psi(\mathbf{p})|^2 d\mathbf{p}. \tag{B.22}$$

To find the orthogonality relation we note that the probability amplitude to find the particle with momentum $\mathbf{p}'$ is given by

$$\psi(\mathbf{p}') = (2\pi\hbar)^{-3}\int d\mathbf{p}\, \langle\mathbf{p}'|\mathbf{p}\rangle\psi(\mathbf{p}). \tag{B.23}$$

Since $|\psi\rangle$ was chosen arbitrary we obtain

$$\langle\mathbf{p}'|\mathbf{p}\rangle = (2\pi\hbar)^3\delta(\mathbf{p}-\mathbf{p}'). \tag{B.24}$$

Using the closure relation (B.12) as well as Eq. (B.18) we find the expression

$$\int d\mathbf{r}\langle\mathbf{p}'|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{p}\rangle = \int d\mathbf{r}\, e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}/\hbar} = (2\pi\hbar)^3\delta(\mathbf{p}-\mathbf{p}'). \tag{B.25}$$

B.1.3 Discrete basis - orbital angular momentum

As an example of a discrete basis, we discuss the case of orbital angular momentum. The three cartesian components of the angular momentum operator $\mathbf{L}$ satisfy the commutation relations

$$[L_x, L_y] = i\hbar L_z,\ [L_y, L_z] = i\hbar L_x \text{ and } [L_z, L_x] = i\hbar L_y. \tag{B.26}$$

These are the generic commutation relations for any type of angular momentum. The Hermitian operators that uniquely define the state of orbital angular momentum are the operators $\mathbf{L}^2$ and L_z. Their shared basis $\{|l, m_l\rangle\}$ is defined by

$$\mathbf{L}^2 |l, m_l\rangle = l(l+1)\hbar^2 |l, m_l\rangle \tag{B.27a}$$

$$L_z |l, m_l\rangle = m_l \hbar |l, m_l\rangle , \tag{B.27b}$$

where the $|l, m_l\rangle$ are abstract (*i.e.*, representation-free) state vectors in Hilbert space, with l and m_l the *rotational quantum numbers.* The basis $\{|l, m_l\rangle\}$ is called the *standard representation* $\{L^2, L_z\}$ of angular momentum. The spherical harmonics

$$Y_l^{m_l}(\theta, \phi) \equiv Y_l^{m_l}(\hat{\mathbf{r}}) = \langle \hat{\mathbf{r}} | l, m_l\rangle \tag{B.28}$$

are the corresponding wavefunctions in the position representation of spherical coordinates.

B.1.4 Spin coordinates, spinor states and spinorbitals

The "wavefunction" $\chi(\sigma)$ of the spin of a particle in the angular momentum state $|\chi\rangle$ is obtained by projection of $|\chi\rangle$ onto one of the eigenstates $\{|\sigma\rangle\}$ of the s_z operator,

$$\chi(\sigma) = \langle \sigma | \chi\rangle = \sum_{m_s=-s}^{s} \langle \sigma | s, m_s\rangle \langle s, m_s | \chi\rangle, \tag{B.29}$$

where σ assumes discrete values in the interval $s \leq \sigma \leq s$. Hence, the function $\chi(\sigma)$ is a function of the discrete variable σ, the *spin coordinate.* For a particle in spin state χ the spinor $\chi(\sigma)$ represents the probability amplitude to detect the particle in the eigenstate σ. For s being *half-integral* it is called a $2s+1$ component *spinor* (to distinguish its rotation properties from scalar and vector functions). The basis states are denoted by the unit spinors

$$\chi_{m_s}(\sigma) \equiv \langle \sigma | s, m_s\rangle = \delta_{m_s,\sigma}, \tag{B.30}$$

where m_s assumes discrete values in the interval $s \leq m_s \leq s$. For the special case of $s = \frac{1}{2}$ the eigenstates are often written in the arrow notation, $\chi_{+1/2}(\sigma) \equiv \chi_{\uparrow}(\sigma)$ and $\chi_{-1/2}(\sigma) \equiv \chi_{\downarrow}(\sigma)$.

As an example we consider the case $s = \frac{1}{2}$, where the summation runs over the values $m_s \in \{-\frac{1}{2}, +\frac{1}{2}\}$,

$$\chi(\sigma) = \chi_{\uparrow}(\sigma)\langle +\tfrac{1}{2}|\chi\rangle + \chi_{\downarrow}(\sigma)\langle -\tfrac{1}{2}|\chi\rangle. \tag{B.31}$$

Note that $\chi(\sigma) = \langle \pm\frac{1}{2}|\chi\rangle$ for $\sigma = \pm\frac{1}{2}$. In the *matrix representation* the $s = \frac{1}{2}$ spinors take the form of a column vector,

$$\chi(\sigma) = \begin{pmatrix} \langle +\frac{1}{2}|\chi\rangle \\ \langle -\frac{1}{2}|\chi\rangle \end{pmatrix} = \langle +\tfrac{1}{2}|\chi\rangle \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \langle -\tfrac{1}{2}|\chi\rangle \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{B.32}$$

and the basis vectors take the form (up to a not observable phase factor)

$$\chi_{\uparrow}(\sigma) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_{\downarrow}(\sigma) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{B.33}$$

The spinor concept is readily extended from *discrete spinor* functions to *spinor fields.* Such an extension is essential to describe particles with both motional and spin degrees of freedom (for example the electron). Since $\boldsymbol{s}$ and $\underline{\mathbf{r}}$ are commuting observables they must share a complete set of basis functions, obtained as the *tensor product* of their eigenstates

$$|\mathbf{r}, \sigma\rangle \equiv |\mathbf{r}\rangle \otimes |\sigma\rangle. \tag{B.34}$$

The tensor product assures that for every eigenvalue of one operator the state can assume all eigenvalues of the other operator. An arbitrary state can be written in the form

$$\psi\left(\mathbf{r},\sigma\right)=\langle\mathbf{r},\sigma|\psi\rangle=\varphi\left(\mathbf{r}\right)\chi(\sigma),\tag{B.35}$$

where $\varphi\left(\mathbf{r}\right)=\langle\mathbf{r}|\varphi\rangle$ is the wavefunction in the position representation and $\chi(\sigma)=\langle\sigma|\chi\rangle$ a discrete spinor.

For the case $s=\frac{1}{2}$ this implies

$$\psi\left(\mathbf{r},\sigma\right)=\varphi\left(\mathbf{r}\right)\langle+\tfrac{1}{2}|\chi\rangle\chi_{\uparrow}(\sigma)+\varphi\left(\mathbf{r}\right)\langle-\tfrac{1}{2}|\chi\rangle\chi_{\downarrow}(\sigma).\tag{B.36}$$

In matrix form this becomes

$$\psi\left(\mathbf{r},\sigma\right)=\begin{pmatrix}\psi\left(\mathbf{r},+1/2\right)\\ \psi\left(\mathbf{r},-1/2\right)\end{pmatrix}=\psi\left(\mathbf{r},+1/2\right)\begin{pmatrix}1\\0\end{pmatrix}+\psi\left(\mathbf{r},-1/2\right)\begin{pmatrix}0\\1\end{pmatrix},\tag{B.37}$$

where $\psi\left(\mathbf{r},\pm1/2\right)$ is a *double-valued* function representing the probability amplitude to observe the particle at position $\mathbf{r}$ in spin state $|\pm\frac{1}{2}\rangle$.

If a particle is prepared in the motional state $|\varphi\rangle=|\mathbf{k}\rangle$ and spin state $|\chi\rangle=|\uparrow\rangle$ the Eq. (B.36) takes the form of a *spinorbital*

$$\psi_{\mathbf{k}\uparrow}\left(\mathbf{r},\sigma\right)=\varphi_{\mathbf{k}}\left(\mathbf{r}\right)\chi_{\uparrow}(\sigma).\tag{B.38}$$

In terms of spinorbitals the spinor field becomes

$$\psi\left(\mathbf{r},\sigma\right)=\psi_{\mathbf{k}\uparrow}\left(\mathbf{r},\sigma\right)\chi(+\tfrac{1}{2})+\psi_{\mathbf{k}\downarrow}\left(\mathbf{r},\sigma\right)\chi(-\tfrac{1}{2}),\tag{B.39}$$

where $\chi(\pm\frac{1}{2})$ is the probability amplitude to observe the particle in spin state $\left|\pm\frac{1}{2}\right\rangle$.

B.2 The Schrödinger and Heisenberg pictures of time evolution

In this section we discuss two alternative views on the time evolution in non-relativistic quantum mechanics. These are known as the *Schrödinger* and the *Heisenberg picture*. To introduce these pictures, we start by recalling that the state of a quantum mechanical system is postulated to be *uniquely* defined by a state vector in Hilbert space (see Appendix B.1.1). At any point in time a quantum mechanical state can be written as a linear superposition of eigenstates. This superposition is (in general) not stationary but evolves in time. In the Schrödinger picture we postulate that the time evolution is *uniquely* defined by a *linear* transformation,

$$|\psi_S(t)\rangle=U(t,t_0)|\psi_S(t_0)\rangle,\tag{B.40}$$

where $|\psi_S(t)\rangle$ is the state of the system at time t. The linearity implies that $|\psi_S(t)\rangle$ is given by a linear superposition of *independently* evolving eigenstates; i.e., the superposition is conserved but the coefficients vary in time. The operator $U(t,t_0)$ is called the evolution operator of the system and accounts for the time dependence of the states over the interval $t_0\to t$. By definition $U(t_0,t_0)=1$. To assure the postulated uniqueness of the state evolution, the transformation has to be *norm conserving*,

$$\langle\psi_S(t)|\psi_S(t)\rangle=\langle\psi_S(t_0)|\psi_S(t_0)\rangle.\tag{B.41}$$

Only in this way we can be sure that a system, initially in state $|\psi_S(t_0)\rangle$, arrives with unit probability at time t in the state $|\psi_S(t)\rangle$. Substituting the transformation (B.40) into (B.41), we find that the norm is conserved if and only if $U^{\dagger}U=\mathbb{1}$; i.e., the evolution has to be *unitary*,

$$U^{\dagger}(t,t_0)=U^{-1}(t,t_0)=U(t_0,t).\tag{B.42}$$

In view of the uniqueness of the time evolution, $U(t, t_0)$ can be written as a product of unitary operators,

$$U(t, t_0) = U(t, t_n)U(t_n, t_{n-1}) \cdots U(t_2, t_1)U(t_1, t_0). \tag{B.43}$$

This shows that the set $\{U(t, t')\}$ forms a group under multiplication, with unit element $U(t, t)$ and inverse $U(t', t)$. In particular, as t is a continuous variable, $U(t, t_0)$ can be written as an *infinite* product of *infinitesimal* evolution operators $U(t + \delta t, t)$. Infinitesimal unitary operators with the property $U(t, t) = 1$ can be expressed in the form

$$U(t + \delta t, t) = \mathbb{1} - (i/\hbar)\mathcal{H}(t)\delta t = e^{-i\mathcal{H}(t)\delta t/\hbar} \quad \text{for } \delta t \to 0, \tag{B.44}$$

where $\mathcal{H}(t)$ has to be a *hermitian* operator to assure the unitarity of U. The factor $1/\hbar$ has been included for future convenience. Note that (for any point in time) the evolution operator commutes with the Hamiltonian,

$$[U(t + \delta t, t), \mathcal{H}(t)] = 0. \tag{B.45}$$

Using $U(t, t) = 1$, we rewrite Eq. (B.44) in the form

$$\lim_{\delta t \to 0} \frac{U(t + \delta t, t) - U(t, t)}{\delta t} = -(i/\hbar)\mathcal{H}(t). \tag{B.46}$$

Multiplying both sides with $U(t, t_0)$ we obtain the differential equation [1]

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = \mathcal{H}(t)U(t, t_0), \tag{B.47}$$

subject to the boundary condition $U = 1$ for $t = t_0$. This equation can be rewritten in the form of an integral equation by integration over the finite time interval $t_0 \to t$,

$$U(t, t_0) = \mathbb{1} - (i/\hbar) \int_{t_0}^{t} dt' \mathcal{H}(t')U(t', t_0). \tag{B.48}$$

This form for the evolution operator is particularly suited for generating iterative solutions for application in time-dependent perturbation theory.

As the time dependences of $U(t, t_0)$ and $|\psi_S(t)\rangle$ are related by the equation

$$i\hbar \frac{\partial}{\partial t} |\psi_S(t)\rangle = \left[i\hbar \frac{\partial}{\partial t} U(t, t_0) \right] |\psi_S(t_0)\rangle \tag{B.49}$$

we find for the time dependence of the state vector

$$i\hbar \frac{\partial}{\partial t} |\psi_S(t)\rangle = \mathcal{H}(t)|\psi_S(t)\rangle, \tag{B.50}$$

with the boundary condition that at $t = t_0$ the system is in the state $|\psi_S(t_0)\rangle$. In this differential equation we recognize the familiar form of the time-dependent Schrödinger equation. In view of this formal similarity the hermitian operator $\mathcal{H}$ is called the Hamiltonian of the quantum mechanical system. In hindsight this explains the factor $1/\hbar$ included in Eq. (B.44). This being said, it should be emphasized that Eq. (B.50) was obtained from the postulates without any reference to the Hamilton formalism of classical mechanics. It shows that the Hamiltonian can be defined, *also in the absence of any correspondence to a classical system*, as the hermitian operator that assures unitary evolution of the system.

Recalling that $U(t, t_0)$ can be written as an infinite product of infinitesimal operators we distinguish three cases

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[1] The time derivative of the operator $U(t, t')$ is defined as

$$\frac{\partial}{\partial t} U(t, t') \equiv \lim_{\delta t \to 0} \frac{U(t + \delta t, t') - U(t, t')}{\delta t}.$$

- *Time-dependent Hamiltonian* with the property $[\mathcal{H}(t), \mathcal{H}(t')] \neq 0$.

$$U(t,t_0) \equiv \lim_{\delta t \to 0} e^{-i\mathcal{H}(t-\delta t)\delta t/\hbar} \cdots e^{-i\mathcal{H}(t_0)\delta t/\hbar} \tag{B.51}$$

- *Time-dependent Hamiltonian* with the property $[\mathcal{H}(t), \mathcal{H}(t')] = 0$. Using the properties of exponential operators (see Appendix C.8)

$$U(t,t_0) \equiv \lim_{\delta t \to 0} e^{-i\mathcal{H}(t-\delta t)\delta t/\hbar} \cdots e^{-i\mathcal{H}(t_0)\delta t/\hbar} = e^{-(i/\hbar)\int_{t_0}^{t} \mathcal{H}(t')dt'} \tag{B.52}$$

- *Time-independent Hamiltonian* $\mathcal{H} = \mathcal{H}_0$ (conservative system). In this case we write $\delta t \equiv (t - t_0)/n$ and obtain with the aid of Eq. (C.33a)

$$U(t,t_0) \equiv \lim_{n \to \infty} \left[e^{-(i/\hbar)\mathcal{H}_0(t-t_0)/n} \right]^n = e^{-i\mathcal{H}(t-t_0)/\hbar}. \tag{B.53}$$

B.2.1 Schrödinger picture

In this section we summarize the primary features of the *Schrödinger picture.* The evolution of the physical system is contained in the time dependence of the state vector,

$$|\psi_S(t)\rangle = U(t,t_0)|\psi_S(t_0)\rangle, \tag{B.54}$$

where $|\psi_S(t)\rangle$ is the *Schrödinger state* of the system at time t. In the Schrödinger picture we write A_S for the operator that represents the dynamical variable A. Likewise, we shall write A_H when turning to the Heisenberg picture. An exception is made for the Hamiltonian because, as we shall see, this operator is the same in both pictures. For this reason we simply write $\mathcal{H}$ rather than $\mathcal{H}_S$ or $\mathcal{H}_H$. The time dependence of the state vectors is governed by the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} |\psi_S(t)\rangle = \mathcal{H}(t)|\psi_S(t)\rangle, \tag{B.55}$$

subject to the boundary condition that at $t = t_0$ the system is in the state $|\psi_S(t_0)\rangle$. According to the postulate of quantum measurement (see Appendix B.1.1), the expectation value of $A_S(t)$ is given by

$$\langle A_S(t)\rangle = \frac{\langle\psi_S(t)|A_S(t)|\psi_S(t)\rangle}{\langle\psi_S(t)|\psi_S(t)\rangle}. \tag{B.56}$$

As the evolution is norm conserving, the time derivative of the expectation value is given by - see Problem B.2

$$i\hbar \frac{d}{dt}\langle A_S(t)\rangle = \langle [A_S(t), \mathcal{H}(t)]\rangle + i\hbar \langle \frac{\partial}{\partial t} A_S(t)\rangle. \tag{B.57}$$

Here the first term arises from the time development of the state and the second one from that of the operator. Note that the latter is only nonzero if the operator depends explicitly on time.

Problem B.2. Show that the equation of motion for the expectation value of a (generally time-dependent) operator $A_S(t)$ is given by

$$i\hbar \frac{d}{dt}\langle A_S(t)\rangle = \langle [A_S(t), \mathcal{H}(t)]\rangle + i\hbar \langle \frac{\partial}{\partial t} A_S(t)\rangle.$$

Solution. The answer is obtained by differentiation of (B.56) using the Leibniz integral rule (C.28). Since the norm of the state is conserved we obtain the following three terms,

$$\frac{d}{dt}\langle A_S(t)\rangle = \left[\frac{\partial}{\partial t}\langle\psi_S(t)|\right] A_S(t)|\psi_S(t)\rangle + \langle\psi_S(t)| \left[\frac{\partial}{\partial t} A_S(t)\right] |\psi_S(t)\rangle + \langle\psi_S\,(t)\,|A_S(t) \left[\frac{\partial}{\partial t}|\psi_S(t)\rangle\right].$$

The first and the third term are evaluated using the Schrödinger equation (B.55) and its hermitian conjugate. The second term is zero unless the operator has an explicit time dependence. Thus we obtain

$$i\hbar\frac{d}{dt}\langle A_S(t)|\rangle = -\langle\psi_S(t)|\left[\mathcal{H}(t)A_S(t) - A_S(t)\mathcal{H}(t)\right]|\psi_S(t)\rangle + i\hbar\langle\psi_S(t)|\left[\frac{\partial}{\partial t}A_S(t)\right]|\psi_S(t)\rangle,$$

which can be rewritten in the form of the desired expression. □

B.2.2 Heisenberg picture

The *Heisenberg picture* is obtained by a unitary transformation of the Schrödinger states and operators in the Hilbert space. This unitary transformation is chosen such that it exactly removes the time dependence from the Schrödinger state $|\psi_S(t)\rangle$ by evolving it back to $t = t_0$,

$$|\psi_H\rangle \equiv U^\dagger(t,t_0)|\psi_S(t)\rangle = |\psi_S(t_0)\rangle. \tag{B.58}$$

The same unitary transformation puts a time dependence on the operators,

$$A_H(t) = U^\dagger(t,t_0)A_S(t)U(t,t_0). \tag{B.59}$$

Note that with this transformation the Heisenberg and Schrödinger pictures coincide at $t = t_0$,

$$A_H(t_0) = A_S(t_0) \quad \text{and} \quad |\psi_H\rangle = |\psi_S(t_0)\rangle. \tag{B.60}$$

Importantly, since $U(t,t_0)$ commutes with the Hamiltonian $\mathcal{H}(t)$, the transformation to the Heisenberg picture leaves the Hamiltonian invariant. For this reason we omit the subscript and simply write $\mathcal{H}(t)$. It is straightforward to show, using Eq. (B.56), that the expectation value $\langle A_H\rangle$ coincides with $\langle A_S\rangle$ at any time t and is given by

$$\langle A_H(t)\rangle = \frac{\langle\psi_H|A_H(t)|\psi_H\rangle}{\langle\psi_H|\psi_H\rangle} = \frac{\langle\psi_H|U^\dagger(t,t_0)A_S(t)U(t,t_0)|\psi_H\rangle}{\langle\psi_H|U^\dagger(t,t_0)U(t,t_0)|\psi_H\rangle} = \langle A_S(t)\rangle. \tag{B.61}$$

As, by construction, $|\psi_H\rangle$ does not depend on time, the time dependence of $\langle A_H(t)\rangle$ is fully determined by the time dependence of $A_H(t)$. The latter is known as the the *Heisenberg equation of motion*. By differentiation of (B.59) we obtain - see Problem B.3

$$i\hbar\frac{d}{dt}A_H(t) = [A_H(t),\mathcal{H}(t)] + i\hbar\frac{\partial}{\partial t}A_H(t), \tag{B.62}$$

where

$$\frac{\partial}{\partial t}A_H(t) \equiv \left(\frac{\partial}{\partial t}A_S(t)\right)_H = U^\dagger(t)\left[\frac{\partial}{\partial t}A_S(t)\right]U(t). \tag{B.63}$$

The correspondence (B.61) shows that the Heisenberg equation of motion is completely equivalent to the Schrödinger equation.

Problem B.3. Consider the Heisenberg operator $A_H(t) = U^\dagger(t)A_S(t)U(t)$. Show that the equation of motion of this operator is given by

$$i\hbar\frac{d}{dt}A_H(t) = [A_H(t),\mathcal{H}(t)] + i\hbar\frac{\partial}{\partial t}A_H(t).$$

Solution. By differentiation of $\langle A_H(t)\rangle$ we obtain three terms using the Leibniz integral rule (C.28)

$$\frac{d}{dt}\langle A_H(t)\rangle = \langle\left[\frac{\partial}{\partial t}U^\dagger(t)\right]A_S(t)U(t) + U^\dagger(t)\left[\frac{\partial}{\partial t}A_S(t)\right]U(t) + U^\dagger(t)A_S(t)\left[\frac{\partial}{\partial t}U(t)\right]\rangle.$$

The first and the third term are evaluated using the differential equation (B.47) and its hermitian conjugate. The second term is zero unless the operator has an explicit time dependence. As the Heisenberg states are time independent we can assign all time dependence to the Heisenberg operators,

$$i\hbar\frac{d}{dt}A_H(t) \equiv -U^{\dagger}(t)\left[\mathcal{H}(t)A_S(t)-A_S(t)\mathcal{H}(t)\right]U(t)+i\hbar U^{\dagger}(t)\frac{\partial}{\partial t}A_S(t)U(t).$$

As $\mathcal{H}(t)$ commutes with the evolution operator this expression simplifies to

$$i\hbar\frac{d}{dt}A_H(t) = [A_H(t),\mathcal{H}(t)]+i\hbar U^{\dagger}(t)\frac{\partial}{\partial t}A_S(t)U(t).$$

Defining

$$\frac{\partial}{\partial t}A_H(t) \equiv \left(\frac{\partial}{\partial t}A_S(t)\right)_H \equiv U^{\dagger}(t)\left[\frac{\partial}{\partial t}A_S(t)\right]U(t)$$

we arrive at the desired expression. □

B.2.3 Interaction picture

Rather than removing the full time dependence, we can also use a unitary transformation that removes only part of it. It may speak for itself that this can be done in many ways. A particularly valuable variant arises when the Hamiltonian of the system can be separated into two parts,

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t), \tag{B.64}$$

where $\mathcal{H}_0$ is the time-independent Hamiltonian of a closed system and $\mathcal{H}_1(t)$ is a (generally time-dependent) perturbation representing some interaction with an external field. To analyze this case, we consider the unitary transformations

$$|\psi_I(t)\rangle = U_0^{\dagger}(t)|\psi_S(t)\rangle, \tag{B.65}$$

and

$$A_I(t) = U_0^{\dagger}(t)A_S(t)U_0(t). \tag{B.66}$$

Here $U_0(t)$ is the evolution operator corresponding to $\mathcal{H}_0$,

$$U_0(t) = e^{-i\mathcal{H}_0(t-t_1)/\hbar}, \tag{B.67}$$

which is the solution of the differential equation

$$i\hbar\frac{\partial}{\partial t}U_0(t) = \mathcal{H}_0U_0(t), \tag{B.68}$$

under the boundary condition $U_0(t) = 1$ for $t = t_1$. With this definition, the state $|\psi_I(t_1)\rangle$ coincides with the Schrödinger state $|\psi_S(t)\rangle$ for $t = t_1$. As we are free to choose the time t_1, we conveniently choose $t_0 = 0$.

The above transformations define the *interaction* picture and the states $|\psi_I(t)\rangle$ are called the *intermediate* states. The operator $A_I(t)$ is called the *intermediate* operator. Note that $U_0(t)$ removes all $\mathcal{H}_0$-related evolution from the state but leaves the part related to $\mathcal{H}_1(t)$. For small $\mathcal{H}_1(t)$ this means that $|\psi_I(t)\rangle$ is "almost" stationary. It follows with the aid of Eqs. (B.65) and (B.56) that the expectation values $\langle A_I\rangle$ and $\langle A_S\rangle$ coincide at all times,

$$\langle A_I\,(t)\rangle = \frac{\langle\psi_I(t)|A_I(t)|\psi_I(t)\rangle}{\langle\psi_I(t)|\psi_I(t)\rangle} = \frac{\langle\psi_I(t)|U_0^{\dagger}(t)A_S(t)U_0(t)|\psi_I(t)\rangle}{\langle\psi_I(t)|U_0^{\dagger}(t)U_0(t)|\psi_I(t)\rangle} = \langle A_S(t)\rangle. \tag{B.69}$$

The time dependence of the intermediate states can be obtained by differentiation of Eq. (B.65) - see Problem B.4,

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = \mathcal{H}_I(t)|\psi_I(t)\rangle, \tag{B.70}$$

where $\mathcal{H}_I(t)$ is defined by

$$\mathcal{H}_I(t) \equiv U_0^\dagger(t)\mathcal{H}_1(t)U_0(t), \tag{B.71}$$

which is consistent with the general case (B.66). In complete analogy with the derivation of the Heisenberg equation of motion we obtain by differentiation of (B.66) the *intermediate* equation of motion,

$$i\hbar\frac{d}{dt}A_I(t) = [A_I(t),\mathcal{H}_0] + i\hbar\frac{\partial}{\partial t}A_I(t), \tag{B.72}$$

where

$$\frac{\partial}{\partial t}A_I(t) \equiv \left(\frac{\partial}{\partial t}A_S(t)\right)_I = U_0^\dagger(t)\left[\frac{\partial}{\partial t}A_S(t)\right]U_0(t). \tag{B.73}$$

Hence, just like the time evolution of A_H follows from the full Hamiltonian, the time dependence of A_I follows from the partial Hamiltonian $\mathcal{H}_0$.

As also the time evolution driven by $\mathcal{H}_I(t)$ has to be uniquely defined the evolution of the intermediate state over the interval $t_0 \to t$ can be written in the form

$$|\psi_I(t)\rangle = U_I(t,t_0)|\psi_I(t_0)\rangle, \tag{B.74}$$

where $U_I(t,t_0)$ is a *unitary* operator and the solution of the differential equation

$$i\hbar\frac{\partial}{\partial t}U_I(t,t_0) = \mathcal{H}_I(t)U_I(t,t_0), \tag{B.75}$$

under the boundary condition $U_I(t_0,t_0) = 1$. This differential equation can be rewritten in the form of an integral equation,

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt_1\mathcal{H}_I(t_1)U_I(t_1,t_0). \tag{B.76}$$

In search for a relation between $U_I(t,t_0)$ and $U(t,t_0)$ we write, with the aid of Eqs. (B.65) and (B.54), the intermediate state in the form

$$|\psi_I(t)\rangle = U_0^\dagger(t)|\psi_S(t)\rangle = U_0^\dagger(t)U(t,t_0)|\psi_S(t_0)\rangle = U_0^\dagger(t)U(t,t_0)U_0(t_0)|\psi_I(t_0)\rangle. \tag{B.77}$$

Comparing this expression with Eq. (B.65) we obtain the following relation between the full and the intermediate evolution operator,

$$U_I(t,t_0) = e^{i\mathcal{H}_0 t/\hbar}U(t,t_0)e^{-i\mathcal{H}_0 t/\hbar}. \tag{B.78}$$

Note that in the intermediate picture the time dependence is divided between the states and the operators. Its operators resemble the Heisenberg operators - compare Eqs. (B.62) and (B.72), whereas its states resemble the Schrödinger states - compare Eqs. (B.55) and (B.70).

Problem B.4. Show that the equation of motion for the expectation value of a (generally time-dependent) intermediate operator $A_I(t)$ is given by

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = \mathcal{H}_I(t)|\psi_I(t)\rangle.$$

Solution. Differentiating (B.65) we obtain with the aid of Eqs. (B.68) and (B.55)

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle &= \left[\frac{\partial}{\partial t}U_0^\dagger(t)\right]|\psi_S(t)\rangle + i\hbar U_0^\dagger(t)\frac{\partial}{\partial t}|\psi_S(t)\rangle \\ &= -\mathcal{H}_0 U_0^\dagger(t)|\psi_S(t)\rangle + U_0^\dagger(t)\mathcal{H}(t)|\psi_S(t)\rangle. \end{aligned}$$

Using Eq. (B.65) and its inverse, this becomes

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = -\mathcal{H}_0|\psi_I(t)\rangle + U_0^\dagger(t)\mathcal{H}(t)U_0(t)|\psi_I(t)\rangle.$$

Since $\mathcal{H}_0 = U_0^\dagger(t)\mathcal{H}_0 U_0(t)$ and $\mathcal{H}_1(t) = \mathcal{H}(t) - \mathcal{H}_0$ this corresponds to

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = U_0^\dagger(t)\mathcal{H}_1(t)U_0(t)|\psi_I(t)\rangle.$$

Defining $\mathcal{H}_I(t) \equiv U_0^\dagger(t)\mathcal{H}_1(t)U_0(t)$ we arrive at the desired form. □

B.2.4 Constants of the motion and "good" quantum numbers

The dynamical variable A of a quantum mechanical system is called a *constant of the motion* if the expectation value $\langle A_S\rangle$ is independent of time, whatever the state of the system. This implies that the Heisenberg operator A_H is stationary as follows by differentiation of (B.61),

$$\frac{d}{dt}\langle A_S\rangle = \langle\frac{d}{dt}A_H\rangle \equiv 0 \quad\Rightarrow\quad \frac{d}{dt}A_H = 0. \tag{B.79}$$

Furthermore, expressing the Heisenberg equation of motion for the operator A_H in terms of the corresponding Schrödinger operator A_S we find with the aid of Eqs. (B.62) and (B.45)

$$i\hbar\frac{d}{dt}A_H = U^\dagger(t,t_0)[A_S,\mathcal{H}]U(t,t_0) + i\hbar U^\dagger(t)\left[\partial A_S(t)/\partial t\right]U(t). \tag{B.80}$$

This shows that the dynamical variable A is a constant of the motion if A_S does not depend explicitly on time, $\partial A_S(t)/\partial t = 0$, and commutes with the Hamiltonian, $[A_S,\mathcal{H}] = 0$.

In particular, suppose that at $t = t_0$ the system is in the eigenstate $|a\rangle$ of A_S with eigenvalue a. In this case we have $\langle A_S\rangle = a$ and a is called a "good" quantum number if this expectation value is conserved in time. This invariance is satisfied if $|a\rangle$ is also an eigenstate of $\mathcal{H}$ (i.e., if $[A_S,\mathcal{H}] = 0$). If a is a good quantum number the time development of the state is given by

$$|\psi(t)\rangle = \exp[-(i/\hbar)\varepsilon_a(t-t_0)]\,|a\rangle\,, \tag{B.81}$$

where $\exp[-(i/\hbar)\varepsilon_a(t-t_0)]$ is called the *dynamical phase* of the state. This shows explicitly that eigenstates are stationary up to the development of the dynamical phase.

Example: To illustrate these concepts we consider a system at $t = 0$ in the state

$$|\psi_0\rangle = |a\rangle = \sqrt{1/2}\,(|\alpha\rangle + |\beta\rangle)\,, \tag{B.82}$$

which is itself *not* an eigenstate of $\mathcal{H}$ but a linear combination of the (normalized) eigenstates $|\alpha\rangle$ and $|\beta\rangle$ of $\mathcal{H}$ with eigenvalues ε_a and ε_b, respectively. By integrating the time-dependent Schrödinger equation we obtain for the time dependence of the state

$$|\psi(t)\rangle = e^{-(i/\hbar)\mathcal{H}t}\,|a\rangle = \sqrt{1/2}\left[e^{-(i/\hbar)\varepsilon_\alpha t}\,|\alpha\rangle + e^{-(i/\hbar)\varepsilon_\beta t}\,|\beta\rangle\right]. \tag{B.83}$$

Note that for $t = 0$ we regain Eq. (B.82). Projecting $|\psi(t)\rangle$ onto the state $|a\rangle$ we find that the occupation of $|a\rangle$ will oscillate in time between 1 and 0 at the frequency corresponding to the energy splitting $\varepsilon_a - \varepsilon_b$ between the levels,

$$|\langle a\,|\psi(t)\rangle\,|^2 = \tfrac{1}{2} + \tfrac{1}{2}\cos[(\varepsilon_\alpha - \varepsilon_\beta)\,t/\hbar]. \tag{B.84}$$

Note that the Hamiltonian is an example of a constant of the motion,

$$\langle\psi(t)|\mathcal{H}\,|\psi(t)\rangle = \tfrac{1}{2}\,(\varepsilon_\alpha + \varepsilon_\beta)\,. \tag{B.85}$$

Let us now turn to the operator A, with $|a\rangle$ representing the eigenstate corresponding to the eigenvalue a,

$$A\,|a\rangle = a\,|a\rangle\,. \tag{B.86}$$

When is A is constant of the motion (and a a good quantum number)?

- If $[A, \mathcal{H}] = 0$ we find with the aid of Eq. (B.83),

$$\langle\psi(t)|A\,|\psi(t)\rangle = a. \tag{B.87}$$

Hence, in this case A is a constant of the motion (and a is a good quantum number).

- If $[A, \mathcal{H}] = -B \neq 0$ we find with the aid of Eq. (C.33b)

$$\begin{aligned}\langle\psi(t)|A\,|\psi(t)\rangle &= \langle a|\, e^{(i/\hbar)\mathcal{H}t} A e^{-(i/\hbar)\mathcal{H}t}\,|a\rangle \\ &= a + \tfrac{1}{2!}(i/\hbar)\,\langle a|\,B\,|a\rangle\, t + \tfrac{1}{3!}(i/\hbar)^2\,\langle a|\,[\mathcal{H}, B]\,|a\rangle\, t^2 + \cdots\,. \end{aligned} \tag{B.88}$$

Hence, in this case A is *not* a constant of the motion (and a *not* a good quantum number).

Problem B.5. Show by explicit calculation the equivalence of the Heisenberg equation of motion and the Schrödinger equation for the example of a particle of mass m moving in the conservative potential energy field $\mathcal{V}(\mathbf{r})$.

Solution. At $t = 0$ the particle is in the state $|\psi_H\rangle$. As the Hamiltonian does not depend on time and the position operator $\underline{\mathbf{r}}$ does not depend *explicitly* on time, the time development of the Heisenberg position operator $\mathbf{r}(t) = \mathbf{r}_H(t)$ is given by Eq. (B.80) in the form

$$i\hbar\frac{d}{dt}\mathbf{r}(t) = [\mathbf{r}(t), \mathcal{H}], \text{ with } \mathcal{H} = -\frac{\underline{\mathbf{p}}^2}{2m} + \mathcal{V}(\underline{\mathbf{r}}).$$

Using $\mathbf{r}(t) = U^\dagger(t, t_0)\underline{\mathbf{r}}U(t, t_0)$ and recalling Eqs. (B.45) and (B.47) we have

$$i\hbar\frac{d}{dt}U^\dagger(t, t_0)\underline{\mathbf{r}}U(t, t_0)\,|\psi_H\rangle = U^\dagger(t, t_0)[\underline{\mathbf{r}}, \mathcal{H}]U(t, t_0)\,|\psi_H\rangle\,.$$

Multiplying from the left with $U(t, t_0)$ and turning to Schrödinger states this becomes

$$i\hbar U(t, t_0)\frac{d}{dt}U^\dagger(t, t_0)\underline{\mathbf{r}}\,|\psi(t)\rangle = [\underline{\mathbf{r}}, \mathcal{H}]\,|\psi(t)\rangle$$

With the aid of the differential equation (B.47) this becomes

$$-\mathcal{H}\underline{\mathbf{r}}\,|\psi(t)\rangle + i\hbar\frac{d}{dt}\underline{\mathbf{r}}\,|\psi(t)\rangle = [\underline{\mathbf{r}}, \mathcal{H}]\,|\psi(t)\rangle\,.$$

Turning to the position representation this becomes the Schrödinger equation,

$$i\hbar\frac{d}{dt}\langle\mathbf{r}\,|\psi(t)\rangle = \mathcal{H}_0\langle\mathbf{r}\,|\psi(t)\rangle\,, \quad \text{with} \quad \mathcal{H}_0 = \langle\mathbf{r}|\mathcal{H}|\mathbf{r}\rangle = -\frac{\hbar^2}{2m}\Delta + \mathcal{V}(\mathbf{r}). \qquad \square$$

B.2.5 Translation as an example of a symmetry operation

In Appendix A.5.3 we introduced the *homogeneity of space* in relation to conservation laws. The evolution of a *closed* mechanical system only depends on the internal state of that system and not on the inertial frame in which the state is observed in space and time. Now let us suppose that the quantum mechanical state of the system is given by de wavefunction

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle,$$

where $\mathbf{r}$ is the position with respect to a cartesian coordinate system $\mathcal{S}$. We now consider a *passive* translation T of the cartesian coordinate system $\mathcal{S}$ defined by the displacement vector $\mathbf{d}$. Denoting the translated coordinate system by $\mathcal{S}' = T\mathcal{S}$, the position $\mathbf{r} = (x, y, z)$ with respect to $\mathcal{S}$ changes into $\mathbf{r}' = (x', y', z')$ with respect to $\mathcal{S}'$, where

$$\mathbf{r}' = T\,\mathbf{r} = \mathbf{r} - \mathbf{d}. \tag{B.89}$$

As the translation is passive the physical state of the system is not affected by the translation, we require

$$\psi'(\mathbf{r}') \equiv \psi(\mathbf{r}), \tag{B.90}$$

or, equivalently,

$$\psi'(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{d}). \tag{B.91}$$

The appearance of the new state ψ' does not come as a surprise. From general quantum mechanics we know that a new coordinate system comes with a new linear combination of eigenstates, $|\psi'\rangle$, which is related to the original linear combination of eigenstates, $|\psi\rangle$, by a *norm-conserving* basis transformation,

$$|\psi'\rangle = \underline{u}|\psi\rangle. \tag{B.92}$$

The transformation $\underline{u}$ has to be norm conserving because $|\psi\rangle$ and $|\psi'\rangle$ represent the *same* state with respect to two *different* bases,

$$\langle \psi | \psi \rangle = \langle \psi' | \psi' \rangle = \langle \psi | \underline{u}^{\dagger} \underline{u} | \psi \rangle \to \underline{u}^{\dagger} \underline{u} = \mathbb{1}. \tag{B.93}$$

This identity shows that the transformation must be unitary, $\underline{u}^{\dagger} = \underline{u}^{-1}$, which implies that the inverse transformation is given by

$$|\psi\rangle = \underline{u}^{\dagger} |\psi'\rangle. \tag{B.94}$$

So let us consider the wavefunction of a *free particle*,

$$\psi'(x) = \underline{u}(\Delta x)\psi(x)$$

$$\begin{aligned}
\psi'(x) &= \psi(x + \Delta x) \\
&= \psi(x) + \Delta x \partial_x \psi(x) + \tfrac{1}{2!} \Delta x^2 \partial_x^2 \psi(x) + \cdots \\
&= e^{\Delta x \partial_x} \psi(x)
\end{aligned}$$

B.3 Density matrix formalism

B.3.1 Density operators for pure states

The *density matrix formalism* provides an alternative for the familiar representation of quantum mechanical states by linear combinations of eigenvectors spanning a Hilbert space. The central quantity of the density matrix formalism is the *density operator.* For a quantum mechanical system in the state $|\psi(t)\rangle$ the density operator is defined as

$$\rho(t) \equiv |\psi(t)\rangle\langle\psi(t)|. \tag{B.95}$$

Note that this operator is *hermitian*, $\rho^\dagger = \rho$, as well as *idempotent*, $\rho^2 = \rho$. The operator ρ can be represented by a (in general *nondiagonal*) square matrix, $\rho_{ij} = \langle i|\rho|j\rangle$, which explains the use of the names *density operator* and *density matrix.* Being hermitian, ρ is free of the phase ambiguity of the state vectors; i.e., a quantum mechanical state is fully defined by its density matrix. As the state kets satisfy the Schrödinger equation (B.50) and the state bras its complex conjugate we have for a time-independent Hamiltonian

$$i\hbar\frac{\partial\rho(t)}{\partial t} = \mathcal{H}|\psi(t)\rangle\langle\psi(t)| - |\psi(t)\rangle\langle\psi(t)|\mathcal{H} = -[\rho(t), \mathcal{H}]. \tag{B.96}$$

Apparently, the density matrix is stationary, $\partial\rho(t)/\partial t = 0$, if it commutes with the Hamiltonian. This has the important consequence that *a stationary density matrix is diagonal in the representation of $\mathcal{H}$.* Furthermore, by diagonalization of a given density matrix we obtain the state of the system and its eigenvalue is unity; i.e., the state of the system is the solution of the eigenvalue equation

$$\rho|\psi\rangle = \rho_0|\psi\rangle \tag{B.97}$$

with eigenvalue $\rho_0 = 1$. In this state, the expectation value of the density operator is unity,

$$\langle\rho\rangle = \langle\psi|\rho|\psi\rangle = 1. \tag{B.98}$$

To demonstrate the calculation of properties of the system in state $|\psi\rangle$, we ask for the *expectation value* of an *arbitrary* operator A,

$$\langle A\rangle = \langle\psi|A|\psi\rangle. \tag{B.99}$$

In some *arbitrarily chosen* alternative representation $\{B\}$, this expectation value can be rewritten (using the closure relation) in the form

$$\langle A\rangle = \sum_i \langle\psi|A|b_i\rangle\langle b_i|\psi\rangle = \sum_i \langle b_i|\psi\rangle\langle\psi|A|b_i\rangle. \tag{B.100}$$

Recognizing the density operator $\rho = |\psi\rangle\langle\psi|$ we find that the expectation value of A for the system in the state $|\psi\rangle$ is given by

$$\langle A\rangle = \sum_i \langle b_i|\rho A|b_i\rangle = \operatorname{tr}\rho A. \tag{B.101}$$

Note that $\operatorname{tr}\rho A = \operatorname{tr} A\rho$. As the representation $\{B\}$ was chosen arbitrarily, the trace is invariant under unitary transformation (a property of square matrices - see Appendix D.2.1). This is expressed by the representation-free form of Eq. (B.101).

To compare the two formalisms a bit further, we reconsider the Parseval relation for the state $|\psi\rangle$ in the representation $\{B\}$,

$$1 = \sum_i |\langle b_i|\psi\rangle|^2 = \sum_i \mathcal{P}_i, \tag{B.102}$$

where

$$\mathbb{1} = \sum_i |b_i\rangle\langle b_i| = \sum_i \rho_i \tag{B.103}$$

is the closure relation in the representation $\{B\}$ and $\mathcal{P}_i$ represents the probability density to observe the system in the eigenstate $|b_i\rangle$. In the *state formalism* we write

$$\mathcal{P}_i = \langle\psi|b_i\rangle\langle b_i|\psi\rangle = \langle\psi|\rho_i|\psi\rangle, \tag{B.104}$$

which is interpreted as the expectation value of the projection operator $\rho_i = |b_i\rangle\langle b_i|$. In the *density matrix formalism*, $\mathcal{P}_i$ is interpreted as the *expectation value of the density operator*,[1]

$$\mathcal{P}_i = \langle b_i|\psi\rangle\langle\psi|b_i\rangle = \langle b_i|\rho|b_i\rangle = \rho_{ii}. \tag{B.105}$$

The representation $\{B\}$ being arbitrary, the Parseval relation takes the representation-free form

$$\operatorname{tr}\rho = 1. \tag{B.106}$$

B.3.2 Density operators for mixed ensembles of states

The importance of the density matrix formalism finds its origin in the probabilistic nature of quantum mechanical measurement. A *single* state-selective measurement (state *filtration*) on a quantum mechanical system is of little value. It tells us whether or not the selected state was observed but nothing more. Only by repeating the measurement many times we can determine the probability of observing that state. If the measurements are done on an ensemble of identically prepared systems, say a beam of particles all prepared in the state $|\psi\rangle$, the probability density of observing this state, $\mathcal{P}_s = |\langle s|\psi\rangle|^2$, is obtained by averaging over the set of measurements. This procedure is called the *ensemble-averaging*. As was shown at the end of the previous section, formally $\mathcal{P}_s$ can be expressed as the *expectation value of the density operator* for the system in state $|s\rangle$, $\mathcal{P}_s = \langle s|\rho|s\rangle$. Such an ensemble of identically prepared systems is called a *pure ensemble*, to distinguish it from *mixed ensembles*, in which the state preparation may vary or is even absent.[2] It may speak for itself that whatever the ensemble we can always determine ensemble averages. Therefore, to refer to an arbitrary type of ensemble averaging we use a different notation for the density matrix, $\rho \to \varrho$, denoting the ensemble-averaged probality to detect the state $|s\rangle$ by $\langle s|\varrho|s\rangle$. If there is no state preparation whatsoever one speaks of a *random ensemble* and $\langle s|\varrho|s\rangle = 1/n$, where n is the order of the density matrix. The value of n cannot exceed the number of measurements but it can be smaller. For instance, measuring spin "up" or "down" on a beam of particles we can do many measurements but $n = 2$.

The relative probability of occurrence of one of the states of a mixed ensemble $\{|s\rangle\}$ is given by the statistical weight w_s, a number between zero and one ($0 \le w_s \le 1$), and subject to the normalization condition

$$\sum_s w_s = 1. \tag{B.107}$$

Here, the probability is defined for a discrete ensemble but can be generalized to the continuous case. Note that orthogonality is neither mentioned nor required for the states of the ensemble $\{|s\rangle\}$.

Let us analyze ensemble averaging in more detail. Knowing the probabilities $\{w_s\}$, we can calculate the *quantum statistical average* for an arbitrary operator A,

$$\bar{A} \equiv \langle\!\langle A\rangle\!\rangle = \sum_s w_s \langle s|A|s\rangle. \tag{B.108}$$

Note that this is the *ensemble average* of the expectation values $\langle A\rangle_s = \langle s|A|s\rangle = A_{ss}$. Choosing an arbitrary representation $\{B\}$, we can use its closure relation to write the quantum-statistical average in the form

$$\bar{A} = \sum_s w_s \sum_i \langle s|A|b_i\rangle\langle b_i|s\rangle = \sum_i \sum_s w_s \langle b_i|s\rangle\langle s|A|b_i\rangle = \sum_i \langle b_i|\varrho A|b_i\rangle, \tag{B.109}$$

---

[1] Notice the difference between the density operator ρ_i and the diagonal matrix element of the density matrix, ρ_{ii}. In our notation $\mathcal{P}_i = \langle\psi|\rho_i|\psi\rangle = \langle\psi|b_i\rangle\langle b_i|\psi\rangle = \langle b_i|\psi\rangle\langle\psi|b_i\rangle = \langle b_i|\rho|b_i\rangle = \rho_{ii}$.

[2] We distinguish between a *mixed ensemble*, which consists of a statistical mixture of states, and a *mixed state*, which is a coherent superposition of states. Beware that some authors use mixed state as an abbreviation for "statistical mixture of states".

where

$$\varrho \equiv \sum_s w_s |s\rangle\langle s| = \sum_s w_s \rho_s \tag{B.110}$$

defines the *statistical operator* of the ensemble defined by the weights $\{w_s\}$, which represents the (by construction *diagonal*) density matrix of a *statistical mixture of states.* Importantly, as for a time-independent mixture the weights $\{w_s\}$ are conserved, it follows in the same way as demonstrated for Eq. B.96 that the time dependence of its density matrix is given by

$$i\hbar \frac{\partial \varrho(t)}{\partial t} = -[\varrho(t), \mathcal{H}]. \tag{B.111}$$

Thus we established that (also) for *mixed* ensembles a *stationary* density matrix is *diagonal* in the representation of $\mathcal{H}$.

Using the statistical operator the quantum statistical average can be written in the representation-free form

$$\bar{A} \equiv \langle\langle A \rangle\rangle = \mathrm{tr}\, \varrho A. \tag{B.112}$$

Substituting $A \to \mathbb{1}$ we find that for mixed ensembles the Parseval relation (B.106) is replaced by

$$\mathrm{tr}\, \varrho = 1. \tag{B.113}$$

Substituting $A \to \rho_s \equiv |s\rangle\langle s|$ we obtain the probability to observe the (pure) state $|s\rangle$ in a measurement on the ensemble,

$$\bar{\rho}_s = \mathrm{tr}\, \varrho \rho_s = \sum_i \langle b_i|\varrho|s\rangle\langle s|b_i\rangle = \langle s|\varrho|s\rangle = \varrho_{ss} = w_s. \tag{B.114}$$

Thus, using the density matrix for mixed ensembles of states, we can calculate quantum statistical averages using the same methods as used for the density matrix of pure states - see Eq. (B.101).[1] The density matrix of a pure state is in general nondiagonal, whereas that of mixed states is by construction diagonal. Furthermore, an important difference is revealed when calculating tr ϱ^2. For *pure* states the density matrix is idempotent, $\rho^2 = \rho$, and we have

$$\mathrm{tr}\, \rho^2 = \mathrm{tr}\, \rho = 1. \tag{B.115}$$

For *mixed* states this is replaced by the inequalities.

$$0 \leq \mathrm{tr}\, \varrho^2 \leq (\mathrm{tr}\, \varrho)^2 = 1. \tag{B.116}$$

B.3.3 Density matrices for quantum-statistical mixtures

Thus far we emphasized ensemble averaging for a real set of measurements; e.g., of the spin states of particles in a beam. Such ensembles of experimental data are called *real* ensembles. Interestingly, density matrices based on *fictitious* ensembles are at least as important. In many-body systems it is simply impossible to measure all particles individually but, as is well known from statistical physics, often this is not necessary. For instance, to calculate the pressure of an ideal gas, all we need to know is the probability of occupation of the single-particle states and this information can be provided by a *fictitious* ensemble such as the canonical distribution over the energy eigenstates of a physical system.

To start the discussion of quantum statistical ensembles we define the entropy of a physical system in terms of its density matrix

$$S/k_B = -\mathrm{tr}\, \varrho \ln \varrho. \tag{B.117}$$

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[1] Many authors do not distinguish between $\langle\langle A \rangle\rangle$ and $\langle A \rangle$ as all relevant information is contained in the form of ϱ.

To explore the plausibility of this definition as a measure for the disorder in the system we choose the representation of $\mathcal{H}$ (in which ϱ is diagonal - see Section B.3.2). Denoting the basis of this representation by $\{|s\rangle\}$ the expression for the entropy can be written in the form

$$S/k_B = -\sum_{s,s'}\langle s|\varrho|s'\rangle\langle s'|\ln\varrho|s\rangle = -\sum_{s}\langle s|\varrho|s\rangle\ln\langle s|\varrho|s\rangle = -\sum_{s}\varrho_{ss}\ln\varrho_{ss}. \tag{B.118}$$

From classical statistical mechanics we recall that zero entropy corresponds to the system being in a single microstate. In quantum statistics this translates to the system being in a pure state. Denoting this pure state by $|\psi\rangle$, its density operator is given by $\varrho = \rho = |\psi\rangle\langle\psi|$ and

$$\varrho_{ss} = \langle s|\varrho|s\rangle = |\langle s|\psi\rangle|^2. \tag{B.119}$$

To avoid the complications of entanglement we restrict ourselves to a single eigenstate of the representation $\{|s\rangle\}$, $|\psi\rangle \to |t\rangle \in \{|s\rangle\}$. In this case we have $\varrho_{ss} = \delta_{s,t}$ and calculate zero entropy, $S = 0$, because either $\varrho_{ss} = 0$ or $\ln\varrho_{ss} = 0$. On the other hand, for a completely random ensemble (where all energy eigenstates have the same probability), the density matrix is given by $\varrho = 1/n$, where n is the size of the ensemble (the order of the density matrix),

$$S/k_B = -\mathrm{tr}\,\frac{1}{n}\ln\frac{1}{n} = \ln n. \tag{B.120}$$

For example, the maximum entropy of a two-level system is $\ln 2$.

In general a statistical mixture will not have maximum entropy. We know from the *statistical principle* for ergodic systems that only states of *equal energy* have to be equally probable. This limits the entropy because, at finite temperature, high-energy states will be less probable. In statistical physics the entropy is determined by a maximization procedure in which one or more constraints are enforced. In a canonical ensemble we search for the maximum entropy under the constraints of given total total energy $E = \langle\mathcal{H}\rangle = \mathrm{tr}\,\varrho\mathcal{H}$ and unit normalization, $\mathcal{N} = \mathrm{tr}\,\varrho = 1$. To describe the procedure, we turn to the representation of $\mathcal{H}$, denoted by $\{|s\rangle\} = \{|1\rangle, \cdots, |n\rangle\}$, because in this representation the density matrix is diagonal. For the sake of the argument we restrict ourselves to discrete systems with a finite-dimensional Hilbert space. The lagrangian for the variation of the diagonal elements of the density matrix $\{\varrho_{ss}\}$, and the multipliers β (for total energy) and γ (for normalization) is stationary if the following conditions are satisfied - see Problem B.6

$$\delta L = \sum_{s=1}^{n}\delta\varrho_{ss}\left[-(\ln\varrho_{ss}+1) - \beta E_s - \gamma\right] = 0, \tag{B.121a}$$

$$\delta E = \sum_{s=1}^{n}\varrho_{ss}E_s - E = 0, \tag{B.121b}$$

$$\delta\mathcal{N} = \sum_{s=1}^{n}\varrho_{ss} - 1 = 0, \tag{B.121c}$$

where $E_s = \langle s|\mathcal{H}|s\rangle$ is the energy of the eigenstate $|s\rangle$. To assure that Eq. (B.121a) be valid for *arbitrary* variations of $\{\delta\varrho_{ss}\}$, we require

$$[(\ln\varrho_{ss}+1) + \beta E_s + \gamma] = 0. \tag{B.122}$$

Renaming the lagrange multiplier $\gamma \to -(1+\beta F)$ we obtain

$$\ln\varrho_{ss} = -\beta(E_s - F), \tag{B.123}$$

which can be written in the form

$$\varrho_{ss} = e^{-\beta(E_s-F)} = \frac{1}{Z}e^{-\beta E_s}. \tag{B.124}$$

Hence, the corresponding density matrix can be defined in the form of a statistical operator,

$$\varrho = \frac{1}{Z} e^{-\beta \mathcal{H}}. \tag{B.125}$$

Imposing the normalization condition (B.121c) we find

$$Z = e^{-\beta F} = \sum_{s=1}^{n} e^{-\beta E_s}. \tag{B.126}$$

By identifying $\beta \equiv 1/k_B T$, we recognize the well-known expression for the canonical partition sum. Note that in the high-temperature limit ($\beta \to 0$) we obtain $Z = n$ and $\varrho_{ss} = 1/n$, which shows that the limiting value for the entropy is that of a random ensemble, $S = \ln n$.

For finite temperature we find for the entropy

$$S/k_B = -\sum_{s=1}^{n} \varrho_{ss} \ln \varrho_{ss} = \beta \sum_{s=1}^{n} \varrho_{ss}(E_s - F) = \beta(E - F), \tag{B.127}$$

where we used Eq. (B.121b). Identifying F with the Helmholtz free energy and E with the internal energy U we obtain the thermodynamic relation

$$F = U - TS. \tag{B.128}$$

Problem B.6. Show that the deviation of the lagrangian of the canonical ensemble of size n vanishes under variation of the $\{\varrho_{ss}\}$, with $s \in \{1, \cdots n\}$ if

$$\delta L = \sum_{s=1}^{n} \delta \varrho_{ss} \left[-(\ln \varrho_{ss} + 1) - \beta E_s - \gamma \right] = 0.$$

Solution. The lagrangian for the variation of the $\{\varrho_{ss}\}$ of the canonical ensemble under the constraints of fixed total total energy $E = \langle \mathcal{H} \rangle = \mathrm{tr}\, \varrho \mathcal{H}$ and normalization, $\mathrm{tr}\, \varrho = 1$, is given by

$$L(\{\varrho_{ss}\}_n, \beta, \gamma) = \sum_{s=1}^{n} \left[-\varrho_{ss} \ln \varrho_{ss} + \beta(E - \varrho_{ss} E_s) + \gamma(1 - \varrho_{ss}) \right].$$

Hence, L is stationary under partial variation of ϱ_{ss} provided

$$\frac{\delta L}{\delta \varrho_{ss}} = -(\ln \varrho_{ss} + 1) - \beta E_s - \gamma = 0$$

and also stationary under partial variation of β and γ provided

$$\frac{\delta L}{\delta \beta} = E - \sum_{s=1}^{n} \varrho_{ss} E_s = 0 \quad \text{and} \quad \frac{\delta L}{\delta \gamma} = 1 - \sum_{s=1}^{n} \varrho_{ss} = 0.$$

Hence, L is stationary under simultaneous variation of of $\{\varrho_{ss}\}_n$, β and γ if

$$\delta L = \sum_{s=1}^{n} \left[-(\ln \varrho_{ss} + 1) - \beta E_s - \gamma \right] \delta \varrho_{ss} = 0, \quad \sum_{s=1}^{n} \varrho_{ss} E_s = E \quad \text{and} \quad \sum_{s=1}^{n} \varrho_{ss} = 1. \qquad \square$$

B.4 Conservation of normalization and current density

The rate of change of normalization of a wave function can be written as a continuity equation

$$\frac{\partial}{\partial t}\left|\Psi(r,t)\right|^2 + \boldsymbol{\nabla}\cdot\mathbf{j} = 0, \tag{B.129}$$

which defines $\mathbf{j}$ as the probability current density of the wave function. With the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t) = H\,\Psi(r,t) \tag{B.130a}$$

$$-i\hbar\frac{\partial}{\partial t}\Psi^*(r,t) = H\,\Psi^*(r,t) \tag{B.130b}$$

we find

$$\begin{aligned}\frac{\partial}{\partial t}\left|\Psi(r,t)\right|^2 &= \Psi^*(r,t)\frac{\partial}{\partial t}\Psi(r,t) + \Psi(r,t)\frac{\partial}{\partial t}\Psi^*(r,t)\\ &= \frac{1}{i\hbar}\left[\Psi^*(H\Psi) - \Psi(H\Psi^*)\right].\end{aligned} \tag{B.131}$$

Hence,

$$\boldsymbol{\nabla}\cdot\mathbf{j} = \frac{i}{\hbar}\left[\Psi^*(H\Psi) - \Psi(H\Psi^*)\right]. \tag{B.132}$$

Hence, together with the continuity equation this equation shows that the normalization of a stationary state is conserved if the Hamiltonian is hermitian.

For a Hamiltonian of the type

$$H = -\frac{\hbar^2}{2m}\Delta + V(r) \tag{B.133}$$

the Eq. (B.132) takes the form

$$\boldsymbol{\nabla}\cdot\mathbf{j} = -\frac{i\hbar}{2m}\left[\psi^*(\boldsymbol{\nabla}^2\psi) - (\boldsymbol{\nabla}^2\psi^*)\psi\right] = -\frac{i\hbar}{2m}\boldsymbol{\nabla}\cdot\left[\psi^*(\boldsymbol{\nabla}\psi) - (\boldsymbol{\nabla}\psi^*)\psi\right]. \tag{B.134}$$

Hence, the continuity equation is satisfied by defining the probability current density as

$$\mathbf{j} = -\frac{i\hbar}{2m}\left(\psi^*\boldsymbol{\nabla}\psi - \psi\boldsymbol{\nabla}\psi^*\right). \tag{B.135}$$

The probability current density is a real quantity,

$$\mathbf{j} = \mathrm{Re}\left[\frac{-i\hbar}{m}\psi^*\boldsymbol{\nabla}\psi\right] = \mathrm{Re}\left[\psi^*\mathbf{v}\psi\right], \tag{B.136}$$

where $\mathbf{v} = \mathbf{p}/m = (-i\hbar/m)\,\boldsymbol{\nabla}$ is the *velocity operator*, in which we recognize the well-known *correspondence rule* $\mathbf{p} \to -i\hbar\boldsymbol{\nabla}$.

Writing ψ as the product of a *position-independent* amplitude $|\psi|$ and a *position-dependent* phase factor, $\psi = |\psi|e^{i\phi}$, we have

$$\mathbf{j} = \frac{i\hbar}{2m}\left(\psi\boldsymbol{\nabla}\psi^* - \psi^*\boldsymbol{\nabla}\psi\right) = \frac{i\hbar}{2m}|\psi|^2\left(e^{i\phi}\boldsymbol{\nabla}e^{-i\phi} - e^{-i\phi}\boldsymbol{\nabla}e^{i\phi}\right) = |\psi|^2\,(\hbar/m)\,\boldsymbol{\nabla}\phi. \tag{B.137}$$

Keeping in mind the flux relation $\mathbf{j} = n\mathbf{v}$, we identify $n = |\psi|^2$ as the *probability density* and

$$\mathbf{v} = (\hbar/m)\,\boldsymbol{\nabla}\phi \tag{B.138}$$

as the *probability-flow velocity*.

C

Properties of functions, series and integrals

C.1 Finite sums of powers

The best known example is the *arithmetic series*:

$$\sum_{k=1}^{n} a_k = \tfrac{1}{2} n(a_n + a_1), \text{ with } a_{n+1} = a_n + v, \tag{C.1}$$

where v is called the difference between successive terms. In particular, for $a_k = k$ this becomes

$$\sum_{k=1}^{n} k = \tfrac{1}{2} n(n+1). \tag{C.2}$$

Related finite sums are

$$\sum_{k=1}^{n} k^2 = \tfrac{1}{6} n(n+1)(2n+1) \tag{C.3}$$

$$\sum_{k=1}^{n} k^3 = \tfrac{1}{4} n^2 (n+1)^2. \tag{C.4}$$

Sums of powers of (generally complex) numbers:

$$\sum_{k=1}^{n} k^n z^k = \left(z \frac{d}{dz} \right)^n \frac{z - z^{n+1}}{1 - z}. \tag{C.5}$$

The best known example is the *geometric series*

$$\sum_{k=1}^{n} a_k = a_1 \frac{1 - r^n}{1 - r}, \text{ with } a_{n+1} = r a_n. \tag{C.6}$$

The factor r is called the ratio of the series; i.e., the ratio of two subsequent terms. Other examples of summations of this type are

$$\sum_{k=1}^{n} k z^k = z \frac{1 - (n+1) z^n + n z^{n+1}}{(1 - z)^2} \tag{C.7}$$

$$\sum_{k=1}^{n} k^2 z^k = z \frac{1 + z - (n+1)^2 z^n + (2n^2 + 2n - 1) z^{n+1} - n^2 z^{n+2}}{(1 - z)^3}. \tag{C.8}$$

C.2 Gamma function

The gamma function is defined for the complex z plane excluding the non-positive integers

$$\int_0^\infty e^{-x} x^{z-1} dx = \Gamma(z). \tag{C.9}$$

For integer values $z - 1 = n = 0, 1, 2, \cdots$ the gamma function coincides with the factorial function,

$$\int_0^\infty e^{-x} x^n dx = \Gamma(n+1) = n! \tag{C.10}$$

Some special values are:

$$\begin{array}{lll} \Gamma(-1/2) = -2\sqrt{\pi} = -3.545, & \Gamma(1/2) = \sqrt{\pi} = 1.772, & \Gamma(1) = 1 \\ \Gamma(-3/2) = \frac{4}{3}\sqrt{\pi} = 2.363, & \Gamma(3/2) = \frac{1}{2}\sqrt{\pi} = 0.886, & \Gamma(2) = 1 \\ & \Gamma(5/2) = \frac{3}{4}\sqrt{\pi} = 1.329, & \Gamma(3) = 2 \\ & \Gamma(7/2) = \frac{15}{8}\sqrt{\pi} = 3.323, & \Gamma(4) = 6. \end{array} \tag{C.11}$$

Some related integrals are

$$\int_0^\infty e^{-x^2} x^{2n+1} dx = \frac{1}{2} n! \tag{C.12}$$

$$\int_0^\infty e^{-x^2} x^{2n} dx = \frac{(2n-1)!!}{2^{n+1}} \sqrt{\pi}. \tag{C.13}$$

A useful integral relation is

$$\int_0^\infty e^{-\ell x^n} x^m dx = \frac{1}{\ell^{(m+1)/n}} \int_0^\infty e^{-x^n} x^m dx. \tag{C.14}$$

C.3 Polylogarithm

The polylogarithm $\mathrm{Li}_\alpha(z)$ is a special function defined over the unit disk in the complex plane by the series expansion

$$\mathrm{Li}_\alpha(z) = \mathrm{PolyLog}[\alpha, z] \equiv \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^\alpha} \qquad (|z| < 1), \tag{C.15}$$

where α is an arbitrary complex number. By analytic continuation the polylogarithm can be defined over a larger range of z. For z and α on the *real axis* and for $\alpha > 1$ the polylogarithm are given by the Bose-Einstein integrals

$$F_\alpha^{\mathrm{BE}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty \frac{x^{\alpha-1}}{z^{-1} e^x - 1} dx \qquad (z < 1) \tag{C.16}$$

and the Fermi-Dirac integrals

$$F_\alpha^{\mathrm{FD}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty \frac{x^{\alpha-1}}{z^{-1} e^x + 1} dx \qquad (z \geq -1). \tag{C.17}$$

Recurrence relations:

$$F_\alpha^{\mathrm{BE/FD}}(z) = z \frac{d}{dz} F_{\alpha+1}^{\mathrm{BE/FD}}(z) \qquad \Leftrightarrow \qquad F_\alpha^{\mathrm{BE/FD}}(e^u) = \frac{d}{du} F_{\alpha+1}^{\mathrm{BE/FD}}(e^u). \tag{C.18}$$

C.4 Bose-Einstein function

The Bose-Einstein (BE) integrals are defined for real z and $\alpha > 1$ as

$$F_\alpha^{\mathrm{BE}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty \frac{x^{\alpha-1}}{z^{-1}e^x - 1} dx \qquad (z < 1). \tag{C.19}$$

The integrals can be expanded in powers of z on the interval $0 < z < 1$,

$$F_\alpha^{\mathrm{BE}}(z) = \frac{1}{\Gamma(\alpha)} \sum_{\ell=1}^{\infty} \int_0^\infty x^{\alpha-1} z^\ell e^{-\ell x} dx = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^\alpha} = g_\alpha(z) = \mathrm{Li}_\alpha(z), \tag{C.20}$$

where $\mathrm{Li}_\alpha(z)$ is the polylogarithm. For *non-integer* values of α the BE-integrals can also be expanded in the form[1]

$$F_\alpha^{\mathrm{BE}}(e^{-u}) = \Gamma(1-\alpha)\, u^{\alpha-1} + \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \zeta(\alpha - n) u^n, \tag{C.21}$$

where the expansion in powers of $u = -\ln z$ is valid on the interval $0 < u < 2\pi$. For *integer* values $\alpha = m \in \{2, 3, 4, \cdots\}$ the BE-integrals the expansion is

$$F_m^{\mathrm{BE}}(e^{-u}) = \frac{(-u)^{m-1}}{(m-1)!} \left(1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{m-1} - \ln u\right) u^{m-1} + \sum_{\substack{n=0 \\ \neq m-1}}^{\infty} \frac{\zeta(m-n)}{n!} u^n, \tag{C.22}$$

with convergence for $0 < u \leq 2\pi$.

C.5 Fermi-Dirac function

The Fermi-Dirac (FD) integrals are defined for real z and $\alpha > 1$ as

$$F_\alpha^{\mathrm{FD}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty \frac{x^{\alpha-1}}{z^{-1}e^x + 1} dx \qquad (z \geq -1). \tag{C.23}$$

The integrals can be expanded in powers of z on the interval $0 < z \leq 1$,

$$F_\alpha^{\mathrm{FD}}(z) = \frac{-1}{\Gamma(\alpha)} \sum_{\ell=1}^{\infty} \int_0^\infty x^{\alpha-1} (-z)^\ell e^{-\ell x} dx = -\sum_{\ell=1}^{\infty} \frac{(-z)^\ell}{\ell^\alpha} = f_\alpha(z) = -\mathrm{Li}_\alpha(-z), \tag{C.24}$$

where $\mathrm{Li}_\alpha(z)$ is the polylogarithm.

C.6 Riemann zeta function

The Riemann zeta function is defined as a Dirichlet series

$$\lim_{z \to 1} g_\alpha(z) = \zeta(\alpha) = \sum_{\ell=1}^{\infty} \frac{1}{\ell^\alpha}. \tag{C.25}$$

Some special values are:

$$\begin{array}{llll} \zeta(1/2) = -1.460, & \zeta(3/2) = 2.612, & \zeta(5/2) = 1.341, & \zeta(7/2) = 1.127, \\ \zeta(1) \to \infty, & \zeta(2) = \pi^2/6 = 1.645, & \zeta(3) = 1.202, & \zeta(4) = \pi^4/90 = 1.082. \end{array}$$

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[1] For a derivation see J.E. Robinson, Phys. Rev. 83, 678 (1951).

C.7 Selected integrals and rules

For $\gamma > 0$ and $\varepsilon > 0$

$$\int_0^\varepsilon \sqrt{x}\,(\varepsilon - x)^{\gamma-1}\,dx = \frac{\sqrt{\pi}\Gamma(\gamma)}{2\,\Gamma\,(3/2+\gamma)}\varepsilon^{1/2+\gamma} \tag{C.26}$$

The *Leibniz integral rule* for moving boundaries is given by

$$\frac{d}{dt}\int_{a(t)}^{b(t)} f(x,t)dx = \int_{a(t)}^{b(t)} \frac{\partial}{\partial t}f(x,t)dx + f(x,t)\frac{d}{dt}b(t) - f(x,t)\frac{d}{dt}a(t) \tag{C.27}$$

In particular, for definite integrals with fixed boundaries this integration rule becomes

$$\frac{d}{dt}\int f(x,t)dx = \int \frac{\partial}{\partial t}f(x,t)dx. \tag{C.28}$$

C.8 Commutator algebra

If A, B, C and D are four arbitrary linear operators the following relations hold:

$$[A,B] = -\,[B,A] \tag{C.29a}$$

$$[A,B+C] = [A,B] + [A,C] \tag{C.29b}$$

$$[A,BC] = [A,B]\,C + B\,[A,C] \tag{C.29c}$$

$$[AB,CD] = A[B,C]D + AC[B,D] + [A,C]DB + C[A,D]B \tag{C.29d}$$

$$0 = [A,[B,C]] + [B,[C,A]] + [C,[A,B]]\,. \tag{C.29e}$$

Commutators containing B^n:

$$[A,B^n] = \sum_{s=0}^{n-1} B^s\,[A,B]\,B^{n-s-1} \tag{C.30a}$$

$$[A,B^n] = nB^{n-1}\,[A,B] \text{ if } B \text{ commutes with } [A,B]. \tag{C.30b}$$

The exponential operator is defined as:

$$e^A \equiv \sum_{n=0}^{\infty}\frac{A^n}{n!}. \tag{C.31}$$

Baker-Campbell-Hausdorff formula:

$$e^A e^B = e^C, \tag{C.32}$$

where

$$C = A + B + \tfrac{1}{2}[A,B] + \tfrac{1}{12}([A,[A,B]] + [[A,B],B]) + \cdots\,.$$

Special cases:

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]} \text{ if } A \text{ and } B \text{ commute with } [A,B] \tag{C.33a}$$

$$e^A B e^{-A} = B + [A,B] + \tfrac{1}{2!}[A,[A,B]] + \tfrac{1}{3!}[A,[A,[A,B]]] + \cdots \tag{C.33b}$$

$$e^A B e^{-A} = B + [A,B] \text{ if } A \text{ commutes with } [A,B] \tag{C.33c}$$

$$e^A B e^{-A} = e^\gamma B \text{ if } [A,B] = \gamma B, \text{ with } \gamma \text{ a constant.} \tag{C.33d}$$

Trotter formula:

$$e^{A+B} = \lim_{N\to\infty}(e^{A/N}e^{B/N})^N. \tag{C.34}$$

Zassenhaus formula:

$$e^{A+B} = e^A e^B \prod_{n=2}^{\infty} e^{C_n}, \tag{C.35}$$

where

$$C_2 = -\tfrac{1}{2}[A,B]; \quad C_3 = \tfrac{1}{6}(2[A,[A,B]] - [[A,B],B]).$$

C.9 Legendre polynomials

The associated Legendre differential equation is given by,

$$\left[\left(1-u^2\right)\frac{d^2}{du^2} - 2u\frac{d}{du} - \frac{m^2}{1-u^2} + l(l+1)\right] P_l^m(u) = 0 \tag{C.36}$$

For $m = 0$ this equation is called the Legendre differential equation and its solutions are the Legendre polynomials, defined by the *Rodrigues formula*:

$$P_l(u) = \frac{1}{2^l l!}\frac{d^l}{du^l}(u^2-1)^l. \tag{C.37}$$

$P_l(u)$ is a real polynomial of *degree* $l \in \{0, 1, 2 \cdots\}$, *parity*

$$P_l(-u) = (-1)^l P_l(u) \tag{C.38}$$

and having l zeros in the interval $-1 \le u \le 1$. The Legendre polynomials of lowest degree are

$$P_0(u) = 1, \quad P_1(u) = u, \quad P_2(u) = \tfrac{1}{2}(3u^2 - 1) \tag{C.39}$$

$$P_3(u) = \tfrac{1}{2}(5u^3 - 3u), \quad P_4(u) = \tfrac{1}{8}(35u^4 - 30u^2 + 3). \tag{C.40}$$

The Legendre polynomials are generated by expansion of the function

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{\sqrt{r^2 - 2urr' + r'^2}} = \frac{1}{r_>}\sum_l \left(\frac{r_<}{r_>}\right)^l P_l(u), \tag{C.41}$$

where $r_> = \max\{r, r'\}$ and $r_< = \min\{r, r'\}$ with $r = |\mathbf{r}|$ and $r' = |\mathbf{r}'|$; further $u = \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}' = \cos\theta$, with θ the angle included by the unit vectors $\hat{\mathbf{r}}$ and $\hat{\mathbf{r}}'$. The expansion (C.41) is called the *multipole expansion.*

For $m \neq 0$ the solutions of Eq. (C.36) are called the associated Legendre functions $P_l^m(u)$. For $m = 0$ they coincide with the Legendre polynomials. For $m > 0$ the $P_l^m(u)$ are obtained by differentiation of the $P_l(u)$,[1]

$$P_l^m(u) = (-1)^m (1-u^2)^{m/2} \frac{d^m}{du^m} P_l(u). \tag{C.42}$$

Note that $P_l^0(u) \equiv P_l(u)$. The differentiation fixes the relative sign of the polynomials of different power. These functions consist of the product of a function $(-1)^m(1-u^2)^{m/2}$ and a polynomial of degree $(l-m)$, parity $(-1)^{l-m}$ with $(l-m)$ zeros in the interval $-1 \le u \le 1$. For crossing from positive to negative m the sign and normalization are fixed by convention,[2]

$$P_l^{-m}(u) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(u), \tag{C.43}$$

---

[1] Here the phase factor $(-1)^m$ is introduced to simplify the definition of the spherical harmonics. This convention is implemented in *Mathematica* but deviates from the convention used in most texts on quantum mechanics. Beware that differences in phase convention affect the recursion relations (C.48) and (C.49).

[2] Note that the phase factor oscillates like $(-1)^m$ for $m > 0 \cdots$ but is always 1 for $m \le 0$. This is the signature of the Condon and Shortley phase convention [11].

where $0 \leq m \leq l$. The $P_l^m(u)$ are nonzero only for $-l \leq m \leq l$; i.e., the index m can assume $2l+1$ possible values for a given value of l. Particular cases are

$$P_l^0(u) = P_l(u), \quad P_l^l(u) = (-1)^{-l}(2l-1)!!(1-u^2)^{l/2}. \tag{C.44}$$

The *orthogonality* of the P_l^m is expressed by

$$\int_{-1}^{1} P_l^m(u) P_{l'}^m(u) du = 0 \qquad (l \neq l') \tag{C.45a}$$

$$\int_{-1}^{1} P_l^m(u) P_l^{m'}(u) du = 0 \qquad (m \neq m'). \tag{C.45b}$$

The *normalization* of the P_l^m is expressed by

$$\int_{-1}^{1} \left[P_l^m(u)\right]^2 du = 2\int_{0}^{1} \left[P_l^m(u)\right]^2 du = \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!}. \tag{C.46}$$

The following recursion *relations* hold for $-l \leq m \leq l$:

$$(2l+1)uP_l^m(u) = (l-m+1)P_{l+1}^m(u) + (l+m)P_{l-1}^m(u) \tag{C.47}$$

$$\sqrt{1-u^2}P_l^{m+1}(u) = -(l-m+1)(l+m)\sqrt{1-u^2}P_l^{m-1}(u) - 2muP_l^m(u) \tag{C.48}$$

and

$$(1-u^2)\frac{d}{du}P_l^m(u) = -luP_l^m(u) + (l+m)P_{l-1}^m(u) \tag{C.49a}$$

$$= (l+1)uP_l^m(u) - (l-m+1)P_{l+1}^m(u) \tag{C.49b}$$

$$= -muP_l^m(u) - \sqrt{1-u^2}P_l^{m+1}(u) \tag{C.49c}$$

$$= +muP_l^m(u) + (l-m+1)(l+m)\sqrt{1-u^2}P_l^{m-1}(u). \tag{C.49d}$$

C.9.1 Spherical harmonics $Y_l^m(\theta,\varphi)$

The *spherical harmonics* are defined as the joint, *normalized* eigenfunctions of $\mathbf{L}^2$ and L_z. Their relation to the associated Legendre polynomials is given by

$$Y_l^m(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\varphi}, \tag{C.50}$$

with $-l \leq m \leq l$. The *orthonormality relation* is

$$\int Y_l^{m*}(\hat{\mathbf{r}})Y_{l'}^{m'}(\hat{\mathbf{r}})d\hat{\mathbf{r}} = \delta_{l'l}\delta_{m'm}. \tag{C.51}$$

Using Eq. (C.43) we find that the *complex conjugation* is given by

$$Y_l^{m*}(\hat{\mathbf{r}}) = (-1)^m Y_l^{-m}(\hat{\mathbf{r}}). \tag{C.52}$$

The *parity* under space inversion, $\hat{\mathbf{r}} = (\theta,\varphi) \to -\hat{\mathbf{r}} = (\pi-\theta, \varphi+\pi)$, is given by

$$Y_l^m(-\hat{\mathbf{r}}) = (-1)^l Y_l^m(\hat{\mathbf{r}}). \tag{C.53}$$

Alternatively, the spherical harmonics can be defined using only associated Legendre functions of positive m,[1]

$$Y_l^m(\theta,\varphi)=\varepsilon\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\varphi}\quad\text{with}\quad\varepsilon=\begin{cases}(-1)^m & \text{for } m\geq 0\\ 1 & \text{for } m<0.\end{cases}\tag{C.54}$$

Note that the spherical harmonics with even l have even parity and those with odd l have odd parity. The lowest order spherical harmonics are:

$$\left.\begin{array}{rll}
 & \sqrt{\frac{4\pi}{2l+1}}Y_l^m(\theta,\varphi)-\mathit{spherical} & \sqrt{\frac{4\pi}{2l+1}}Y_l^m(x,y,z)-\mathit{cartesian}\\
Y_0^0= & 1 & \Leftrightarrow\ 1\\
Y_1^0= & \cos\theta & \Leftrightarrow\ z/r\\
Y_1^{\pm1}= & \mp\sqrt{\tfrac12}\sin\theta\ e^{\pm i\varphi} & \Leftrightarrow\mp\sqrt{\tfrac12}\,(x\pm iy)\,/r\\
Y_2^0= & \tfrac12\left(3\cos^2\theta-1\right) & \Leftrightarrow\ \tfrac12\left(3z^2-r^2\right)/r\\
Y_2^{\pm1}= & \sqrt{\tfrac32}\sin\theta\cos\theta\ e^{\pm i\varphi} & \Leftrightarrow\ \sqrt{\tfrac32}\,(x\pm iy)\,z/r^2\\
Y_2^{\pm2}= & \sqrt{\tfrac32\tfrac12}\sin^2\theta\ e^{\pm 2i\varphi} & \Leftrightarrow\ \sqrt{\tfrac32\tfrac12}\,(x\pm iy)^2\,/r^2\\
Y_3^0= & \tfrac12\left(2\cos^3\theta-3\cos\theta\sin^2\theta\right) & \Leftrightarrow\ \tfrac12\left(5z^2-3r^2\right)z/r^3\\
Y_3^{\pm1}= & \mp\sqrt{\tfrac{3}{16}}\left(4\cos^2\theta\sin\theta-\sin^3\theta\right)e^{\pm i\varphi} & \Leftrightarrow\mp\sqrt{\tfrac{3}{16}}\,(x\pm iy)\left(5z^2-r^2\right)/r^3\\
Y_3^{\pm2}= & \sqrt{\tfrac{15}{2}\tfrac12}\cos\theta\sin^2\theta\ e^{\pm 2i\varphi} & \Leftrightarrow\ \sqrt{\tfrac{15}{2}\tfrac12}\,(x\pm iy)^2\,z/r^3\\
Y_3^{\pm3}= & \mp\sqrt{\tfrac52}\sqrt{\tfrac18}\sin^3\theta\ e^{\pm 3i\varphi} & \Leftrightarrow\mp\sqrt{\tfrac52}\sqrt{\tfrac18}\,(x\pm iy)^3\,/r^3.
\end{array}\right\}\tag{C.55}$$

Note that

$$Y_l^m(\theta,\varphi)|_{\grave{\theta}=0}=\sqrt{\frac{2l+1}{4\pi}}\delta_{m,0}.$$

Furthermore, the phase factor oscillates like $(-1)^m$ for $m=1,3,5,\cdots 0$ but is always 1 for $m<0$; this is the signature of the Condon and Shortley phase convention.

The *addition theorem* relates the angle θ_{12} between two directions $\hat{\mathbf{r}}_1=(\theta_1,\varphi_1)$ and $\hat{\mathbf{r}}_2=(\theta_2,\varphi_2)$ relative to a coordinate system of choice,

$$\frac{2l+1}{4\pi}P_l(\cos\theta_{12})=\sum_{m=-l}^{l}Y_l^{m*}(\hat{\mathbf{r}}_1)Y_l^m(\hat{\mathbf{r}}_2).\tag{C.56}$$

The product of two spherical harmonics can be expressed in terms of Wigner $3j$ symbols

$$Y_l^m(\hat{\mathbf{r}})Y_{l'}^{m'}(\hat{\mathbf{r}})=\sum_{L=|l-l'|}^{l+l'}\sum_{M=-L}^{L}(-1)^M\sqrt{\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}}\times\begin{pmatrix}l\,l'\,L\\0\,0\,0\end{pmatrix}\begin{pmatrix}l & l' & L\\m & m' & M\end{pmatrix}Y_L^{-M}(\hat{\mathbf{r}}),\tag{C.57}$$

---

[1] Note that the phase factor $(-1)^m$ is only included for positive m. This is the signature of the Condon and Shortley phase convention [11].

An important relation is the *integral over three spherical harmonics* [26]

$$\int Y_{l_1}^{m_1}(\hat{\mathbf{r}})Y_{l_2}^{m_2}(\hat{\mathbf{r}})Y_{l_3}^{m_3}(\hat{\mathbf{r}})d\hat{\mathbf{r}} = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \qquad (C.58)$$

In Dirac notation this becomes

$$\langle l'm'|\, Y_k^q(\hat{\mathbf{r}})\, |lm\rangle = (-1)^{m'} \sqrt{\frac{(2l'+1)(2k+1)(2l+1)}{4\pi}} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix}. \qquad (C.59)$$

Some special cases are:

- $k=0$: The $3j$ symbols are zero unless $l'=l$ and $m'=m$; hence, we find

$$\langle l'm'|\, \sqrt{4\pi}\, Y_0^0(\hat{\mathbf{r}})\, |lm\rangle = \delta_{l',l}\delta_{m',m} \qquad (C.60)$$

- $k=1$: The first $3j$ symbol is zero unless $l'=l\pm 1$; hence, we find

$$\langle l'm'|\, \sqrt{4\pi/3}\, Y_1^q(\hat{\mathbf{r}})\, |lm\rangle = (-1)^{m'+\max(l,l')} \sqrt{\max(l,l')} \begin{pmatrix} l' & 1 & l \\ -m' & q & m \end{pmatrix} \delta_{l',l\pm 1} \qquad (C.61)$$

- $k=2$: The first $3j$ symbol is zero unless $l'=l,\ l\pm 2$; hence, we find

$$\langle l'm'|\, \sqrt{4\pi/5}\, Y_2^q(\hat{\mathbf{r}})\, |lm\rangle = \begin{cases} (-1)^{m'+l+1} \sqrt{\dfrac{l\,(l+1)\,(2l+1)}{(2l+3)(2l-1)}} \begin{pmatrix} l & 2 & l \\ -m' & q & m \end{pmatrix} & l'=l \\ (-1)^{m'+l} \sqrt{\dfrac{3}{4}\dfrac{l+l'}{l+l'+1}} \sqrt{\max(l,l')} \begin{pmatrix} l' & 2 & l \\ -m' & q & m \end{pmatrix} & l'=l\pm 2. \end{cases} \qquad (C.62)$$

C.10 Hermite polynomials

The Hermite differential equation is given by

$$y'' - 2xy' + 2ny = 0. \qquad (C.63)$$

For $n = 0, 1, 2, \ldots$ the solutions satisfy the Rodrigues formula

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}(e^{-x^2}). \qquad (C.64)$$

These solutions are polynomials of *degree* n known as *Hermite polynomials*. Examples:

$$\begin{array}{ll} H_0\,(x) = 1 & H_4\,(x) = 16x^4 - 48x^2 + 12 \\ H_1\,(x) = 2x & H_5\,(x) = 32x^5 - 160x^3 + 120x \\ H_2\,(x) = 4x^2 - 2 & H_6\,(x) = 64x^6 - 480x^4 + 720x^2 - 120 \\ H_3\,(x) = 8x^3 - 12x & H_7\,(x) = 128x^7 - 1344x^5 + 3360x^3 - 1680x\,. \end{array} \qquad (C.65)$$

The generating function is

$$e^{2tx-t^2} = \sum_{n=0}^{\infty} H_n\,(x)\,\frac{t^n}{n!}. \qquad (C.66)$$

Useful recursion relations are

$$H_{n+1}\,(x) = 2xH_n\,(x) - 2nH_{n-1}\,(x) \qquad (C.67)$$

$$H_n'\,(x) = 2nH_{n-1}\,(x) \qquad (C.68)$$

and the orthogonality relation is given by

$$\int_{-\infty}^{\infty} e^{-x^2} H_m\,(x)\,H_n\,(x) = 2^n n! \sqrt{\pi}\delta_{mn}\,. \qquad (C.69)$$

C.11 Laguerre polynomials

Generalized Laguerre polynomials satisfy the following differential equation

$$xy'' + (\alpha + 1 - x)y' + 2ny = 0. \tag{C.70}$$

For $n = 0, 1, 2, \ldots$ the solutions satisfy the Rodrigues formula[1]

$$L_n^\alpha(x) = \frac{1}{n!} e^x x^{-\alpha} \frac{d^n}{dx^n}(e^{-x} x^{n+\alpha}) \tag{C.71}$$

$$= \sum_{m=0}^{n} (-1)^m \binom{n+\alpha}{n-m} \frac{x^m}{m!}$$

$$= \sum_{m=0}^{n} \frac{\Gamma(\alpha+n+1)}{\Gamma(\alpha+m+1)} \frac{(-1)^m}{(n-m)!} \frac{x^m}{m!} \tag{C.72}$$

These polynomials are well-defined also for real $\alpha > -1$ because the ratio of two gamma functions differing by an integer is well-defined, $(\beta)_n = \beta(\beta+1)(\beta+2)\cdots(\beta+n-1) = \Gamma(\beta+n)/\Gamma(\beta)$. The *Laguerre polynomials* of lowest *degree* are given by

$$L_0^\alpha(x) = 1, \quad L_1^\alpha(x) = \alpha + 1 - x, \quad L_2^\alpha(x) = \tfrac{1}{2}(\alpha+1)(\alpha+2) - (\alpha+2)x + \tfrac{1}{2}x^2. \tag{C.73}$$

Some special cases for $\alpha = 0$ and $\alpha = -n$ are

$$L_0(x) = 1, \quad L_1(x) = 1 - x, \quad L_2(x) = 1 - 2x + \tfrac{1}{2}x^2, \quad L_n^{-n}(x) = (-1)^n \frac{x^n}{n!}. \tag{C.74}$$

The generating function is

$$\frac{(-1)^m\, t^m}{(1-t)^{m+1}} e^{-x/(1-t)} = \sum_{n=m}^{\infty} L_n^m\,(x)\,\frac{t^n}{n!}. \tag{C.75}$$

The generalized Laguerre polynomials satisfy the orthogonality relation

$$\int_0^\infty x^\alpha e^{-x} L_n^\alpha(x) L_m^\alpha(x) dx = 0 \text{ for } m \neq n \text{ (orthogonality relation)} \tag{C.76}$$

$$\int_0^\infty x^\alpha e^{-x} L_n^\alpha(x) dx = \Gamma(\alpha+1)\delta_{0,n}\,. \tag{C.77}$$

Useful recursion relations are:

$$xL_n^\alpha(x) = (2n+\alpha+1)L_n^\alpha(x) - (n+\alpha)L_{n-1}^\alpha(x) - (n+1)L_{n+1}^\alpha \tag{C.78}$$

$$\frac{d}{dx}L_n^\alpha(x) = -L_{n-1}^{\alpha+1}(x) = -[1 + L_1^\alpha(x) + \cdots + L_{n-1}^\alpha(x)]. \tag{C.79}$$

Series expansions:

$$L_n^{\alpha+1}(x) = \sum_{m=0}^{n} L_m^\alpha(x) \tag{C.80a}$$

$$\frac{d}{dx}L_n^\alpha(x) = -\sum_{m=0}^{n-1} L_m^\alpha(x) \tag{C.80b}$$

$$\frac{d^2}{dx^2}L_n^\alpha(x) = \sum_{m=0}^{n-2} (n-m-1)\, L_m^\alpha(x). \tag{C.80c}$$

---

[1] Different definitions can be found in the literature. Here we adhere to the definition of the generalized Laguerre polynomials as used in the *Handbook of Mathematical functions* by Abramowitz and Stegun (Eds.), Dover Publications, New York 1965. This definition is also used by *Mathematica*.

Further, it is practical to introduce a generalized normalization integral

$$J_\nu(m,\alpha)=\int_0^\infty x^{\alpha+\nu}e^{-x}[L_m^\alpha(x)]^2dx. \tag{C.81}$$

Some special cases are given by

$$J_0(m,\alpha)=\int_0^\infty x^{\alpha}e^{-x}[L_m^\alpha(x)]^2dx=\frac{\Gamma(\alpha+m+1)}{m!} \tag{C.82}$$

$$J_1(m,\alpha)=\int_0^\infty x^{\alpha+1}e^{-x}[L_m^\alpha(x)]^2dx=\frac{\Gamma(\alpha+m+1)}{m!}(2m+\alpha+1) \tag{C.83}$$

$$J_2(m,\alpha)=\int_0^\infty x^{\alpha+2}e^{-x}[L_m^\alpha(x)]^2dx=\frac{\Gamma(\alpha+m+1)}{m!}[6m(m+\alpha+1)+\alpha^2+3\alpha+2] \tag{C.84}$$

$$J_{-1}(m,\alpha)=\int_0^\infty x^{\alpha-1}e^{-x}[L_m^\alpha(x)]^2dx=\frac{1}{\alpha}\int_0^\infty x^{\alpha}e^{-x}[L_m^\alpha(x)]^2dx=\frac{\Gamma(\alpha+m+1)}{m!}\frac{1}{\alpha} \tag{C.85}$$

The integrals $J_\nu(m,\alpha)$ with $\nu>0$ are obtained from Eq. (C.82) by repetitive use of the recursion relation (C.78) and orthogonality relation (C.76); integrals $J_\nu(m,\alpha)$ with $\nu<0$ are obtained from Eq. (C.82) by partial integration and use of the recursion relation (C.79), the orthogonality relation (C.76) and the special integral (C.77).
Selected ratios for $m=n-l-1$ and $\alpha=2l+1$:

$$J_4/J_1=\frac{1}{n}[35n^2(n^2-1)-30n^2(l+2)(l-1)+3(l+2)(l+1)l(l-1)] \tag{C.86}$$

$$J_3/J_1=2\left[5n^2+1-3l(l+1)\right] \tag{C.87}$$

$$J_2/J_1=\frac{1}{n}\left[3n^2-l(l+1)\right] \tag{C.88}$$

$$J_1/J_1=1 \tag{C.89}$$

$$J_0/J_1=\frac{1}{2n} \tag{C.90}$$

$$J_{-1}/J_1=\frac{1}{2n}\frac{1}{2l+1} \tag{C.91}$$

$$J_{-2}/J_1=\frac{1}{8}\frac{1}{(l+1)(l+1/2)l} \tag{C.92}$$

$$J_{-3}/J_1=\frac{1}{32n}\frac{3n^2-l(l+1)}{(l+3/2)(l+1)(l+1/2)l(l-1/2)}. \tag{C.93}$$

C.12 Bessel functions

C.12.1 Spherical Bessel functions and Hankel functions

The spherical Bessel differential equation is given by

$$x^2y''+2xy'+\left[x^2-l(l+1)\right]y=0. \tag{C.94}$$

The general solution is a linear combination of two particular solutions, solutions $j_l\,(x)$, regular (as x^l) at the origin and known as spherical Bessel functions of the first kind, and solutions $n_l($ $x)$, irregular at the origin and known as spherical Bessel function of the second kind (also called Neumann functions). The spherical Bessel functions and the Neumann functions are real. The general solution can also be written as a linear combination of two complex functions called Hankel functions of the first (+) and second (−) type,

$$h_l^\pm(x)=n_l\,(x)\pm ij_l\,(x) \tag{C.95}$$

or, vice versa

$$j_l\,(x) = \frac{1}{2} i \left[h_l^-(x) - h_l^+(x)\right] \tag{C.96a}$$

$$n_l\,(x) = \frac{1}{2} \left[h_l^-(x) + h_l^+(x)\right]. \tag{C.96b}$$

The spherical Bessel functions and Neumann functions are real and Hankel functions can be expressed in the form

$$j_l\,(x) = R_l \frac{\sin x}{x} + S_l \frac{\cos x}{x} \tag{C.97}$$

$$n_l\,(x) = R_l \frac{\sin x}{x} - S_l \frac{\cos x}{x} \tag{C.98}$$

$$h_l^\pm(x) = (R_l \pm iS_l)\, \frac{e^{\pm ix}}{x}, \tag{C.99}$$

where R_l and S_l are polynomials in $1/x$ with real coefficients. In the case of R_l the polynomial is of degree l and has parity $(-1)^l$; the polynomial S_l is of degree $l-1$ and has parity $(-1)^{l-1}$. For real x the polynomial $(R_l \pm iS_l)$ is of the form

$$R_l \pm iS_l = \sum_{s=0}^{l} \frac{(\pm i)^{s-l}}{2^s s!} \frac{(l+s)!}{(l-s)!} \left(\frac{1}{x}\right)^s. \tag{C.100}$$

For real argument x the functions $j_l\,(x)$ and $n_l\,(x)$ are real and the Hankel functions satisfy the relation

$$h_l^\pm(x) = h_l^\mp(x)^*.$$

The parity relations for the spherical Bessel, spherical Neumann and spherical Hankel functions are

$$j_l(-z) = (-1)^l j_l(z) \tag{C.101}$$

$$n_l(-z) = (-1)^{l-1} n_l(z) \tag{C.102}$$

$$h_l^\pm(-z) = (-1)^{l-1} h_l^\mp(z). \tag{C.103}$$

An integral representation of the spherical Bessel function is

$$j_l\,(kr) = \tfrac{1}{2}(-1)^l \int_{-1}^{1} e^{ikr\cos\theta} P_l(\cos\theta) d\cos\theta \tag{C.104}$$

Some special cases are given by

- Lowest orders:

$$\begin{aligned} j_0\,(x) &= \frac{\sin x}{x}, & n_0\,(x) &= \frac{\cos x}{x}, & h_0^\pm(x) &= \frac{e^{\pm ix}}{x}, \\ j_1\,(x) &= \frac{\sin x}{x^2} - \frac{\cos x}{x}, & n_1\,(x) &= \frac{\cos x}{x^2} + \frac{\sin x}{x}, & h_1^\pm(x) &= \left(\frac{1}{x^2} \mp i\frac{1}{x}\right) \frac{e^{\pm ix}}{x}. \end{aligned} \tag{C.105a}$$

- Asymptotic forms for $x \to \infty$

$$j_l\,(x) \underset{x\to\infty}{\sim} \frac{1}{x} \sin(x - \tfrac{1}{2} l\pi) \tag{C.106a}$$

$$n_l\,(x) \underset{x\to\infty}{\sim} \frac{1}{x} \cos(x - \tfrac{1}{2} l\pi) \tag{C.106b}$$

$$h_l^\pm(x) \underset{x\to\infty}{\sim} \frac{e^{\pm i(x - \frac{1}{2} l\pi)}}{x} \left[1 \pm i \frac{l(l+1)}{2x}\right]. \tag{C.106c}$$

- Asymptotic forms for $x \to 0$

$$j_l\left(x\right) \underset{x\to 0}{\sim} \frac{x^l}{(2l+1)!!}\left[1-\frac{x^2}{2(2l+3)}+\cdots\right] \tag{C.107a}$$

$$n_l\left(x\right) \underset{x\to 0}{\sim} \frac{(2l+1)!!}{(2l+1)}\left(\frac{1}{x}\right)^{l+1}\left[1+\frac{x^2}{2(2l-1)}+\cdots\right]. \tag{C.107b}$$

- Orthogonality relations

$$\int_0^\infty j_l\left(k_1 r\right) j_l\left(k_2 r\right) r^2 dr = \frac{\pi}{2k_1^2}\delta(k_1-k_2) \tag{C.108}$$

$$\int_{-\infty}^{\infty} j_l\left(x\right) j_{l'}\left(x\right) dx = \frac{\pi}{2l+1}\delta_{l'l}. \tag{C.109}$$

C.12.1.1 Relation to Ricatti functions

The Ricatti functions $\hat{\jmath}_l\left(x\right)$, $\hat{n}_l\left(x\right)$ and $\hat{h}_l^{\pm}(x)$ are defined as

$$\hat{\jmath}_l\left(x\right) = x j_l\left(x\right) \tag{C.110a}$$

$$\hat{n}_l\left(x\right) = x n_l\left(x\right) \tag{C.110b}$$

$$\hat{h}_l^{\pm}(x) = x h_l^{\pm}(x). \tag{C.110c}$$

C.12.1.2 Relation to Bessel functions

The spherical Bessel functions are related to half-integer Bessel functions

$$j_l\left(x\right) = \sqrt{\frac{\pi}{2x}} J_{l+\frac{1}{2}}(x) \text{ for } l=0,1,2,\ldots \tag{C.111}$$

$$n_l(x) = (-)^l \sqrt{\frac{\pi}{2x}} J_{-l-\frac{1}{2}}(x) \text{ for } l=0,1,2,\ldots \tag{C.112}$$

C.12.2 Bessel functions

The Bessel differential equation is given by

$$x^2 y'' + x y' + \left(x^2-n^2\right) y = 0. \tag{C.113}$$

The general solution is a linear combination of two particular solutions

$$y = A J_n(x) + B J_{-n}(x) \text{ for } n \neq 0,1,2,\cdots \tag{C.114a}$$

$$y = A J_n(x) + B Y_n(x) \text{ for all integer } n \tag{C.114b}$$

where A and B are arbitrary constants and $J_{\pm n}(x)$ are Bessel functions, which are defined by

$$J_{\pm n}(x) = \sum_{p=0}^{\infty} \frac{(-1)^p\,(x/2)^{2p\pm n}}{p!\Gamma\left(1+p\pm n\right)}. \tag{C.115}$$

The $Y_n(x)$ are Neumann functions and are defined by

$$Y_n\left(x\right) = \frac{J_n(x)\cos n\pi - J_{-n}(x)}{\sin n\pi} \text{ for } n \neq 0,1,2,\cdots \tag{C.116}$$

$$Y_n\left(x\right) = \lim_{p\to n} \frac{J_n(x)\cos p\pi - J_{-n}(x)}{\sin p\pi} \text{ for } n = 0,1,2,\cdots. \tag{C.117}$$

Extracting the leading term from the Bessel expansion (C.115) results in

$$J_{\pm n}(x) = \frac{(x/2)^{\pm n}}{\Gamma(1 \pm n)} \left(1 - \frac{(x/2)^2}{(1 \pm n)} + \cdots \right). \tag{C.118}$$

The generating function is of the form

$$e^{x(z-1/z)/2} = \sum_{n=-\infty}^{\infty} J_n(x) z^n, \tag{C.119}$$

in particular for $z = 1$

$$\sum_{n=-\infty}^{\infty} J_n(x) = 1.$$

Some differential recursion relations are for any $n \in \mathbb{Z}$

$$2J_n'(x) = J_{n-1}(x) - J_{n+1}(x) \tag{C.120a}$$

$$\frac{2n}{x} J_n(x) = J_{n+1}(x) + J_{n-1}(x) \tag{C.120b}$$

$$\frac{d}{dx}\left[x^n J_n(x)\right] = x^n J_{n-1}(x). \tag{C.120c}$$

Some integral recursion relations are for any $n \in \mathbb{Z}$

$$\int x^{n+1} J_n(x) dx = x^{n+1} J_{n+1}(x) \tag{C.121}$$

$$\int x^{-n+1} J_n(x) dx = -x^{-n+1} J_{n+1}(x). \tag{C.122}$$

Completeness relations for any $m \neq 0$

$$J_0^2(x) + 2\sum_{n=1}^{\infty} J_n^2(x) = 1 \tag{C.123}$$

$$\sum_{n=-\infty}^{\infty} J_{n+m}(x) J_n(x) = 0. \tag{C.124}$$

Addition relation

$$J_n(x+y) \sum_{m=-\infty}^{\infty} J_m(x) J_{n-m}(y) \tag{C.125}$$

Special cases:

Bessel functions with negative integer index

$$J_{-n}(x) = (-1)^n J_n(x) \text{ for } n = 0, 1, 2, \cdots$$
$$Y_{-n}(x) = (-1)^n Y_n(x) \text{ for } n = 0, 1, 2, \cdots .$$

Bessel function of $n = 1/4$

$$J_{1/4}(x) = \frac{(x/2)^{1/4}}{\Gamma(5/4)} (1 - \frac{(x/2)^2 \Gamma(5/4)}{\Gamma(9/4)} + \cdots) \tag{C.126}$$

$$J_{-1/4}(x) = \frac{(x/2)^{-1/4}}{\Gamma(3/4)} (1 - \frac{(x/2)^2 \Gamma(3/4)}{\Gamma(7/4)} + \cdots) \tag{C.127}$$

Asymptotic expansions:

$$J_n(x) \underset{x\to\infty}{\simeq} \sqrt{\frac{2}{\pi}\frac{1}{x}}\cos\left(x - n\frac{\pi}{2} - \frac{\pi}{4}\right) \tag{C.128}$$

$$Y_n(x) \underset{x\to\infty}{\simeq} \sqrt{\frac{2}{\pi}\frac{1}{x}}\sin\left(x - n\frac{\pi}{2} - \frac{\pi}{4}\right) \tag{C.129}$$

Integral expressions for $\mu + \nu + 1 > \lambda > 0$

$$\int_0^\infty \frac{1}{r^\lambda} J_\mu(kr) J_\nu(kr) dr = \frac{k^{\lambda-1}\Gamma(\lambda)\Gamma\left(\frac{\mu+\nu-\lambda+1}{2}\right)}{2^\lambda \Gamma\left(\frac{\mu-\nu+\lambda+1}{2}\right)\Gamma\left(\frac{\mu+\nu+\lambda+1}{2}\right)\Gamma\left(\frac{\nu-\mu+\lambda+1}{2}\right)}. \tag{C.130}$$

Special cases $2\mu + 1 > \lambda > 0$

$$\int_0^\infty \frac{1}{r^\lambda}\left[J_\mu(kr)\right]^2 dr = \frac{k^{\lambda-1}\Gamma(\lambda)\Gamma\left(\frac{2\mu-\lambda+1}{2}\right)}{2^\lambda\left[\Gamma\left(\frac{\lambda+1}{2}\right)\right]^2\Gamma\left(\frac{2\mu+\lambda+1}{2}\right)}. \tag{C.131}$$

C.12.3 Jacobi-Anger expansion and related expressions

The Jacobi-Anger expansions are is given by

$$e^{iz\cos\theta} = \sum_{n=-\infty}^{n=\infty} i^n J_n(z) e^{in\theta} \tag{C.132}$$

$$e^{iz\sin\theta} = \sum_{n=-\infty}^{n=\infty} i^n J_n(z) e^{in(\theta-\pi/2)} = \sum_{n=-\infty}^{n=\infty} J_n(z) e^{in\theta}, \tag{C.133}$$

where n assumes only integer values. Using $\int_{-\pi}^{\pi} e^{in\alpha} d\alpha = \delta_{n,0}$ this leads to the following integral representation of the Bessel function

$$\int_{-\pi}^{\pi} e^{iz\sin\theta} e^{-im\theta} d\theta = \sum_{n=-\infty}^{n=\infty} J_n(z)\int_{-\pi}^{\pi} e^{in\theta} e^{-im\theta} d\theta = J_n(z), \tag{C.134}$$

in particular

$$J_0(z) = \int_{-\pi}^{\pi} e^{iz\sin\theta} d\theta = \int_{-\pi}^{\pi} e^{iz\cos\theta'} d\theta'. \tag{C.135}$$

This relation can be rewritten in several closely related forms

$$e^{iz\sin\theta} = J_0(z) + \sum_{n=1}^{n=\infty} J_n(z)[e^{in\theta} + (-1)^n e^{-in\theta}] \tag{C.136}$$

$$\cos(z\sin\theta) = \Re(e^{iz\sin\theta}) = J_0(z) + 2\sum_{n=2,4,\cdots}^{n=\infty} J_n(z)\cos(n\theta) \tag{C.137}$$

$$\sin(z\sin\theta) = \Im(e^{iz\sin\theta}) = 2\sum_{n=1,3,\cdots}^{n=\infty} J_n(z)\sin(n\theta). \tag{C.138}$$

C.13 The Wronskian and Wronskian Theorem

Let us consider a second-order differential equation of the following general form

$$\chi'' + F(r)\chi = 0 \tag{C.139}$$

and look for some general properties of this eigenvalue equation. The only restrictions will be that $F(r)$ is bounded from below and continuous over the entire interval $(-\infty, +\infty)$. To compare full solutions of Eq. (C.139) with approximate solutions the analysis of their *Wronskian* is an important tool. The Wronskian of two functions $\chi_1(r)$ and $\chi_2(r)$ is defined as

$$W(\chi_1, \chi_2) \equiv \chi_1\chi_2' - \chi_1'\chi_2. \tag{C.140}$$

Problem C.1. If the Wronskian of two functions $\chi_1(r)$ and $\chi_2(r)$ is vanishing at a given value of r, then the logarithmic derivative of these two functions are equal at that value of r.

Solution. The Wronskian $W(\chi_1, \chi_2)$ is vanishing at position r if $\chi_1\chi_2' - \chi_1'\chi_2 = 0$. This can be rewritten as

$$\frac{d\ln\chi_1}{dr} = \frac{\chi_1'}{\chi_1} = \frac{\chi_2'}{\chi_2} = \frac{d\ln\chi_2}{dr}.$$

Hence, the logarithmic derivatives are equal. □

Problem C.2. Show that the derivative of the Wronskian of two functions $\chi_1(r)$ and $\chi_2(r)$, which are (over an interval $a < r < b$) solutions of two differential equations $\chi_1'' + F_1(r)\chi_1 = 0$ and $\chi_2'' + F_2(r)\chi_2 = 0$, is given by

$$dW(\chi_1, \chi_2)/dr = [F_1(r) - F_2(r)]\chi_1\chi_2.$$

This is the differential form of the Wronskian theorem.

Solution. The two functions $\chi_1(r)$ and $\chi_2(r)$ are solutions (over an interval $a < r < b$) of the equations

$$\chi_1'' + F_1(r)\chi_1 = 0 \tag{C.141}$$
$$\chi_2'' + F_2(r)\chi_2 = 0, \tag{C.142}$$

Multiplying the upper equation by χ_2 and the lower one by χ_1, we obtain after subtracting the two equations

$$dW(\chi_1, \chi_2)/dr = \chi_1\chi_2'' - \chi_2\chi_1'' = [F_1(r) - F_2(r)]\chi_1\chi_2.$$

In integral form this expression is known as the *Wronskian theorem,*

$$W(\chi_1, \chi_2)|_a^b = \int_a^b [F_1(r) - F_2(r)]\chi_1(r)\chi_2(r)dr. \tag{C.143}$$

The Wronskian theorem expresses the overall variation of the Wronskian of two functions over a given interval of their joint variable. □

Problem C.3. Show that the derivative of the Wronskian of two functions $\chi_1(r)$ and $\chi_2(r)$, which are (over an interval $a < r < b$) solutions of two differential equations $\chi_1'' + F_1(r)\chi_1 + f_1(r) = 0$ and $\chi_2'' + F_2(r)\chi_2 + f_2(r) = 0$, is given by

$$dW(\chi_1, \chi_2)/dr = [F_1(r) - F_2(r)]\chi_1\chi_2 + f_1(r)\chi_2 - f_2(r)\chi_1.$$

Solution. The two functions $\chi_1(r)$ and $\chi_2(r)$ are solutions (over an interval $a < r < b$) of the equations

$$\chi_1'' + F_1(r)\chi_1 + f_1(r) = 0 \tag{C.144}$$

$$\chi_2'' + F_2(r)\chi_2 + f_2(r) = 0, \tag{C.145}$$

Multiplying the upper equation by χ_2 and the lower one by χ_1, we obtain after subtracting the two equations

$$dW(\chi_1,\chi_2)/dr = [F_1(r) - F_2(r)]\chi_1\chi_2 + f_1(r)\chi_2 - f_2(r)\chi_1.$$

In integral form this expression becomes

$$W(\chi_1,\chi_2)|_a^b = \int_a^b [F_1(r) - F_2(r)]\chi_1\chi_2 dr + \int_a^b [f_1(r)\chi_2 - f_2(r)]\chi_1 dr. \tag{C.146}$$

The Wronskian theorem expresses the overall variation of the Wronskian of two functions over a given interval of their joint variable. □

For two functions $\chi_1(r,\varepsilon_1)$ and $\chi_2(r,\varepsilon_2)$, which are solutions of the 1D-Schrödinger equation (C.139) on the interval $a < r < b$ for energies ε_1 and ε_2, the Wronskian Theorem takes the form

$$W(\chi_1,\chi_2)|_a^b = (\varepsilon_1 - \varepsilon_2)\int_a^b \chi_1(r)\chi_2(r)dr. \tag{C.147}$$

Likewise, for two functions $\chi_1(r)$ and $\chi_2(r)$, which are (on the interval $a < r < b$) solutions for energy ε of the 1D-Schrödinger equation (C.139) with potential $U_1(r)$ and $U_2(r)$, respectively, the Wronskian Theorem takes the form

$$W(\chi_1,\chi_2)|_a^b = \int_a^b [U_2(r) - U_1(r)]\,\chi_1(r)\chi_2(r)dr. \tag{C.148}$$

C.14 Total differentials and partial derivatives

In this section we consider the function u, which is function of the variables x, y and z,

$$u = u(x,y,z) \tag{C.149}$$

in the presence of a single constraint

$$g(x,y,z) = 0. \tag{C.150}$$

In thermodynamics the constraint is given by the equation of state of the system under consideration. In view of the constraint we can express x, y, z and u in terms of (y,z), (y,z) or (x,y), respectively,

$$z = z(x,y) \quad \text{or} \quad y = y(x,z) \quad \text{or} \quad x = x(y,z) \tag{C.151}$$

$$u = u(x,y) \quad \text{or} \quad u = u(x,z) \quad \text{or} \quad u = x(y,z). \tag{C.152}$$

C.14.1 Total differential

The *total differential* (also called *exact differential*),

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{C.153}$$

can always be written in the form

$$dz = A(x,y)dx + B(x,y)dy, \tag{C.154}$$

where

$$A(x,y) \equiv \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad B(x,y) \equiv \left(\frac{\partial z}{\partial y}\right)_x, \tag{C.155}$$

which implies

$$\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}. \tag{C.156}$$

Properties:
Path invariance: The integral $\int A(x,y)dx + \int B(x,y)dy$ is independent of the integration path in the x, y plane but only depends on the value of the function z at the beginning and the end point,

$$\int_{x_1,y_1}^{x_2,y_2} A(x,y)dx + \int_{x_1,y_1}^{x_2,y_2} B(x,y)dy = \int_{z_1}^{z_2} dz = z_2 - z_1, \tag{C.157}$$

where $z_1 = z(x_1, y_1)$ and $z_2 = z(x_2, y_2)$.

Minus 1 rule: The variables x, y, z satisfy the relation (see Problem C.4)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{C.158}$$

Problem C.4. Derive the minus 1 rule.

Solution. This rule follows by substituting the total differential

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{C.159}$$

into Eq. (C.153)

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz. \tag{C.160}$$

Since

$$\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x = 1 \tag{C.161}$$

the differential is only satisfied if

$$\left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z = 0, \tag{C.162}$$

which can be rewritten in the form of the *minus 1 rule.* □

Inversely, the expression (C.154) is in general *not* a total differential. Interpreting $A(x,y)$ and $B(x,y)$ as partial derivatives,

$$A(x,y) \equiv \left(\frac{\partial z_A}{\partial x}\right)_y \quad \text{and} \quad B(x,y) \equiv \left(\frac{\partial z_B}{\partial y}\right)_x, \tag{C.163}$$

we find that in general

$$\left(\frac{\partial A}{\partial y}\right)_x \neq \left(\frac{\partial B}{\partial x}\right)_y. \tag{C.164}$$

For this case we use the notation:

$$đz = A(x,y)dx + B(x,y)dy. \tag{C.165}$$

Only if the condition (C.156) holds the functions $z_A(x,y)$ and $z_B(x,y)$ are equal (up to a constant) and Eq. (C.154) becomes a total differential.

D

Square matrices

D.1 Nomenclature and notation

In this section we summarize the nomenclature and properties of *complex* square matrices of *order* n. An arbitrary $n \times n$ matrix A and its *inverse* are written as

$$A \equiv (a^i_j) \text{ and } A^{-1} \equiv (a^i_j)^{-1} \equiv (\bar{a}^i_j), \tag{D.1}$$

where a^i_j and $\bar{a}^i_j$ represent the elements of these matrices with the convention that the *upper* or *contravariant* index is the *row* index and the *lower* or *covariant* index is the *column* index. We define the index order, *upper precedes lower.* Conforming to the standard matrix notation, the *first* index is the *row* index of the matrix (a^i_j) and the *second* index the *column* index. The *transposed* matrix

$$A^T \equiv \tilde{A} \equiv (\tilde{a}^i_j) = (a^j_i) \tag{D.2}$$

is obtained by exchanging rows and columns, the *complex conjugate*

$$A^* \equiv (a^i_j)^* = (a^{i*}_j) \tag{D.3}$$

by taking the complex conjugate of all elements, and the *hermitian conjugate* or *conjugate transpose*

$$A^\dagger \equiv (a^i_j)^\dagger = (a^{j*}_i) = \tilde{A}^* \tag{D.4}$$

is obtained by complex conjugation of the transposed matrix. The trace of the matrix A is defined as

$$\mathrm{tr}A = \sum_{i=1}^{n} a^i_i. \tag{D.5}$$

The determinant of the matrix A is defined by the *Leibniz expansion*

$$|A| \equiv \det A = \det(a^i_j) = \sum_P (-1)^p a^{i_1}_1 \cdots a^{i_n}_n = \varepsilon_{i_1,\cdots i_n} a^{i_1}_1 \cdots a^{i_n}_n, \tag{D.6}$$

where the summation runs over all permutations P of the indices $(i_1, \cdots i_n) = (1, \cdots n)$ and $p \in \{\text{even}, \text{odd}\}$ is the order of the permutation; $\varepsilon_{i_1,\cdots i_n}$ is a generalized Levi-Civita symbol.

With each element a^i_j of the matrix we can associate a *cofactor*, cofactor(a^i_j), which is defined as the *minor* (sub-determinant) $\det A^i_j$ corresponding to the sub-matrix A^i_j of that element, including its sign $(-1)^{i+j}$. The determinant $\det A$ can be expanded in terms of its minors $\det A^i_j$, *c.q.* cofactors, with respect to row i,

$$\det A = \sum_{i=1}^{n} (-1)^{i+j} a^i_j \det A = \sum_{i=1}^{n} a^i_j \mathrm{cofactor}(a^i_j). \tag{D.7}$$

This is called the *Laplace expansion.* Replacing the elements of the transposed matrix by their cofactors we obtain the *adjoint* matrix, in which the elements are the cofactors of the *transposed* matrix

$$\mathrm{Adj}(a^i_j) = \mathrm{cofactor}(a^j_i) = (-1)^{i+j} \det A^j_i. \tag{D.8}$$

For square matrices we define the following special cases:

$$\begin{array}{rlrcll}
\textit{complex:} & \textit{hermitian} & A = A^\dagger & \Leftrightarrow & a^i_j = a^{j*}_i & \text{(D.9)} \\
 & \textit{unitary} & A^{-1} = A^\dagger & \Leftrightarrow & \bar{a}^i_j = a^{j*}_i & \text{(D.10)} \\
 & \textit{real} & A = A^* & \Leftrightarrow & a^i_j = a^{i*}_j & \text{(D.11)} \\
\textit{real:} & \textit{symmetrical} & A = \tilde{A} & \Leftrightarrow & a^i_j = a^j_i & \text{(D.12)} \\
 & \textit{orthogonal} & A^{-1} = \tilde{A} & \Leftrightarrow & \bar{a}^i_j = a^j_i & \text{(D.13)}
\end{array}$$

D.2 Properties

If the inverse exists, the matrix A satisfies the following properties:

- The determinant of an $n \times n$ matrix (a^j_i) is invariant under addition to a given column (or row) a scalar multiple of *another* column (or rows)

  $$\begin{vmatrix} a^1_1 \cdots a^n_1 \\ \vdots \qquad \vdots \\ a^1_n \cdots a^n_n \end{vmatrix} = \begin{vmatrix} a^1_1 + ka^j_1 \cdots a^n_1 \\ \vdots \qquad\qquad \vdots \\ a^1_n + ka^j_1 \cdots a^n_n \end{vmatrix} = \begin{vmatrix} a^1_1 & \cdots & a^n_1 \\ \vdots & & \vdots \\ a^1_n + ka^1_i & \cdots & a^n_n + ka^n_i \end{vmatrix}. \tag{D.14}$$

- The determinant of a *triangular* $n \times n$ matrix (a^j_i), *i.e.* $a^j_i = 0$ for $i > j$ (or $j > i$), is equal to the product of the diagonal elements,

  $$\begin{vmatrix} a^1_1 & \cdots & a^n_1 \\ 0 & \ddots & \vdots \\ 0 & 0 & a^n_n \end{vmatrix} = \prod_{i=1}^{n} a^i_i\,. \tag{D.15}$$

  This follows from the Leibniz expansion because the only nonzero product of n matrix elements is the diagonal one.

- The determinant of the blockdiagonal $(n+m) \times (n+m)$ matrix of the $n \times n$ matrix A and the $m \times m$ matrix B is equal to the product of the determinants of the matrices A and B,

  $$\begin{vmatrix} A & C \\ 0 & B \end{vmatrix} = \begin{vmatrix} a^1_1 \cdots a^n_1 & c^1_1 \cdots c^m_1 \\ \vdots \qquad \vdots & \vdots \qquad \vdots \\ a^1_n \cdots a^n_n & c^1_n \cdots c^m_m \\ & b^1_1 \cdots b^m_1 \\ 0 & \vdots \qquad \vdots \\ & b^1_m \cdots b^m_m \end{vmatrix} = \det A \det B. \tag{D.16}$$

  This follows from the Leibniz expansion because the only nonzero product of $n+m$ matrix elements are the ones containing only elements of the submatrices A and B. Note that the r.h.s. is independent of C because the elements of the submatrix C appear in the determinant only in combination with elements of the zero block.

- The product rule for the determinants of two $n \times n$ matrices, A and B,

$$\det AB = \det A \, \det B. \tag{D.17}$$

- The determinant of A is non-zero

$$\det A = \det(a^i_j) = \Delta \neq 0. \tag{D.18}$$

Proof: Because the inverse exists, $(\bar{a}^i_j) = (a^i_j)^{-1}$, we have $(a^i_j)(\bar{a}^i_j) = \mathbb{1}$. Thus we obtain with the aid of the product rule $1 = \det[(a^i_j)(\bar{a}^i_j)] = \Delta \det(\bar{a}^i_j)$. This implies $\Delta \neq 0$.

- The determinant of A^{-1} equals the inverse of the determinant of A,

$$\det A^{-1} = \det(\bar{a}^i_j) = \Delta^{-1}. \tag{D.19}$$

Proof: Because the inverse exists we have (with the aid of the product rule) $1 = \det[(a^i_j)(\bar{a}^i_j)] = \Delta \det(\bar{a}^i_j)$ with $\Delta \neq 0$. This can be rewritten in the form (D.19).

- The determinant of A^* equals the complex conjugate of $\det A$,

$$\det A^* = \det(a^{i*}_j) = \det(a^i_j)^* = \Delta^*. \tag{D.20}$$

Proof: $\det(a^{i*}_j) = \varepsilon_{i_1,\cdots i_n} a^{i_1*}_1 \cdots a^{i_n*}_n = (\varepsilon_{i_1,\cdots i_n} a^{i_1}_1 \cdots a^{i_n}_n)^* = [\det(a^i_j)]^*$.

- The determinant of A is invariant under transposition

$$\det \tilde{A} = \det A. \tag{D.21}$$

Proof: $\det(a^i_j) = \varepsilon_{i_1,\cdots i_n} a^{i_1*}_1 \cdots a^{i_n*}_n = \varepsilon_{i_1,\cdots i_n} a^1_{i_1} \cdots a^n_{i_n} = \det(a^j_i)$.

- *Kronecker property:*

$$a^i_k \bar{a}^k_j = \delta^i_j \text{ and } \bar{a}^i_{i'} a^{i'}_j = \delta^i_j \tag{D.22}$$

Proof:[1] $\mathbb{1} = (a^i_j)(\bar{a}^i_j) = (a^i_k \bar{a}^k_j) \Rightarrow (a^i_k \bar{a}^k_j) = \delta^i_j$ and $\mathbb{1} = (\bar{a}^i_j)(a^i_j) = (\bar{a}^i_k a^k_j) \Rightarrow \bar{a}^i_k a^k_j = \delta^i_j$.

- The elements of the inverse matrix are given by

$$\bar{a}^i_j = \Delta^{-1} \mathrm{Adj}(a^i_j), \tag{D.23}$$

where $\mathrm{Adj}(a^i_j)$ is the *adjoint* matrix of (a^i_j), *i.e.* $\mathrm{Adj}(a^i_j) = \mathrm{cofactor}(a^j_i) = (-1)^{i+j} \det(A^j_i)$.
Proof: Let $B = (\alpha^i_j) = \mathrm{Adj}(a^i_j)$ be the *adjoint* matrix of (a^i_j). Then, the product of the matrices A and B is given by

$$AB = (a^i_j)(\alpha^i_j) = (a^i_k \alpha^k_j) = \sum_{i=1}^{n} a^i_k \mathrm{cofactor}(a^j_k) = (\delta^i_j) \det A = \mathbb{1}\, \Delta. \tag{D.24}$$

To arrive at the result we used Eq. (D.7) and further $\sum_{i=1}^{n} a^i_k \mathrm{cofactor}(a^j_k) = 0$ for $i \neq j$.[2] Rewriting Eq. (D.24) we obtain at $A^{-1} = B/\Delta$, which had to be proven.

---

[1] Note that $a^i_k b^k_j \neq a^k_i b^j_k$. Therefore we need a convention. In matrix multiplication we use the *column on row* summation convention $(c^i_j) = (a^i_j)(b^i_j) = (a^i_k b^k_j)$. This means that we sum over the column index of the left matrix and the row index of the right matrix.

[2] Note that this expression corresponds to a determinant with two identical columns.

- The trace of the commutator of two $(n \times n)$ matrices, A and B, is zero,

  $$\operatorname{tr}[A, B] = 0 \tag{D.25}$$

  Proof: The trace $\operatorname{tr} AB$ of the product of the matrices A and B is given by

  $$\operatorname{tr} AB = \operatorname{tr}(a^i_k b^k_j) = \sum_{i,k=1}^{n} a^i_k b^k_i = \sum_{i,k=1}^{n} b^k_i a^i_k = \operatorname{tr}(b^k_i a^i_l) = \operatorname{tr} BA.$$

  Since $[A, B] = AB - BA$ and $\operatorname{tr}(A + B) = \operatorname{tr}A + \operatorname{tr}B$ this completes the proof.

- The trace of the product of three $(n \times n)$ matrices A, B and C is invariant under cyclic permutation of these matrices,

  $$\operatorname{tr} ABC = \operatorname{tr} CAB = \operatorname{tr} BCA \tag{D.26}$$

  Proof: This follows by direct application of property D.25.

D.2.1 Unitary matrices

Let $U = (u^{i'}_i)$ be a unitary $n \times n$ matrix, $U^{-1} = U^\dagger \equiv \tilde{U}^* \Leftrightarrow \bar{u}^i_{i'} = u^{i'*}_i$. The unitarity implies the following properties:

- *Kronecker property*: The Kronecker property takes the following form

  $$u^{i'*}_i u^i_{j'} = \delta^{i'}_{j'} \text{ and } u^i_{i'} u^{i'*}_j = \delta^i_j. \tag{D.27}$$

  Proof: Substituting the unitarity condition $\bar{u}^i_{i'} = u^{i'*}_i$ in Eq. (D.22) yields the desired result.

- *Determinant* - The determinant of a unitary $n \times n$ matrix U equals a complex number of unit norm,

  $$\Delta \equiv \det U = e^{i\varphi}. \tag{D.28}$$

  where $\varphi \in \mathbb{R}$. For the special case $\varphi = 0$ the matrix U is called the *special unitary matrix.*
  Proof: Using the properties D.20, D.30 and D.19 we find $\Delta^* = \det U^* = \det U^\dagger = \det U^{-1} = 1/\Delta \to |\Delta|^2 = 1$, which implies (D.28).

- *Matrix inversion rule*: The elements of the inverse matrix are given by

  $$u^{i*}_{i'} = e^{-i\varphi} \text{cofactor}(u^{i'}_i), \tag{D.29}$$

  Proof: This follows from Eq. (D.23) by substitution of $\Delta = e^{i\varphi}$.

- *Determinant of hermitian conjugate*: The determinant of $U^\dagger$ follows with Eq. (D.21),

  $$\det U^\dagger = \det \tilde{U}^* = \det U^* = e^{-i\varphi}. \tag{D.30}$$

  Proof: This follows from Eq. (D.21) and substitution of $\Delta = e^{i\varphi}$.

- *Invariance of determinant under unitary transformation:* The determinant of an arbitrary $n \times n$ matrix A is invariant under unitary transformation

  $$\det UAU^\dagger = \det A. \tag{D.31}$$

  Proof: Using the properties D.17 and D.28 we find $\det UAU^\dagger) = \det U \det A \det U^\dagger = e^{i\varphi} \det A \, e^{-i\varphi} = \det A$.

- *Invariance of trace under unitary transformation:* The trace of an arbitrary $n \times n$ matrix A is invariant under unitary transformation

  $$\operatorname{tr} UAU^\dagger = \operatorname{tr}A. \tag{D.32}$$

  Proof: Using the properties D.26 and D.10 we find $\operatorname{tr} UAU^\dagger = \operatorname{tr} U^\dagger UA = \operatorname{tr} U^{-1}UA = \operatorname{tr}A$.

E

Vector relations

E.1 Inner and outer products

$$(\mathbf{u},\mathbf{v},\mathbf{w}) = \mathbf{u}\cdot(\mathbf{v}\times\mathbf{w}) = \mathbf{v}\cdot(\mathbf{w}\times\mathbf{u}) = \mathbf{w}\cdot(\mathbf{u}\times\mathbf{v}) \tag{E.1}$$

$$\mathbf{u}\times(\mathbf{v}\times\mathbf{w}) = (\mathbf{u}\cdot\mathbf{w})\mathbf{v} - (\mathbf{u}\cdot\mathbf{v})\mathbf{w} \tag{E.2}$$

$$\mathbf{u}\times(\mathbf{v}\times\mathbf{w}) = -\,(\mathbf{v}\times\mathbf{w})\times\mathbf{u} \tag{E.3}$$

$$(\mathbf{u}\times\mathbf{v})\cdot(\mathbf{w}\times\mathbf{z}) = (\mathbf{u}\cdot\mathbf{w})(\mathbf{v}\cdot\mathbf{z}) - (\mathbf{u}\cdot\mathbf{z})(\mathbf{v}\cdot\mathbf{w}) \tag{E.4}$$

E.2 Gradient, divergence and curl

E.2.1 Helmholtz theorem

Any vector $\mathbf{A}$ can be separated in an *irrotational* part $\mathbf{A}_{\|}$ and a *rotational (solenoidal)* part $\mathbf{A}_{\perp}$, defined by

$$\mathbf{A} = \mathbf{A}_{\perp} + \mathbf{A}_{\|} \text{ with } \boldsymbol{\nabla}\cdot\mathbf{A}_{\perp} = 0 \text{ and } \boldsymbol{\nabla}\times\mathbf{A}_{\|} = 0. \tag{E.5}$$

E.2.2 Vector identities with a single vector differential operator

$$\boldsymbol{\nabla}\cdot(\mathbf{A}\phi) = (\mathbf{A}\cdot\boldsymbol{\nabla}\phi) + \phi(\boldsymbol{\nabla}\cdot\mathbf{A}) \tag{E.6}$$

$$\boldsymbol{\nabla}\times(\mathbf{A}\phi) = -(\mathbf{A}\times\boldsymbol{\nabla}\phi) + \phi(\boldsymbol{\nabla}\times\mathbf{A}) \tag{E.7}$$

$$\boldsymbol{\nabla}\cdot(\mathbf{A}\times\mathbf{B}) = \mathbf{B}\cdot(\boldsymbol{\nabla}\times\mathbf{A}) + \mathbf{A}\cdot(\boldsymbol{\nabla}\times\mathbf{B}) \tag{E.8}$$

$$\boldsymbol{\nabla}\times(\mathbf{A}\times\mathbf{B}) = (\mathbf{B}\cdot\boldsymbol{\nabla})\mathbf{A} - \mathbf{B}(\boldsymbol{\nabla}\cdot\mathbf{A}) - (\mathbf{A}\cdot\boldsymbol{\nabla})\mathbf{B} + \mathbf{A}(\boldsymbol{\nabla}\cdot\mathbf{B}) \tag{E.9}$$

$$\boldsymbol{\nabla}(\mathbf{A}\cdot\mathbf{B}) = (\mathbf{B}\cdot\boldsymbol{\nabla})\mathbf{A} + (\mathbf{A}\cdot\boldsymbol{\nabla})\mathbf{B} + \mathbf{B}\times(\boldsymbol{\nabla}\times\mathbf{A}) + \mathbf{A}\times(\boldsymbol{\nabla}\times\mathbf{B}) \tag{E.10}$$

Examples:

$$\boldsymbol{\nabla}\cdot\mathbf{r} = 3 \Leftrightarrow \partial_i r_i = 3 \tag{E.11}$$

$$\boldsymbol{\nabla}\times\mathbf{r} = \mathbf{0} \Leftrightarrow \varepsilon_{ijk}\partial_j r_k = \mathbf{0} \tag{E.12}$$

$$(\mathbf{A}\cdot\boldsymbol{\nabla})\mathbf{r} = \mathbf{A} \Leftrightarrow A_i\nabla_i r_k = A_k \tag{E.13}$$

$$\boldsymbol{\nabla}\cdot\dot{\mathbf{r}} = \boldsymbol{\nabla}\times\dot{\mathbf{r}} = (\mathbf{A}\cdot\boldsymbol{\nabla})\dot{\mathbf{r}} = \mathbf{0} \tag{E.14}$$

Combining Eqs. (E.10), (E.12) and (E.13) we find

$$\boldsymbol{\nabla}(\mathbf{r}\cdot\mathbf{A}) = \mathbf{A} + (\mathbf{r}\cdot\boldsymbol{\nabla})\mathbf{A} + \mathbf{r}\times(\boldsymbol{\nabla}\times\mathbf{A}). \tag{E.15}$$

Likewise we find by combining Eqs. (E.10) with Eq. (E.9)

$$\boldsymbol{\nabla}(\dot{\mathbf{r}}\cdot\mathbf{A}) = (\dot{\mathbf{r}}\cdot\boldsymbol{\nabla})\mathbf{A} + \dot{\mathbf{r}}\times(\boldsymbol{\nabla}\times\mathbf{A}) \tag{E.16}$$

$$\frac{d}{dt}\mathbf{A} = \frac{\partial}{\partial t}\mathbf{A} + (\dot{\mathbf{r}}\cdot\nabla)\mathbf{A}. \tag{E.17}$$

Special case:

$$\boldsymbol{\nabla} r^n = nr^{n-1}\,(\mathbf{r}/r) = nr^{n-1}\hat{\mathbf{r}}. \tag{E.18}$$

For $n \geq 0$ this expression is valid everywhere, including the origin. For $n < 0$ the expression is irregular in the origin. In particular we have

$$\boldsymbol{\nabla}\frac{1}{r} = -\frac{\mathbf{r}}{r^3}. \tag{E.19}$$

Since

$$\boldsymbol{\nabla}|\mathbf{r}-\mathbf{r}'| = \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} = -\boldsymbol{\nabla}'|\mathbf{r}-\mathbf{r}'| \tag{E.20}$$

(as is easily verified in cartesian coordinates) we can generalize Eq. (E.18) to

$$\boldsymbol{\nabla}|\mathbf{r}-\mathbf{r}'|^n = n|\mathbf{r}-\mathbf{r}'|^{n-1}\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} = -\boldsymbol{\nabla}'|\mathbf{r}-\mathbf{r}'|^n. \tag{E.21}$$

E.2.3 Expressions with second derivatives

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\phi) = 0 \tag{E.22}$$

$$\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\times\mathbf{A}) = 0 \tag{E.23}$$

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{A}) = \boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{A}) - \boldsymbol{\nabla}^2\mathbf{A} \tag{E.24}$$

Expressions for the laplacian:

$$\Delta r^n = \boldsymbol{\nabla}\cdot\boldsymbol{\nabla} r^n = nr^{n-2}\,(\boldsymbol{\nabla}\cdot\mathbf{r}) + n\mathbf{r}\cdot\boldsymbol{\nabla} r^{n-2} = 3nr^{n-2} + n(n-2)r^{n-2}. \tag{E.25}$$

We distinguish three cases:

$$\Delta r^n = n(n+1)r^{n-2} \ \text{ is regular everywhere } \begin{cases} \text{for } n \geq 0 \ \textit{also} \text{ at the origin} \\ \text{for } n < 0 \ \textit{outside} \text{ at the origin} \end{cases} \tag{E.26}$$

Note that for $n = -1$ this expression yields $\boldsymbol{\nabla}^2(1/r) = 0$ everywhere outside the origin. The case $n = -1$ is special at the origin because the laplacian produces a flux out of any sphere centered around the origin. With the Gauss divergence theorem we calculate for this flux

$$-\int \boldsymbol{\nabla}\left(1/r^3\right)\mathbf{r}\cdot d\mathbf{r} = -\oint\left(1/r^3\right)\mathbf{r}\cdot\hat{\mathbf{r}}dS = -4\pi. \tag{E.27}$$

Thus, Δr^{-1} can be regarded as a distribution and we write

$$\boldsymbol{\nabla}^2(1/r) = -4\pi\delta(\mathbf{r}). \tag{E.28}$$

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