Elements of Quantum Gases: Thermodynamic and Collisional Properties of Trapped Atomic Gases

Bachellor course at honours level

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Contents

Preface

When I was scheduled to give an introductory course on the modern quantum gases I was full of ideas about what to teach. The research in this field has flourished for more than a full decade and many experimental results and theoretical insights have become available. An enormous body of literature has emerged with in its wake excellent review papers, summer school contributions and books, not to mention the relation with a hand full of recent 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 good students - a proper common language was absent 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 given in the form of 8 lectures of 1.5 hours to bachelor students at honours 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 in the summer of 2006 for a group of 60 masters students at an international predoc school organized together with Dr. Philippe Verkerk at the Centre de Physique des Houches in the French Alps.

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 course was scheduled for 3 EC points severe choices had 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, was 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. 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 Stringari and Pitaevskii on *Bose-Einstein Condensation* as well as many papers from the research literature.

The starting point of the course is the quasi-classical gas at low densities. 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 kinetic properties. All these aspects meet in a discussion 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.

In Chapter 8 we turn to the quantum gases be it in the absence of interactions. 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. At this point we also introduce the concept of bosons and fermions. Next we expand to many-body states and the occupation number representation. Using the grand canonical ensemble we derive the Bose-Einstein and Fermi-Dirac distributions and show how they give rise to a distortion of the density profile of a harmonically trapped gas and ultimately to Bose-Einstein condensation.

Chapter 2 is included to prepare for treating the 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. I could not resist including the Wronskian theorem because in this way some valuable extras could be included in the next chapter.

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 zero-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. 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. More excitingly, 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.

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. Here one would like to continue and apply all this in the quantum kinetic equation. However this is a bridge too far for a course of only 3EC points.

I thank the students who inspired me to write up this course and Dr. Mikhail Baranov who was invaluable as a sparing partner in testing my own understanding of the material and who shared with me several insights that appear in the text.

Amsterdam, January 2007, *Jook Walraven.*

In the spring of 2007 several typos and unclear passages were identified in the manuscript. I thank the students who gave me valuable feedback and tipped me on improvements of various kinds. When giving the lectures in 2008 the section on the ideal Bose gas was improved and a section on BEC in low-dimensional systems was included. In Chapter 3 the Wronskian theorem was moved to an appendix. Chapter 4 was extended with sections on power-law potentials. Triggered by the work of Tobias Tiecke and Servaas Kokkelmans I expanded the section on Feshbach resonances into a separate chapter. At the School in Les Houches in 2008, again organized with Dr. Philippe Verkerk I made some minor modifications.

Over the winter break I added sections on field operators and improved the section on the grand cannonical ensemble. These improvements enabled to add a section on the weakly-interacting Bose gas in which most of the lecture material comes together in the derivation of the Gross-Pitaevskii equation.

Amsterdam, January 2009, *Jook Walraven.*

In the spring and summer of 2009 I worked on improvement of chapters 3 and 4. The section on the weakly-interacting Bose gas was expanded to a small chapter. Further, I added a Chapter on the Boltzmann equation, which makes it possible to give a better introduction in the kinetic phenomena.

Amsterdam, January 2010, *Jook Walraven.*

1

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 *kinetics.* For example they affect the relation between pressure and temperature; *i.e.,* the thermodynamic *equation of state.* On the kinetic 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*, *nearly ideal* or *weakly interacting.*[1]

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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.

Kinetically the interactions give rise to *collisions.* To calculate the *collision rate* as well as the *mean-free-path* travelled by an atom in between two collisions we need the size of the atoms. As a rule of thumb we expect the *kinetic diameter* of an atom to be approximately equal to the range of the interaction potential. From this follows directly an estimate for the (binary) *collision cross section*

$$\sigma = \pi r_0^2, \tag{1.2}$$

for the *mean-free-path*

$$\ell = 1/n\sigma \tag{1.3}$$

and for the *collision rate*

$$\tau_c^{-1} = n\bar{v}_r\sigma. \tag{1.4}$$

Here $\bar{v}_r = \sqrt{16k_BT/\pi m}$ is the average relative atomic *speed.* In many cases estimates based on 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 focussed 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 *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,

$$H = \sum_i \left(\frac{p_i^2}{2m} + \mathcal{U}(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i,j}{}' \mathcal{V}(r_{ij}), \tag{1.5}$$

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[2] 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 very 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,

$$H^{(i)} = H_0\left(\mathbf{r}_i, \mathbf{p}_i\right) + \frac{1}{2}\sum_j{}' \mathcal{V}(r_{ij}) \qquad \text{with } H_0\left(\mathbf{r}_i, \mathbf{p}_i\right) = \frac{p_i^2}{2m} + \mathcal{U}(\mathbf{r}_i). \tag{1.6}$$

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. As a consequence, the same total energy $H^{(i)}$ of atom i can be obtained for many different configurations of the gas.

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 will 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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[2] Position and momentum cannot be determined to infinite accuracy, the states are quantized. Moreover, also from a practical point of view the task is hopeless when dealing with a large number of atoms.

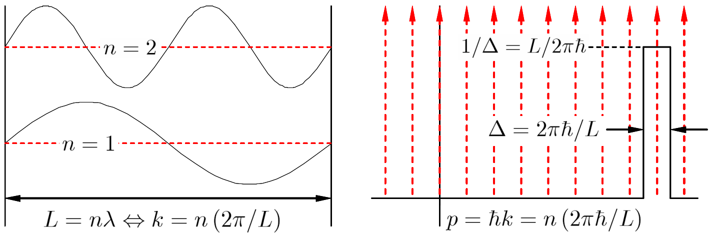

Figure 1.1: *Left*: Periodic boundary conditions illustrated for the one-dimensional case. *Right*: Periodic boundary conditions give rise to a discrete spectrum of momentum states, which may be represented by a quasi-continuous distribution if we approximate the deltafunction by a distribution of finite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

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}\,(\mathbf{r}) = \varepsilon_k\psi_{\mathbf{k}}\,(\mathbf{r})\,, \tag{1.7}$$

where the eigenfunctions and corresponding eigenvalues are given by

$$\psi_{\mathbf{k}}\,(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}} \text{ and } \varepsilon_k = \frac{\hbar^2k^2}{2m}. \tag{1.8}$$

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 $V = L^3$, $\langle\mathbf{p}|\mathbf{p}\rangle = \int d\mathbf{r}|\langle\mathbf{r}|\mathbf{p}\rangle|^2 = 1$. For the free particle this implies a discrete set of plane wave eigenstates

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{1.9}$$

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

$$\langle\mathbf{p}|\mathbf{p}'\rangle = \delta_{\mathbf{p},\mathbf{p}'} \qquad \text{and} \qquad \underline{1} = \sum_{\mathbf{p}}|\mathbf{p}\rangle\langle\mathbf{p}|, \tag{1.10}$$

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 and closure relations take the form

$$\langle\mathbf{p}|\mathbf{p}'\rangle = (2\pi\hbar/L)^3\,f_L(\mathbf{p}-\mathbf{p}') \qquad \text{and} \qquad \underline{1} = (2\pi\hbar)^{-3}\int d\mathbf{r}d\mathbf{p}\,|\mathbf{p}\rangle\langle\mathbf{p}|, \tag{1.11}$$

where

$$f_L(0) = (L/2\pi\hbar)^3 \quad \text{and} \quad \lim_{L\to\infty} f_L(\mathbf{p}-\mathbf{p}') = \delta(\mathbf{p}-\mathbf{p}'). \tag{1.12}$$

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 inverse cubic Planck constant. Thus the continuum transition does not affect the dimension! For finite L the Eqs. (1.10) remain valid to good approximation and can be used to replace discrete state summation by the mathematically often more convenient phase-space integration

$$\sum_{\mathbf{p}} \rightarrow \frac{1}{(2\pi\hbar)^3} \int d\mathbf{r} d\mathbf{p}. \tag{1.13}$$

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 $(L/2\pi\hbar)^3$. 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 (1.5); *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,

$$P_0(\varepsilon) = C_0 \Omega^{(0)}(\varepsilon), \tag{1.14}$$

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 will 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:

$$P_0(\varepsilon) = C_0 \Omega_1(\varepsilon) \Omega(E_{tot} - \varepsilon). \tag{1.15}$$

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 very 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

$$P_0(\varepsilon_s) = \Omega_1(\varepsilon_s) P_s, \tag{1.16}$$

because the statistical principle requires $P_{s'} = P_s$ for all states s' with $\varepsilon_{s'} = \varepsilon_s$. Therefore, comparing Eqs. (1.16) and (1.15) we find that the probability P_s for the atom to be in a specific *state* s is given by

$$P_s = C_0 \Omega(E_{tot} - \varepsilon_s) = C_0 \Omega(E^*). \tag{1.17}$$

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*.[3] Because $\varepsilon_s \lll E^*$ we may approximate $\ln \Omega(E^*)$ with a Taylor expansion to first order in ε_s,

$$\ln \Omega(E^*) = \ln \Omega\left(E_{tot}\right) - \varepsilon_s \left(\partial \ln \Omega(E^*)/\partial E^*\right)_{\mathcal{U},N^*}. \tag{1.18}$$

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

$$P_s = C_0 \Omega\left(E_{tot}\right) e^{-\beta\varepsilon_s} = Z_1^{-1} e^{-\beta\varepsilon_s}. \tag{1.19}$$

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*

$$Z_1 = \textstyle\sum_s e^{-\beta\varepsilon_s}. \tag{1.20}$$

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 (1.14) into a product of the form of Eq. (1.15). For such a subsystem the canonical partition function is written as

$$Z = \textstyle\sum_s e^{-\beta E_s}, \tag{1.21}$$

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 (1.5) invariant.[4] This yields for the N-particle canonical distribution

$$P_s = C_0 \Omega\left(E_{tot}\right) e^{-\beta E_s} = \left(N! Z_N\right)^{-1} e^{-\beta E_s}, \tag{1.22}$$

with the N-particle canonical partition function given by

$$Z_N = (N!)^{-1} \textstyle\sum_s^{(cl)} e^{-\beta E_s}. \tag{1.23}$$

Here the summation runs over all classically distinguishable states. This approach may be justified in quantum mechanics as long as multiple occupation of the same single-particle state is negligible. In Section 1.4.5 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.

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[3] 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 probabilites, to the thermodynamic quantity entropy, which is an extensive, *i.e. additive* property.

[4] Omission of this correction gives rise to the paradox of Gibbs, see *e.g.* F. Reif, *Fundamentals of statistical and thermal physics*, McGraw-Hill, Inc., Tokyo 1965. Arguably this famous paradox can be regarded - in hindsight - as a first indication of the modern concept of indistinguishability of identical particles.

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

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

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 corresponds to the state of maximum entropy, $S^* + S = \text{max}$, where S is the entropy of the small system. Next we recall the thermodynamic relation

$$dS = \frac{1}{T}dU - \frac{1}{T}dW - \frac{\mu}{T}dN, \tag{1.24}$$

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*

$$P_{s_2}/P_{s_1} = e^{-\Delta\varepsilon/k_BT}, \tag{1.25}$$

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

$$P_s = (N!Z_N)^{-1} e^{-E_s/k_BT} \tag{1.26}$$

where

$$Z_N = (N!)^{-1} \textstyle\sum_s e^{-E_s/k_BT} \tag{1.27}$$

is the N-particle canonical partition function. With Eq. (1.26) the average energy of the small N-body system can be expressed as

$$\overline{E} = \textstyle\sum_s E_sP_s = (N!Z_N)^{-1} \sum_s E_s e^{-E_s/k_BT} = k_BT^2 \left(\partial \ln Z_N/\partial T\right)_{\mathcal{U},N}. \tag{1.28}$$

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

$$U = k_BT^2 \left(\partial \ln Z_N/\partial T\right)_{\mathcal{U},N} = T\left[\partial \left(k_BT\ln Z_N\right)/\partial T\right]_{\mathcal{U},N} - k_BT\ln Z_N. \tag{1.29}$$

Introducing the energy

$$F = -k_BT\ln Z_N \quad\Leftrightarrow\quad Z_N = e^{-F/k_BT} \tag{1.30}$$

we note that $F = U + T\left(\partial F/\partial T\right)_{\mathcal{U},N}$. Comparing this expression with the thermodynamic relation $F = U - TS$ we recognize in F with the Helmholtz free energy F. 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 $dF = đW - SdT + \mu dN$,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{\mathcal{U},N} \quad\text{and}\quad \mu = \left(\frac{\partial F}{\partial N}\right)_{\mathcal{U},T}. \tag{1.31}$$

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

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{1.32}$$

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. (1.15) 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

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

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 (1.26) 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

$$\varepsilon = H_0(\mathbf{r},\mathbf{p}) = \frac{p^2}{2m} + \mathcal{U}(\mathbf{r}). \tag{1.33}$$

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 (1.26), which with $N = 1$ and Z_1 takes the form $P_s = Z_1^{-1} e^{-\varepsilon_s/k_BT}$. As the classical hamiltonian (1.33) 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*

$$P(\mathbf{r},\mathbf{p}) = (2\pi\hbar)^{-3} Z_1^{-1} e^{-H_0(\mathbf{r},\mathbf{p})/k_BT} \tag{1.34}$$

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 (1.13). In this quasi-classical limit the single-particle canonical partition function takes the form

$$Z_1 = \frac{1}{(2\pi\hbar)^3} \int e^{-H_0(\mathbf{r},\mathbf{p})/k_BT} d\mathbf{p} d\mathbf{r}. \tag{1.35}$$

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*

$$n(\mathbf{r},\mathbf{p}) = NP(\mathbf{r},\mathbf{p}) = (2\pi\hbar)^{-3} f(\mathbf{r},\mathbf{p}). \tag{1.36}$$

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

$$N = \frac{1}{(2\pi\hbar)^3} \int f(\mathbf{r},\mathbf{p}) d\mathbf{p} d\mathbf{r}. \tag{1.37}$$

Thus, in the center of phase space we have

$$f\,(0,0)=(2\pi\hbar)^3\,NP\,(0,0)=N/Z_1\equiv D \tag{1.38}$$

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*.[5] 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 $\mathbf{r}$

$$n(\mathbf{r})=\frac{1}{(2\pi\hbar)^3}\int f(\mathbf{r},\mathbf{p})d\mathbf{p}=f\,(0,0)\,e^{-\mathcal{U}(\mathbf{r})/k_BT}\frac{1}{(2\pi\hbar)^3}\int_0^\infty e^{-(p/\alpha)^2}4\pi p^2dp \tag{1.39}$$

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. (1.39) in the form

$$n(\mathbf{r})=n_0e^{-\mathcal{U}(\mathbf{r})/k_BT} \tag{1.40}$$

and using the definition (1.38) we may identify

$$n_0=n(0)=D/(2\pi\hbar)^3\int_0^\infty e^{-(p/\alpha)^2}4\pi p^2dp \tag{1.41}$$

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 (1.40) holds for both collisionless and hydrodynamic conditions as long as the ideal gas approximation is valid. Evaluating the momentum integral using (B.3) we obtain

$$\int_0^\infty e^{-(p/\alpha)^2}4\pi p^2dp=\pi^{3/2}\alpha^3=(2\pi\hbar/\Lambda)^3\,, \tag{1.42}$$

where $\Lambda\equiv[2\pi\hbar^2/(mk_BT)]^{1/2}$ 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. (1.42) into (1.41) we find that the degeneracy parameter is given by

$$D=n_0\Lambda^3. \tag{1.43}$$

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

$$N=\int n(\mathbf{r})d\mathbf{r}=n_0\int e^{-\mathcal{U}(\mathbf{r})/k_BT}d\mathbf{r}. \tag{1.44}$$

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,

$$V_e\equiv N/n_0=\int e^{-\mathcal{U}(\mathbf{r})/k_BT}d\mathbf{r}. \tag{1.45}$$

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

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. (1.45) 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.(1.38) we have

$$N = n_0 \Lambda^3 Z_1. \tag{1.46}$$

Eliminating N using Eq. (1.45) the mentioned relation is found to be

$$Z_1 = V_e \Lambda^{-3}. \tag{1.47}$$

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

$$dW = -p_0 dV_e, \tag{1.48}$$

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,

$$P_{\mathrm{M}}(\mathbf{p}) = \int P(\mathbf{r},\mathbf{p}) d\mathbf{r} = Z_1^{-1} \frac{e^{-(p/\alpha)^2}}{(2\pi\hbar)^3} \int e^{-\mathcal{U}(\mathbf{r})/k_B T} d\mathbf{r} = (\Lambda/2\pi\hbar)^3 e^{-(p/\alpha)^2} = \frac{e^{-(p/\alpha)^2}}{\pi^{3/2}\alpha^3}, \tag{1.49}$$

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 $\bar{v}_{th} = \sqrt{8 k_B T / \pi m}$, 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. (1.49) we obtain using the definite integral (B.4)

$$\bar{p} = \frac{1}{\pi^{3/2}\alpha^3} \int e^{-(p/\alpha)^2} 4\pi p^3 dp = \frac{4\alpha}{\pi^{1/2}} \int e^{-x^2} x^3 dx = \sqrt{8 m k_B T/\pi} \, . \blacktriangleright \tag{1.50}$$

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

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. (1.49) we obtain using the definite integral (B.4)

$$\overline{p^2} = \frac{1}{\pi^{3/2}\alpha^3} \int e^{-(p/\alpha)^2} 4\pi p^4 dp = \frac{4\alpha^2}{\pi^{1/2}} \int e^{-x^2} x^4 dx = 3 m k_B T \, . \blacktriangleright \tag{1.51}$$

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

$$\langle (p - \bar{p})^2 \rangle = (3 - 8/\pi) \, m k_B T \simeq m k_B T/2,$$

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

$$\langle (p-\bar{p})^2 \rangle = \langle p^2 \rangle - 2\langle p \rangle \bar{p} + \bar{p}^2 = \overline{p^2} - \bar{p}^2, \tag{1.52}$$

where $\bar{p}$ and $\overline{p^2}$ are the first and second moments of the momentum distribution. Substituting Eqs. (1.50) and (1.51) we obtain the requested 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

$$E_Z(\mathbf{r}) = -\boldsymbol{\mu} \cdot \mathbf{B}(\mathbf{r}) \tag{1.53}$$

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

$$E_Z(\mathbf{r}) = 2\mu_B m_s B(\mathbf{r}), \tag{1.54}$$

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

$$\mathcal{U}(r) = \tfrac{1}{2}\mu_B B''(0)r^2 = \tfrac{1}{2}m\omega^2 r^2, \tag{1.55}$$

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 *harmonic 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,

$$n(r) = n_0 e^{-(r/R)^2}. \tag{1.56}$$

Note that for harmonic traps the density distribution of a classical gas has a *gaussian shape* in the ideal-gas limit. Comparing with Eq. (1.40) we find for the *thermal radius*

$$R = \sqrt{\frac{2k_BT}{m\omega^2}}. \tag{1.57}$$

Substituting Eq. (1.55) into Eq. (1.45) we obtain after integration for the *effective volume* of the gas

$$V_e = \int e^{-(r/R)^2} 4\pi r^2 dr = \pi^{3/2} R^3 = \left(\frac{2\pi k_BT}{m\omega^2}\right)^{3/2}. \tag{1.58}$$

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. (B.3)

$$E_P = \int \mathcal{U}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} = n_0 k_BT \int_0^\infty (r/R)^2 e^{-(r/R)^2} 4\pi r^2 dr = \frac{3}{2} N k_BT. \tag{1.59}$$

Similarly we calculate for the kinetic energy

$$E_K = \int \left(p^2/2m\right) n(\mathbf{p})d\mathbf{p} = \frac{Nk_BT}{\pi^{3/2}\alpha^3}\int_0^\infty \left(p/\alpha\right)^2 e^{-(p/\alpha)^2} 4\pi p^2 dp = \frac{3}{2}Nk_BT. \tag{1.60}$$

Hence, the total energy is given by

$$E = 3Nk_BT. \tag{1.61}$$

Problem 1.6 *An isotropic harmonic trap has the same curvature of* $m\omega^2/k_B = 2000$ *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 $T = 10$ μ*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 velocity 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

$$f(\mathbf{r},\mathbf{p}) = \int d\varepsilon' \, f(\varepsilon')\, \delta[\varepsilon' - H_0(\mathbf{r},\mathbf{p})]. \tag{1.62}$$

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*

$$\rho(\varepsilon) \equiv (2\pi\hbar)^{-3} \int d\mathbf{r} d\mathbf{p}\, \delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})], \tag{1.63}$$

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. (1.63) over $\mathbf{p}$ the density of states takes the form[6]

$$\rho(\varepsilon) = \frac{2\pi(2m)^{3/2}}{(2\pi\hbar)^3} \int_{\mathcal{U}(\mathbf{r})\leq\varepsilon} \sqrt{\varepsilon - \mathcal{U}(\mathbf{r})} d\mathbf{r}, \tag{1.64}$$

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

$$\rho(\varepsilon) = \frac{4\pi m\, V}{(2\pi\hbar)^3}\sqrt{2m\varepsilon}, \tag{1.65}$$

where V is the volume of the system. As a second example we consider the harmonically trapped gas. Substituting Eq. (1.55) into Eq. (1.64) we find after a straightforward integration for the density of states

$$\rho(\varepsilon) = \tfrac{1}{2}(1/\hbar\omega)^3\varepsilon^2. \tag{1.66}$$

Problem 1.10 *Show the relation*

$$\int d\mathbf{r}d\mathbf{p}\, f(\mathbf{r},\mathbf{p})\delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})] = f(\varepsilon)\rho(\varepsilon) = f(\varepsilon)\int d\mathbf{r}d\mathbf{p}\,\delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})]. \tag{1.67}$$

Solution: Substituting Eq. (1.62) into the left hand side of Eq.(1.67) we obtain using the definition for the density of states

$$(2\pi\hbar)^{-3}\int d\varepsilon'\, f(\varepsilon')\int d\mathbf{r}d\mathbf{p}\,\delta[\varepsilon' - H_0(\mathbf{r},\mathbf{p})]\,\delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})] = \int d\varepsilon'\, f(\varepsilon')\,\rho(\varepsilon')\,\delta\,(\varepsilon - \varepsilon') = f(\varepsilon)\rho(\varepsilon). \blacktriangleright \tag{1.68}$$

1.3.4 Power-law traps

Let us analyze *isotropic power-law traps*, *i.e.* power-law traps for which the potential can be written as

$$\mathcal{U}(\mathbf{r}) = \mathcal{U}_0\,(r/r_e)^{3/\gamma} \equiv w_0 r^{3/\gamma}, \tag{1.69}$$

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 $w_0 = \mathcal{U}_0 r_e^{-3/\gamma}$, where $\mathcal{U}_0$ is the *trap strength* and r_e the *characteristic trap size*. In the 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*, which are represented by potentials of the type[7]

$$\mathcal{U}(x,y,z) = w_1\,|x|^{1/\gamma_1} + w_2\,|y|^{1/\gamma_2} + w_3\,|z|^{1/\gamma_3} \quad \text{with } \gamma = \sum_i \gamma_i, \tag{1.70}$$

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

[7] See V. Bagnato, D.E. Pritchard and D. Kleppner, *Phys.Rev. A* **35,** 4354 (1987).

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

	square well	harmonic trap	linear trap	square root dimple trap
w_0	$\mathcal{U}_0 r_e^{-3/\gamma}$ with $\gamma \to 0$	$\frac{1}{2}m\omega^2$	$\mathcal{U}_0 r_e^{-1}$	$\mathcal{U}_0 r_e^{-1/2}$
γ	0	3/2	3	6
α_{PL}	$\frac{4}{3}\pi r_e^3$	$\left(2\pi k_B/m\omega^2\right)^{3/2}$	$\frac{4}{3}\pi r_e^3\, 3!\, (k_B/\mathcal{U}_0)^3$	$\frac{4}{3}\pi r_e^3\, 6!(k_B/\mathcal{U}_0)^6$
A_{PL}	$\frac{2\sqrt{2}}{3\pi}(m^{1/2}r_e/\hbar)^3$	$\frac{1}{2}(1/\hbar\omega)^3$	$\frac{32\sqrt{2}}{105\pi}(m^{1/2}r_e/\hbar)^3\mathcal{U}_0^{-3}$	$\frac{2048\sqrt{2}}{9009\pi}(m^{1/2}r_e/\hbar)^3\mathcal{U}_0^{-6}$

where γ is again the *trap parameter*. Substituting the power-law potential (1.69) into Eq. (1.45) we calculate (see problem 1.11) for the volume

$$V_e(T) = \alpha_{PL} T^{\gamma}, \tag{1.71}$$

where the coefficients α_{PL} are included in Table 1.1 for some typical cases of γ. Similarly, substituting Eq. (1.69) into Eq. (1.64) we find (see problem 1.12) for the density of states

$$\rho(\varepsilon) = A_{PL}\varepsilon^{1/2+\gamma}. \tag{1.72}$$

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*

$$V_e = \frac{4}{3}\pi r_e^3 \Gamma(\gamma+1)\left(\frac{k_B T}{\mathcal{U}_0}\right)^{\gamma},$$

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 $w_0 = \mathcal{U}_0 r_e^{-3/\gamma}$

$$V_e = \int e^{-w_0 r^{3/\gamma}/k_B T} 4\pi r^2 dr = \frac{4}{3}\pi r_0^3 \gamma \left(\frac{k_B T}{\mathcal{U}_0}\right)^{\gamma} \int e^{-x} x^{\gamma-1} dx,$$

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

Problem 1.12 *Show that the density of states of an isotropic power-law trap is given by*

$$\rho(\varepsilon) = \sqrt{\frac{2}{\pi}}\frac{\left(m^{1/2}r_e/\hbar\right)^3}{3\mathcal{U}_0^{\gamma}}\frac{\Gamma(\gamma+1)}{\Gamma(\gamma+3/2)}\varepsilon^{1/2+\gamma}.$$

Solution: The density of states is defined as $\rho(\varepsilon) = 2\pi(2m)^{3/2}/(2\pi\hbar)^3 \int_{\mathcal{U}(\mathbf{r})\leq\varepsilon} \sqrt{\varepsilon - \mathcal{U}(\mathbf{r})} d\mathbf{r}$. Substituting $\mathcal{U}(\mathbf{r}) = w_0 r^{3/\gamma}$ for the potential with $w_0 = \mathcal{U}_0 r_e^{-3/\gamma}$ and introducing the dummy variable $x = \varepsilon - w_0 r^{3/\gamma}$ this can be written as

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

Using the integral (B.17) this leads to the requested result. ▶

1.3.5 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 (1.70). 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

$$Z_N = \frac{1}{N!}(2\pi\hbar)^{-3N} \int e^{-H(\mathbf{p}_1,\mathbf{r}_1;\cdots;\mathbf{p}_N,\mathbf{r}_N)/k_BT} d\mathbf{p}_1 \cdots d\mathbf{p}_N d\mathbf{r}_1 \cdots d\mathbf{r}_N. \tag{1.73}$$

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

$$Z_N = \frac{Z_1^N}{N!}. \tag{1.74}$$

Here Z_1 is the single-particle canonical partition function given by Eq. (1.35). In terms of the density of states it takes the form[8]

$$Z_1 = (2\pi\hbar)^{-3} \int \{ \int e^{-\varepsilon/k_BT} \delta[\varepsilon - H_0(\mathbf{r},\mathbf{p})] d\varepsilon \} d\mathbf{p} d\mathbf{r} = \int e^{-\varepsilon/k_BT} \rho(\varepsilon) d\varepsilon. \tag{1.75}$$

Substituting the power-law expression Eq. (1.72) for the density of states we find for power-law traps

$$Z_1 = A_{PL} (k_BT)^{(\gamma+3/2)} \int e^{-x} x^{(\gamma+1/2)} dx = A_{PL} \Gamma(\gamma + 3/2) (k_BT)^{(\gamma+3/2)}, \tag{1.76}$$

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

$$Z_1 = (k_BT/\hbar\omega)^3. \tag{1.77}$$

First we calculate the total energy. Substituting Eq. (1.74) into Eq. (1.29) we find

$$E = Nk_BT^2 (\partial \ln Z_1/\partial T) = (3/2 + \gamma) Nk_BT, \tag{1.78}$$

where γ is the trap parameter defined in Eq. (1.70). 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. (1.78) 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

$$E_P = \gamma N k_BT. \tag{1.79}$$

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. (1.74) can be written in the form

$$Z_N \simeq \left(\frac{Z_1 e}{N} \right)^N \quad \text{for } N \ggg 1. \tag{1.80}$$

Substituting this result into expression (1.30) we find for the Helmholtz free energy

$$F = -Nk_BT[1 + \ln(Z_1/N)] \quad \Leftrightarrow \quad Z_1 = Ne^{-(1+F/Nk_BT)}. \tag{1.81}$$

As an example we derive a thermodynamic expression for the degeneracy parameter. First we recall Eq. (1.46), which relates D to the single-particle partition function,

$$D = n_0\Lambda^3 = N/Z_1. \tag{1.82}$$

---

[8] 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. (1.81) we obtain

$$n_0\Lambda^3 = e^{1+F/Nk_BT}, \tag{1.83}$$

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

$$n_0\Lambda^3 = \exp\left[E/Nk_BT - S/Nk_B + 1\right]. \tag{1.84}$$

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. (1.48),

$$p_0 = -\left(\partial F/\partial V_e\right)_{T,N}. \tag{1.85}$$

Substituting Eq. (1.47) into Eq. (1.81) the free energy can be written as

$$F = -Nk_BT[1 + \ln V_e - 3\ln\Lambda - \ln N]. \tag{1.86}$$

Thus, combining (1.85) and (1.86), we obtain for the *central pressure* the well-known expression,

$$p_0 = (N/V_e)\, k_BT = n_0k_BT. \tag{1.87}$$

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

$$\mu = -k_BT\ln(Z_1/N) \Leftrightarrow \mu = k_BT\ln(n_0\Lambda^3). \tag{1.88}$$

Solution: Starting from Eq. (1.31) we evaluate the chemical potential as a partial derivative of the Helmholz free energy,

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

Recalling Eq. (1.47), $Z_1 = V_e\Lambda^{-3}$, we see 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. ▶

1.3.6 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 ($đQ = TdS = 0$).[9]

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.

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[9] 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. (1.78) the degeneracy parameter can be written for this case as

$$n_0\Lambda^3 = \exp\left[5/2 + \gamma - S/Nk_B\right], \tag{1.89}$$

implying that $n_0\Lambda^3$ is conserved provided the cloud shape remains constant ($\gamma =$ constant). Under these conditions the temperature changes with central density and effective volume according to

$$T(t) = T_0\left[n_0(t)/n_0\right]^{2/3}. \tag{1.90}$$

To analyze what happens if we adiabatically change the power-law potential

$$\mathcal{U}(\mathbf{r}) = \mathcal{U}_0(t)\,(r/r_e)^{3/\gamma} \tag{1.91}$$

by varying the trap strength $\mathcal{U}_0(t)$ as a function of time. In accordance, also the central density n_0 and the effective volume V_e become functions of time (see Problem 1.11)

$$\frac{n_0}{n_0(t)} = \frac{V_e(t)}{V_0} = \left(\frac{T(t)/T_0}{\mathcal{U}_0(t)/\mathcal{U}_0}\right)^{\gamma}. \tag{1.92}$$

Substituting this expression into Equation (1.90) we obtain

$$T(t) = T_0\left[\mathcal{U}_0(t)/\mathcal{U}_0\right]^{\gamma/(\gamma+3/2)}, \tag{1.93}$$

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. (1.90) that the central density will change like

$$n_0\,(t) = n_0\left[\mathcal{U}_0(t)/\mathcal{U}_0\right]^{\gamma/(1+2\gamma/3)}. \tag{1.94}$$

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. (1.89) 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 r_e 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[10] or even substantially[11], adiabatic variation will typically not allow to change D by more than two orders of magnitude in trapped gases.

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[10] P.W.H. Pinkse, A. Mosk, M. Weidemüller, M.W. Reynolds, T.W. Hijmans, and J.T.M. Walraven, *Phys. Rev. Lett.* **78** (1997) 990.

[11] D. M. Stamper-Kurn, H.-J. Miesner, A. P. Chikkatur, S. Inouye, J. Stenger, and W. Ketterle, *Phys. Rev. Lett.* **81**, (1998) 2194.

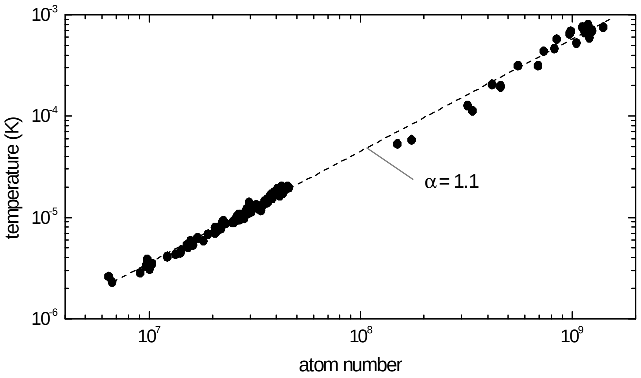

Figure 1.2: Measurement of evaporative cooling of a ^{87}Rb cloud in a Ioffe-Pritchard trap. In this example the efficiency parameter was observed to be slightly larger than unity ($\alpha = 1.1$). See further K. Dieckmann, *Thesis*, University of Amsterdam (2001).

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 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*[12] in which 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

$$\tau_{th} \simeq \tau_c = (n\bar{v}_r\sigma)^{-1}, \tag{1.95}$$

where $\bar{v}_r$ is the average relative speed given by Eq. (1.106). 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 $\exp[-\varepsilon_{tr}/k_BT]$. Hence, the evaporation rate may be estimated with

$$\tau_{ev}^{-1} \simeq n\bar{v}_r\sigma e^{-\varepsilon_{tr}/k_BT}.$$

Let us analyze evaporative cooling for the case of a harmonic trap[13], where the total energy is given by Eq. (1.61). 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

$$\dot{E} = 3\dot{N}k_BT + 3Nk_B\dot{T}. \tag{1.96}$$

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[12] Proposed by H. Hess, Phys. Rev. B **34** (1986) 3476. First demonstrated experimentally by H. Hess et al. Phys. Rev. Lett. **59** (1987) 672.

[13] 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, *Adv. At. Mol. Opt. Phys.* **36** (1997); C. Cohen Tannoudji, *Course 96/97 at College de France*; J.T.M. Walraven in: *Quantum Dynamics of Simple Systems*, G.-L. Oppo, S.M. Barnett, E. Riis and M. Wilkinson (Eds.) IOP Bristol 1996).

Suppose next that we continuously remove the tail of atoms of potential energy $\varepsilon_{tr} = \eta k_B T$ with $\eta \gg 1$. Under such conditions the loss rate of total energy is given by[14]

$$\dot{E} = (\eta + 1)\dot{N} k_B T. \tag{1.97}$$

Equating Eqs.(1.96) and (1.97) we obtain the relation

$$\dot{T}/T = \tfrac{1}{3}(\eta - 2)\dot{N}/N. \tag{1.98}$$

This relation shows that the temperature decreases with the number of atoms provided $\eta > 2$, which is easily arranged. The solution of Eq. (1.98) can be written as[15]

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

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

$$\dot{n}_0/n_0 = \dot{N}/N - \dot{V}_e/V_e. \tag{1.99}$$

Substituting Eq. (1.58) for the effective volume in a harmonic trap Eq. (1.99) takes the form

$$\dot{n}_0/n_0 = \dot{N}/N - \tfrac{3}{2}\dot{T}/T, \tag{1.100}$$

and after substitution of Eq. (1.98)

$$\dot{n}_0/n_0 = \tfrac{1}{2}\left(4 - \eta\right)\dot{N}/N. \tag{1.101}$$

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 $\dot{D} = \dot{n}_0 \Lambda^3 + 3 n_0 \Lambda^2 \dot{\Lambda}$ and arrive at

$$\dot{D}/D = \left(3 - \eta\right)\dot{N}/N \tag{1.102}$$

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.

Interestingly, with increasing density the evaporation rate

$$\dot{N}/N = -\tau_{ev}^{-1} \simeq -n_0 \bar{v}_r \sigma e^{-\eta}, \tag{1.103}$$

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.

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

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[14] Naively one might expect $\dot{E} = (\eta + 3/2)\dot{N} k_B T$. The expression given here results from a kinetic analysis of evaporative cooling in the limit $\eta \to \infty$, see O.J. Luiten *et al.*, *Phys. Rev.* A **53** (1996) 381.

[15] Eq.(1.98) 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.

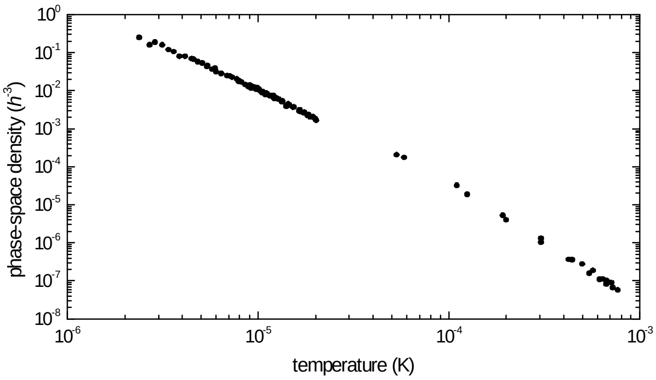

Figure 1.3: Example of the increase in phase-space density with decreasing temperature as observed with a cloud of ^{87}Rb atoms in a Ioffe-Pritchard trap. In this example the gas reaches a temperature of 2.4 μK and a phase-space density of 0.24. Further cooling results in Bose-Einstein condensation.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

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* $T \leq 500$ μ*K 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 like for 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.1),

$$\varepsilon = H(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) = \frac{P^2}{2M} + \frac{p^2}{2\mu} + \mathcal{U}_2\left(\mathbf{R}, \mathbf{r}\right) + \mathcal{V}(r), \tag{1.104}$$

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, $\mathcal{U}_2\left(\mathbf{R}, \mathbf{r}\right) = \mathcal{U}(\mathbf{R} + \frac{1}{2}\mathbf{r}) + \mathcal{U}(\mathbf{R} - \frac{1}{2}\mathbf{r})$ 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

$$P(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r}) = \frac{1}{2}(2\pi\hbar)^{-6} Z_2^{-1} e^{-H(\mathbf{P}, \mathbf{R}; \mathbf{p}, \mathbf{r})/k_B T}, \tag{1.105}$$

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

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

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

$$\bar{v}_r = \int_0^\infty \frac{p}{\mu} P_{\mathrm{M}}(\mathbf{p})d\mathbf{p} = \frac{1}{\mu}\frac{\int_0^\infty pe^{-(p/\alpha)^2}4\pi p^2dp}{\int_0^\infty e^{-(p/\alpha)^2}4\pi p^2dp} = \sqrt{8k_BT/\pi\mu}, \tag{1.106}$$

where where $\alpha = \sqrt{2\mu k_BT}$. Here we used the definite integrals (B.3) and (B.4) 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 a 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 (1.105) over $\mathbf{P}$ and $\mathbf{p}$,

$$P(\mathbf{R},\mathbf{r}) = \int P(\mathbf{P},\mathbf{R};\mathbf{p},\mathbf{r})d\mathbf{P}d\mathbf{p}, \tag{1.107}$$

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*,

$$P(\mathbf{R},\mathbf{r}) = \frac{1}{2}(2\pi\hbar)^{-6}\int Z_2^{-1}e^{-H(\mathbf{P},\mathbf{R};\mathbf{p},\mathbf{r})/k_BT}d\mathbf{P}d\mathbf{p} = J_{12}^{-1}V_e^{-2}e^{-[\mathcal{U}_2(\mathbf{R},\mathbf{r})+\mathcal{V}(r)]/k_BT}, \tag{1.108}$$

and V_e the effective volume of the gas as defined by Eq. (1.45). Further, we introduced the normalization integral

$$J_{12} \equiv V_e^{-2}\int e^{-[\mathcal{U}_2(\mathbf{R},\mathbf{r})+\mathcal{V}(r)]/k_BT}d\mathbf{r}d\mathbf{R} \tag{1.109}$$

as an integral over the pair configuration. The integration of Eq. (1.108) over momentum space is straightforward because the pair hamiltonian (1.104) 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 very short relative distances $r \lesssim r_0$. This suggests to split the configuration space for the relative position in 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

$$J_{12} = V_e^{-2}\int e^{-\mathcal{U}_2(\mathbf{R},\mathbf{r})/k_BT}d\mathbf{r}d\mathbf{R} + V_e^{-2}\int e^{-\mathcal{U}_2(\mathbf{R},\mathbf{r})/k_BT}\left[e^{-\mathcal{V}(r)/k_BT} - 1\right]d\mathbf{r}d\mathbf{R}. \tag{1.110}$$

The first term on the r.h.s. is a free-space integration yielding unity.[16] 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

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[16] Note that $\int e^{-\mathcal{U}_2(\mathbf{R},\mathbf{r})/k_BT}d\mathbf{r}d\mathbf{R} = \int e^{-\mathcal{U}(\mathbf{r}_1)/k_BT}d\mathbf{r}_1e^{-\mathcal{U}(\mathbf{r}_2)/k_BT}d\mathbf{r}_2 = V_e^2$ because the Jacobian of the transformation $d\mathbf{r}d\mathbf{R} = \left|\frac{\partial(\mathbf{r},\mathbf{R})}{\partial(\mathbf{r}_1,\mathbf{r}_2)}\right|d\mathbf{r}_1d\mathbf{r}_2$ is unity (see Problem A.1).

separate the configuration integral into a product of integrals over the relative and the center of mass coordinates. Comparing with Eq. (1.44) 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 the configuration integral can be written as

$$J_{12} = 1 + v_{int}V_{2e}/V_e^2, \tag{1.111}$$

where

$$v_{int} \equiv \int \left[e^{-\mathcal{V}(r)/k_BT} - 1\right] 4\pi r^2 dr \equiv \int \left[g\,(r) - 1\right] 4\pi r^2 dr \tag{1.112}$$

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 *radial distribution function* of the pair.

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

$$\bar{\mathcal{V}} \equiv \int \mathcal{V}(r)P(\mathbf{R},\mathbf{r})d\mathbf{r}d\mathbf{R} = J_{12}^{-1}V_e^{-2}\int \mathcal{V}(r)e^{-[\mathcal{U}_2(\mathbf{R},\mathbf{r})+\mathcal{V}(r)]/k_BT}d\mathbf{r}d\mathbf{R}. \tag{1.113}$$

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. (1.113) reduces to

$$\bar{\mathcal{V}} = V_e^{-2}\int e^{-2\mathcal{U}(\mathbf{R})/k_BT}d\mathbf{R}\,J_{12}^{-1}\int \mathcal{V}(r)e^{-\mathcal{V}(r)/k_BT}d\mathbf{r} \simeq k_BT^2\frac{\partial \ln J_{12}}{\partial T}, \tag{1.114}$$

which is readily verified by substituting Eq. (1.111). 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

$$\tilde{U} \equiv \int \mathcal{V}(r)e^{-\mathcal{V}(r)/k_BT}d\mathbf{r} = \int \mathcal{V}(r)g(r)d\mathbf{r} \tag{1.115}$$

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

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

In Eq. (1.115) the interaction strength is expressed for *thermally* distributed pairs of classical atoms. More generally the volume integral (1.115) 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,

$$E_{int} = \frac{1}{2}N\,(N-1)\,\bar{\mathcal{V}}. \tag{1.116}$$

Presuming $N \gg 1$ we may approximate $N\,(N-1)\,/2 \simeq N^2/2$ and using definition (1.45) 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

$$\varepsilon_{int} = E_{int}/N = \frac{1}{2}\frac{V_{2e}}{J_{12}V_e}n_0\tilde{U}. \tag{1.117}$$

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

$$n|\tilde{U}| \ll k_BT. \tag{1.118}$$

Problem 1.16 *Show that the trap-averaged interaction energy per atom as given by Eq. (1.117) 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 $n(\mathbf{r}) = n_0 e^{-\mathcal{U}(\mathbf{r})/k_BT}$ and using $V_e = N/n_0$ we obtain

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

Problem 1.17 *Show that for a harmonically trapped dilute gas*

$$V_{2e}/V_e = V_e(T/2)/V_e(T) = (1/2)^{3/2}. \tag{1.119}$$

Solution: The result follows directly with Eq. (1.45). ▶

1.4.4 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),

$$\mathcal{V}(r) = \infty \text{ for } r \le r_c \text{ and } \mathcal{V}(r) = -C_6/r^6 \text{ for } r > r_c, \tag{1.120}$$

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 1.4.6). Note that the model potential (1.120) 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, $k_BT \gg \mathcal{V}_0$, we have

$$\tilde{U} = \int \mathcal{V}(r)e^{-\mathcal{V}(r)/k_BT} d\mathbf{r} \simeq \int_{r_c}^{\infty} \mathcal{V}(r)4\pi r^2 dr = -4\pi r_c^3\mathcal{V}_0\int_1^{\infty} 1/x^4 dx = b\mathcal{V}_0, \tag{1.121}$$

where $x = r/r_c$ is a dummy variable. Note that the integral only converges for power-law potentials of power $p > 3$, *i.e.* short-range potentials. The trap-averaged interaction energy (1.117) is given by

$$\varepsilon_{int} = \frac{1}{2}\frac{V_{2e}}{V_e}n_0\tilde{U}. \tag{1.122}$$

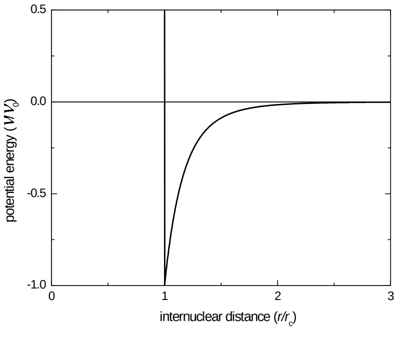

Figure 1.4: Model potential with hard core of diameter r_c and Van der Waals tail.

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

$$v_{int} \equiv \int_{r_c}^{\infty} \left[e^{-\mathcal{V}(r)/k_BT} - 1 \right] 4\pi r^2 dr \simeq -\frac{1}{k_BT} \int_{r_c}^{\infty} \mathcal{V}(r) 4\pi r^2 dr = b\frac{\mathcal{V}_0}{k_BT} \ll V_e. \tag{1.123}$$

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. (1.121) was obtained for temperatures $k_BT \gg \mathcal{V}_0$.

1.4.5 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

$$Z_N = \frac{1}{N!}(2\pi\hbar)^{-3N} \int e^{-H(\mathbf{p}_1,\mathbf{r}_1;\cdots;\mathbf{p}_N,\mathbf{r}_N)/k_BT} d\mathbf{p}_1 \cdots d\mathbf{p}_N d\mathbf{r}_1 \cdots d\mathbf{r}_N. \tag{1.124}$$

After integration over momentum space, which is straightforward because the pair hamiltonian (1.104) shows complete separation of the momentum variables $\{\mathbf{p}_i\}$, we obtain

$$Z_N = \frac{1}{N!}\Lambda^{-3N} \int e^{-U(\mathbf{r}_1,\cdots,\mathbf{r}_N)/k_BT} d\mathbf{r}_1 \cdots d\mathbf{r}_N = \frac{Z_1^N}{N!}\mathcal{J}, \tag{1.125}$$

where we substituted the single-atom partition function (1.47) and introduced the configuration integral $\mathcal{J} \equiv V_e^{-N} \int e^{-U(\mathbf{r}_1,\cdots,\mathbf{r}_N)/k_BT} d\mathbf{r}_1 \cdots d\mathbf{r}_N$, with $U(\mathbf{r}_1,\cdots,\mathbf{r}_N) = \sum_i \mathcal{U}(\mathbf{r}_i) + \sum_{i<j} \mathcal{V}(r_{ij})$. 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[17]

$$\mathcal{J} = (1 - Nb/V_e)^{N-2} \prod\nolimits_{i<j} J_{ij}, \tag{1.126}$$

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

$$Z_N = \frac{Z_1^N}{N!} (1 - Nb/V_e)^{N-2} J_{12}^{N(N-1)/2}. \tag{1.127}$$

1.4.6 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 (1.120). In view of Eq. (1.127) 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. (1.127) we have for the canonical partition function of a nearly-ideal gas in the high-temperature limit

$$Z_N = \frac{Z_1^N}{N!} \left(1 - N\frac{b}{V_e}\right)^N \left(1 + \frac{b}{V_e}\frac{V_{2e}}{V_e}\frac{\mathcal{V}_0}{k_BT}\right)^{N^2/2}. \tag{1.128}$$

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. (1.31),

$$p_0 = -\left(\partial F/\partial V_e\right)_{T,N} = k_BT \left(\partial \ln Z_N/\partial V_e\right)_{T,N}. \tag{1.129}$$

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

Then using Eq. (1.47) we obtain for the *pressure* under conditions where $\tilde{U}/k_BT \ll 1$ and $Nb \ll 1$

$$p_0 = k_BT\left(\frac{N}{V_e} + b\frac{N^2}{V_e^2} - b\frac{N^2}{2V_e^2}\frac{\mathcal{V}_0}{k_BT}\frac{V_{2e}}{V_e}\right). \tag{1.130}$$

This expression may be written in the form

$$\frac{p_0}{n_0k_BT} = 1 + B(T)n_0, \tag{1.131}$$

where $B(T) \equiv b[1-(1/2)^{5/2}\,\mathcal{V}_0/k_BT] = b-(V_{2e}/V_e)\,\tilde{U}/2k_BT$ 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

$$\frac{1}{V_e} + b\frac{N}{V_e^2} \simeq \frac{1}{V_e - Nb}, \tag{1.132}$$

we can bring Eq. (1.130) in the form of the *Van der Waals equation of state*,

$$\left(p_0 + a\frac{N^2}{V_e^2}\right)(V_e - Nb) = Nk_BT, \tag{1.133}$$

with $a = -\,(V_{2e}/V_e)\,\tilde{U}/2$ a positive constant. This famous equation of state was the first expression containing the essential ingredients to describe the *gas to liquid phase transition* for decreasing temperatures.[18] 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. (1.28),

$$U = k_BT^2\,(\partial \ln Z_N/\partial T)_{\mathcal{U},N}\,.$$

Then using Eqs.(1.127) and (1.114) we find for $k_BT \gg \mathcal{V}_0$

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

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

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[18] See for instance F. Reif, *Fundamentals of statistical and thermal physics*, McGraw-Hill, Inc., Tokyo 1965.

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 for Δp the rms momentum spread around the average momentum in a thermal gas, $\Delta p = [\langle (p - \bar{p})^2 \rangle]^{1/2} \simeq [mk_BT/2]^{1/2}$ (see Problem 1.5), the uncertainty in position is given by $\Delta l \simeq \hbar/\Delta p = [2\hbar^2/(mk_BT)]^{1/2}$. The quantum resolution limit is reached when Δl approaches the interatomic spacing,

$$\Delta l \simeq \hbar/\Delta p = [2\hbar^2/(mk_BT)]^{1/2} \simeq n_0^{-1/3}.$$

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 $\Lambda \equiv [2\pi\hbar^2/(mk_BT)]^{1/2}$ is the *thermal* de Broglie wavelength introduced in Section 1.3.1 (note that Λ and Δl coincide within a factor 2).

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 will 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. These states are *metastable.* With increasing density, when 3-body collisions become important, the system becomes instable 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 kinetic 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 $T = 1$ μK.*
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 $T = 1$ μK?

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

2.1 Introduction

The motion of particles in a *central* potential field plays an important role in atomic and molecular physics. First of all, to understand the properties of the individual atoms we rely on careful analysis of the electronic motion in the presence of Coulomb interaction with the nucleus. Further, also many properties related to interactions between atoms, like 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[1] summarize in this chapter the derivation of the Schrödinger equation for the motion of two particles interacting through a *central* potential $\mathcal{V}(r)$, $r = |\mathbf{r}_1 - \mathbf{r}_2|$ being the radial distance between the particles. In view of the central symmetry and in the absence of externally applied fields the relative motion of the particles, say of masses m_1 and m_2, can be reduced to the motion of a single particle of *reduced mass* $\mu = m_1 m_2/(m_1 + m_2)$ in the same potential field (see appendix A.1). 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 2.2). Knowing the hamiltonian we can write down the Schrödinger equation (Section 2.3) 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. In Section 2.4 we show that the radial wave equation can be written in the form of a one-dimensional Schrödinger equation, which simplifies the mathematical analysis of the radial motion.

2.2 Hamiltonian

The classical hamiltonian for the motion of a particle of (reduced) mass μ in the central potential $\mathcal{V}(r)$ is given by

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

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 $\mathbf{p} = \mu\mathbf{v}$ is the momentum of the particle and the hamiltonian

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[1] The approach of this chapter is mostly based on Albert Messiah *Quantum Mechanics*, North-Holland Publishing company, Amsterdam 1970.

can be written as[2]

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

Turning to position and momentum operators in the *position representation* ($\mathbf{p} \to -i\hbar\boldsymbol{\nabla}$ and $\mathbf{r} \to \mathbf{r}$) the quantum mechanical hamiltonian takes the familiar form of the *Schrödinger hamiltonian*,

$$\mathcal{H}_0 = -\frac{\hbar^2}{2\mu}\Delta + \mathcal{V}(r). \tag{2.3}$$

To fully exploit the central symmetry we rewrite the classical hamiltonian in a form in which the *angular momentum*, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, and the *radial momentum*, $p_r = \hat{\mathbf{r}} \cdot \mathbf{p}$ with $\hat{\mathbf{r}} = \mathbf{r}/r$ the unit vector in radial direction (see Fig. 2.1), appear explicitly,

$$H = \frac{1}{2\mu}\left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) + \mathcal{V}(r). \tag{2.4}$$

This form enables us to separate the description of the angular motion from that of the radial motion of the reduced mass, which is a great simplification of the problem. In Section 2.2.7 we show how Eq. (2.4) follows from Eq. (2.1) and derive the operator expression for p_r^2. However, first we derive expressions for the operators $\mathbf{L}_z$ and $\mathbf{L}^2$. In Sections 2.3 and 2.4 we formulate Schrödinger equations for the radial motion.

2.2.1 Symmetrization of non-commuting operators - commutation relations

With the reformulation of the hamiltonian for the orbital motion in the form (2.4) we should watch out for ambiguities in the correspondence rules $\mathbf{p} \to -i\hbar\boldsymbol{\nabla}$ and $\mathbf{r} \to \underline{\mathbf{r}}$. [3] Whereas in classical mechanics the expressions $p_r = \hat{\mathbf{r}} \cdot \mathbf{p}$ and $p_r = \mathbf{p} \cdot \hat{\mathbf{r}}$ are identities 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. The risk of such ambiguities in making the transition from the classical to the quantum mechanical description is not surprising because non-commutativity of position and momentum is at the core of quantum mechanics.

To deal with non-commutativity the operator algebra has to be completed with expressions for the relevant commutators. For the *cartesian* components of the position r_i and momentum p_j the commutators are

$$[r_i, p_j] = i\hbar\delta_{ij}\,, \qquad \text{with } i,j \in \{x,y,z\}. \tag{2.5}$$

This follows easily in the position representation by evaluating the action of the operator $[r_i, p_j]$ on an arbitrary function of position $\phi(r_x, r_y, r_z)$,

$$[r_i, p_j]\,\phi = -i\hbar\left(r_i\partial_j - \partial_j r_i\right)\phi = -i\hbar\left(r_i\partial_j\phi - r_i\partial_j\phi - \phi\delta_{ij}\right) = i\hbar\delta_{ij}\phi. \tag{2.6}$$

Here $\partial_j = \partial/\partial r_j$ is a shorthand notation for the partial derivative operator. Note that the commutation relations in the form (2.5) are specific for cartesian coordinates; in general their form will be different.

For the anti-commutator $\{r_i, p_j\}$, by construction, no ambiguity appears in the correspondence rule since $\{r_i, p_j\} = \{p_j, r_i\}$ both in classical mechanics and in quantum mechanics. Hence, after symmetrization with respect to non-commuting dynamical variables, *e.g.* $p_r \equiv \frac{1}{2}(\hat{\mathbf{r}} \cdot \mathbf{p} + \mathbf{p} \cdot \hat{\mathbf{r}})$, the correspondence rules allow unambiguous construction of quantum mechanical operators starting from their classical counter parts.

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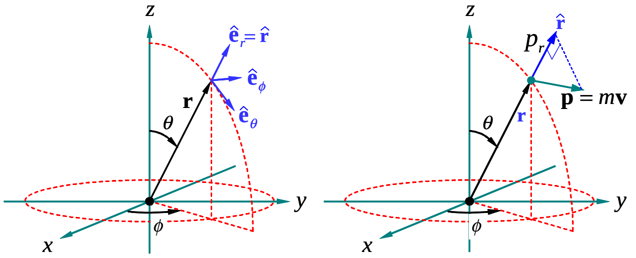
[2] In the presence of an external electromagnetic field the *non-relativistic* momentum of a *charged* particle of mass m and charge q is given by $\mathbf{p} = m\mathbf{v} + q\mathbf{A}$, with $m\mathbf{v}$ its *kinetic* momentum and $q\mathbf{A}$ its *electromagnetic* momentum.

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



(a) (b)

Figure 2.1: (a) We use the unit vector convention: $\hat{\mathbf{r}} = \hat{\mathbf{e}}_r = \hat{\mathbf{e}}_x \sin\theta\cos\phi + \hat{\mathbf{e}}_y \sin\theta\sin\phi + \hat{\mathbf{e}}_z\cos\theta$; $\hat{\mathbf{e}}_\theta = \hat{\mathbf{e}}_x\cos\theta\cos\phi + \hat{\mathbf{e}}_y\cos\theta\sin\phi - \hat{\mathbf{e}}_z\sin\theta$, $\hat{\mathbf{e}}_\phi = -\hat{\mathbf{e}}_x\sin\phi + \hat{\mathbf{e}}_y\cos\phi$; (b) vector diagram indicating the direction $\hat{\mathbf{r}}$ and amplitude p_r of the radial momentum vector.

2.2.2 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 rule ($\mathbf{p} \to -i\hbar\boldsymbol{\nabla}$ and $\mathbf{r} \to \underline{\mathbf{r}}$). Interestingly, explicit symmetrization in the form $\mathbf{L} = \frac{1}{2}(\mathbf{r}\times\mathbf{p} - \mathbf{p}\times\mathbf{r})$ is not required,

$$\mathbf{L} = -i\hbar\mathbf{r}\times\boldsymbol{\nabla}. \tag{2.7}$$

This is easily verified using the cartesian vector components,[4]

$$L_i = -i\hbar\tfrac{1}{2}\left(\varepsilon_{ijk}r_j\partial_k - \varepsilon_{ijk}\partial_j r_k\right) = -i\hbar\varepsilon_{ijk}r_j\partial_k. \tag{2.8}$$

Here we used the Einstein summation convention[5] and ε_{ijk} is the Levi-Civita tensor[6].

Having identified Eq. (2.7) as the proper operator expression for the orbital angular momentum we can turn to arbitrary *orthogonal* curvilinear coordinates $\{u, v, w\}$. In this case the gradient vector is given by $\boldsymbol{\nabla} = \{h_u^{-1}\partial_u, h_v^{-1}\partial_v, h_w^{-1}\partial_w\}$, where $h_a = |\partial\mathbf{r}/\partial a|$, $\partial_a \equiv \partial/\partial a$ and the unit vectors are defined by $\hat{\mathbf{a}} \equiv \hat{\mathrm{e}}_a = h_a^{-1}\partial_a\mathbf{r}$ with $a \in \{u, v, w\}$. The angular momentum operator can be decomposed in the following form

$$\mathbf{L} = -\,i\hbar(\mathbf{r}\times\boldsymbol{\nabla}) = -\,i\hbar\begin{vmatrix} \hat{\mathbf{u}} & \hat{\mathbf{v}} & \hat{\mathbf{w}} \\ r_u & r_v & r_w \\ h_u^{-1}\partial_u & h_v^{-1}\partial_v & h_w^{-1}\partial_w \end{vmatrix}, \tag{2.9}$$

For *spherical coordinates* we have $h_r = |\partial\mathbf{r}/\partial r| = 1$, $h_\phi = |\partial\mathbf{r}/\partial\phi| = r\sqrt{\sin^2\theta\sin^2\phi + \sin^2\theta\cos^2\phi} = r\sin\theta$ and $h_\theta = |\partial\mathbf{r}/\partial\theta| = r\sqrt{\cos^2\theta\cos^2\phi + \cos^2\theta\sin^2\phi + \sin^2\theta} = r$. The components of the radius vector are $r_r = r$ and $r_\theta = r_\phi = 0$. Working out the determinant in Eq. (2.9), *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

$$\mathbf{L} = -i\hbar(\mathbf{r}\times\boldsymbol{\nabla}) = i\hbar\left(\hat{\mathbf{e}}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} - \hat{\mathbf{e}}_\phi\frac{\partial}{\partial\theta}\right). \tag{2.10}$$

Here both $\hat{\mathbf{e}}_\theta$ and $\hat{\mathbf{e}}_\phi$ are unit vectors of the spherical coordinate system (see Fig. 2.1). 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.

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[4] Note that $-\varepsilon_{ijk}\partial_j r_k = -\varepsilon_{ijk}r_k\partial_j = \varepsilon_{ikj}r_k\partial_j = \varepsilon_{ijk}r_j\partial_k$ for cartesian coordinates because for $j \neq k$ the operators r_j and ∂_k commute and for $j = k$ one has $\varepsilon_{ijk} = 0$.

[5] In the Einstein convention summation is done over repeating indices.

[6] $\varepsilon_{ijk} = \pm 1$ for all even $(+)$ or odd $(-)$ permutations of $i, j, k = x, y, z$ and $\varepsilon_{ijk} = 0$ for two equal indices.

2.2.3 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, $L_z = \hat{\mathbf{e}}_z \cdot \mathbf{L}$. From Eq. (2.10) we see that

$$L_z = i\hbar \left((\hat{\mathbf{e}}_z \cdot \hat{\mathbf{e}}_\theta) \frac{1}{\sin\theta} \frac{\partial}{\partial\phi} - (\hat{\mathbf{e}}_z \cdot \hat{\mathbf{e}}_\phi) \frac{\partial}{\partial\theta} \right).$$

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

$$L_z = -i\hbar \frac{\partial}{\partial\phi}. \tag{2.11}$$

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

$$-i\hbar \frac{\partial}{\partial\phi} \Phi_m(\phi) = m\hbar\ \Phi_m(\phi). \tag{2.12}$$

Here, the eigenvalue is called the m quantum number for the projection of the angular momentum $\mathbf{L}$ on the quantization axis.[7] The eigenfunctions are

$$\Phi_m(\phi) = a_m e^{im\phi}. \tag{2.13}$$

Because the wavefunction must be invariant under rotation of the atom over 2π we have the boundary condition $e^{im\phi} = e^{im(\phi+2\pi)}$. Thus we require $e^{im2\pi} = 1$, which implies $m = 0,\ \pm1,\ \pm2, \ldots$ With the normalization

$$\int_0^{2\pi} \left|\Phi_m(\phi)^2\right| d\phi = 1$$

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

2.2.4 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

$$[L_x, L_y] = i\hbar L_z,\ [L_y, L_z] = i\hbar L_x \text{ and } [L_z, L_x] = i\hbar L_y. \tag{2.14}$$

These expressions are readily derived with the help of some elementary commutator algebra (see appendix B.7). We show 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 $L_i = \varepsilon_{ijk} r_j p_k$ we use subsequently the distributive rule (B.18b), the multiplicative rule (B.18d) and the commutation relation (2.5),

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

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

$$[L_x, \mathbf{L}^2] = 0,\ [L_y, \mathbf{L}^2] = 0,\ [L_z, \mathbf{L}^2] = 0. \tag{2.15}$$

---

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

We verify this explicitly for L_z. Since $\mathbf{L}^2 = \mathbf{L}\cdot\mathbf{L} = L_x^2 + L_y^2 + L_z^2$ we obtain with the multiplicative rule (B.18c)

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

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

2.2.5 The operators $L_\pm$

The operators

$$L_\pm = L_x \pm iL_y \tag{2.16}$$

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

$$L_\pm = i\hbar\left([(\hat{\mathbf{e}}_x\cdot\hat{\mathbf{e}}_\theta) \pm i\,(\hat{\mathbf{e}}_y\cdot\hat{\mathbf{e}}_\theta)]\,\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} - [(\hat{\mathbf{e}}_x\cdot\hat{\mathbf{e}}_\phi) \pm i\,(\hat{\mathbf{e}}_y\cdot\hat{\mathbf{e}}_\phi)]\,\frac{\partial}{\partial\theta}\right),$$

as follows directly with Eq. (2.10). Substituting the unit vector decompositions $\hat{\mathbf{e}}_\phi = -\hat{\mathbf{e}}_x\sin\phi + \hat{\mathbf{e}}_y\cos\phi$ and $\hat{\mathbf{e}}_\theta = \hat{\mathbf{e}}_x\cos\theta\cos\phi + \hat{\mathbf{e}}_y\cos\theta\sin\phi - \hat{\mathbf{e}}_z\sin\theta$ we obtain

$$L_\pm = \hbar e^{\pm i\phi}\left(i\cot\theta\frac{\partial}{\partial\phi} \pm \frac{\partial}{\partial\theta}\right). \tag{2.17}$$

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 Problem 2.1).

Several useful relations for $L_\pm$ follow straightforwardly. Using the commutation relations (2.14) we obtain

$$[L_z, L_\pm] = [L_z, L_x] \pm i\,[L_z, L_y] = i\hbar L_y \pm \hbar L_x = \pm\hbar L_\pm. \tag{2.18}$$

Further we have

$$L_+L_- = L_x^2 + L_y^2 - i\,[L_x, L_y] = L_x^2 + L_y^2 + \hbar L_z = \mathbf{L}^2 - L_z^2 + \hbar L_z \tag{2.19a}$$

$$L_-L_+ = L_x^2 + L_y^2 + i\,[L_x, L_y] = L_x^2 + L_y^2 - \hbar L_z = \mathbf{L}^2 - L_z^2 - \hbar L_z, \tag{2.19b}$$

where we used again one of the commutation relations (2.14). Subtracting these equations we obtain

$$[L_+, L_-] = 2\hbar L_z \tag{2.20}$$

and by adding Eqs. (2.19) we find

$$\mathbf{L}^2 = L_z^2 + \tfrac{1}{2}\left(L_+L_- + L_-L_+\right). \tag{2.21}$$

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

To derive an expression for the operator $\mathbf{L}^2$ we use the operator relation (2.21). Substituting Eqs. (2.11) and (2.17) we obtain after some straightforward but careful manipulation

$$\mathbf{L}^2 = -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})\right]. \tag{2.22}$$

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

$$-\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})\right]Y(\theta,\phi)=\lambda\hbar^2Y(\theta,\phi). \tag{2.23}$$

Because $\mathbf{L}^2$ commutes with L_z the θ and ϕ variables separate, *i.e.* we can write

$$Y(\theta,\phi)=P(\theta)\Phi_m(\phi), \tag{2.24}$$

where the function $\Phi_m(\phi)$ is an eigenfunction of the L_z operator and the properties of the function $P(\theta)$ are to be determined. Evaluating the second derivative $\partial^2/\partial\phi^2$ in Eq. (2.23) we obtain

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})-\frac{m^2}{\sin^2\theta}+\lambda\right]P(\theta)=0. \tag{2.25}$$

Using the notation $u\equiv\cos\theta$ and $\lambda=l(l+1)$ this equation takes the form of the Legendre differential equation (B.22),

$$\left[\left(1-u^2\right)\frac{d^2}{du^2}-2u\frac{d}{du}-\frac{m^2}{1-u^2}+l(l+1)\right]P_l^m(u)=0. \tag{2.26}$$

The solutions are the *associated Legendre polynomials* $P_l^m(u)$, with $|m|\leq l$; *i.e.,* $2l+1$ possible values of m for given value of l. They are obtained, see Eq. (B.23), by differentiation of the *Legendre polynomials* $P_l(u)$, with $P_l(u)=P_l^0(u)$. The lowest order Legendre polynomials are

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

The *spherical harmonics* are defined (see Section B.8.1) as the normalized joint eigenfunctions of $\mathbf{L}^2$ and L_z in the position representation. Hence, we have

$$\mathbf{L}^2Y_l^m(\theta,\phi)=l(l+1)\hbar^2Y_l^m(\theta,\phi) \tag{2.27}$$

and

$$L_zY_l^m(\theta,\phi)=m\hbar Y_l^m(\theta,\phi). \tag{2.28}$$

Angular momentum and Dirac notation

In the Dirac notation we identify $Y_l^m(\theta,\phi)=\langle\hat{\mathbf{r}}\,|l,m\rangle$ and write

$$\mathbf{L}^2\,|l,m\rangle=l(l+1)\hbar^2\,|l,m\rangle \tag{2.29}$$

$$L_z\,|l,m\rangle=m\hbar\,|l,m\rangle\,, \tag{2.30}$$

where the $|l,m\rangle$ are abstract state vectors in Hilbert space for the joint eigenstates of $\mathbf{L}^2$ and L_z as defined by the quantum numbers l and m. The actions of the shift operators $L_\pm$ are derived in Problem 2.1.

$$L_\pm\,|l,m\rangle=\sqrt{l\,(l+1)-m(m\pm1)}\hbar\,|l,m\pm1\rangle\,. \tag{2.31}$$

Expressions analogous to those given for $\mathbf{L}^2$, L_z and $L_\pm$ hold for any hermitian operator satisfying the basic commutation relations (2.14). Such operators are called *angular momentum operators.* Another famous example is the operator $\mathbf{S}$ for the electronic spin. Using the commutation relations it is readily verified that Eq. (2.21) is a special case of the more general *inner product rule* for two momentum operators $\mathbf{L}$ and $\mathbf{S}$,

$$\mathbf{L}\cdot\mathbf{S}=L_zS_z+\tfrac{1}{2}\left(L_+S_-+L_-S_+\right). \tag{2.32}$$

Note that the L_zS_z operator as well as the operators L_+S_- and L_-S_+ conserve the total angular momentum along the quantization axis $m=m_l+m_s$.

Problem 2.1 *Show that the action of the shift operators* $L_{\pm}$ *is given by*

$$L_{\pm}\left|l,m\right\rangle=\sqrt{l\left(l+1\right)-m(m\pm1)}\hbar\left|l,m\pm1\right\rangle . \tag{2.33}$$

Solution: We show this for L_+, for L_- the proof proceeds analogously. Using the commutation relations (B.18c) we have

$$L_zL_+\left|l,m\right\rangle=\left(L_+L_z+\left[L_z,L_+\right]\right)\left|l,m\right\rangle=\left(L_+m\hbar+\hbar L_+\right)\left|l,m\right\rangle=\left(m+1\right)\hbar L_+\left|l,m\right\rangle$$

Comparison with $L_z\left|l,m+1\right\rangle=\left(m+1\right)\hbar\left|l,m+1\right\rangle$ shows that $L_+\left|l,m\right\rangle=c_+\left(l,m\right)\hbar\left|l,m+1\right\rangle$. Similarly we obtain $L_-\left|l,m\right\rangle=c_-\left(l,m\right)\hbar\left|l,m-1\right\rangle$. The constants $c_{\pm}\left(l,m\right)$ remain to be determined. For this we write the expectation value of L_+L_- in the form

$$\left\langle l,m\right|L_-L_+\left|l,m\right\rangle=c_-\left(l,m+1\right)c_+\left(l,m\right)\hbar^2. \tag{2.34}$$

On the other hand we have, using Eq. (2.19a)

$$\left\langle l,m\right|L_-L_+\left|l,m\right\rangle=\left\langle l,m\right|\mathbf{L}^2-L_z^2-\hbar L_z\left|l,m\right\rangle=\left[l\left(l+1\right)-m(m+1)\right]\hbar^2 \tag{2.35}$$

Next we note $c_+\left(l,m\right)=c_-^*\left(l,m+1\right)$ and $c_-\left(l,m\right)=c_+^*\left(l,m-1\right)$ because L_x and L_y are hermitian, and $L_{\pm}$ the hermitian conjugates of $L_{\mp}$. For L_+ we have

$$\begin{aligned}\left\langle l,m+1\right|L_+\left|l,m\right\rangle&=\left\langle l,m+1\right|L_x\left|l,m\right\rangle+\left\langle l,m+1\right|iL_y\left|l,m\right\rangle\\&=\left\langle l,m\right|L_x\left|l,m+1\right\rangle^*-i\left\langle l,m\right|L_y\left|l,m+1\right\rangle^*\\&=\left\langle l,m\right|L_-\left|l,m+1\right\rangle^* .\end{aligned}$$

Hence, combining this with Eqs. (2.34) and (2.35) we obtain

$$c_-\left(l,m+1\right)c_+\left(l,m\right)=\left|c_+\left(l,m\right)\right|^2=\left[l\left(l+1\right)-m(m+1)\right],$$

which is the square of the eigenvalue we were looking for. ▶

2.2.7 Radial momentum operator p_r

The radial momentum operator in the position representation is given by

$$p_r\equiv\tfrac{1}{2}\left(\hat{\mathbf{r}}\cdot\mathbf{p}+\mathbf{p}\cdot\hat{\mathbf{r}}\right)=-\frac{i\hbar}{2}\left[\frac{\mathbf{r}}{r}\cdot\boldsymbol{\nabla}+\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{r}}{r}\right)\right], \tag{2.36}$$

which in spherical coordinates takes the form

$$p_r\psi=-i\hbar\left(\frac{\partial}{\partial r}+\frac{1}{r}\right)\psi=-i\hbar\frac{1}{r}\frac{\partial}{\partial r}(r\psi) \tag{2.37}$$

and implies the commutation relation

$$[r,p_r]=i\hbar. \tag{2.38}$$

Importantly, p_r^2 commutes with L_z and $\mathbf{L}^2$,

$$\left[p_r^2,L_z\right]=0\quad\text{and}\quad\left[p_r^2,\mathbf{L}^2\right]=0, \tag{2.39}$$

because p_r is independent of θ and ϕ and L is independent of r, see Eq. (2.10).

In the position representation the squared radial momentum operator takes the form

$$p_r^2\psi=-\hbar^2\left(\frac{\partial}{\partial r}+\frac{1}{r}\right)^2\psi=-\hbar^2\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)\psi=-\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(r\psi\right). \tag{2.40}$$

In Problem 2.2 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 the *physically relevant solutions* for the (radial) wavefunction.

To demonstrate how Eq. (2.4) follows from Eq. (2.1) we express the *classical* expression for $\mathbf{L}^2/r^2$ in terms of $\mathbf{r}$ and $\mathbf{p}$ using cartesian coordinates,[8]

$$\begin{aligned}\mathbf{L}^2/r^2 &= (\varepsilon_{ijk}r_jp_k)(\varepsilon_{ilm}r_lp_m)/r^2 = (\delta_{jl}\delta_{km}-\delta_{jm}\delta_{kl})\,r_jp_kr_lp_m/r^2\\ &= [(r_jr_j)(p_kp_k) - r_jp_jp_kr_k]/r^2 = [(r_jr_j)(p_kp_k) - (r_jp_j)^2]/r^2\\ &= [r^2\mathbf{p}^2 - (\mathbf{r}\cdot\mathbf{p})^2]/r^2 = \mathbf{p}^2 - (\hat{\mathbf{r}}\cdot\mathbf{p})^2 .\end{aligned} \tag{2.41}$$

Before constructing the quantum mechanical operator for $\mathbf{L}^2/r^2$ in the position representation we first symmetrize the classical expression,

$$\frac{\mathbf{L}^2}{r^2} = \mathbf{p}^2 - \frac{1}{4}(\hat{\mathbf{r}}\cdot\mathbf{p} + \mathbf{p}\cdot\hat{\mathbf{r}})^2 . \tag{2.42}$$

Using Eq. (2.36) we obtain after elimination of $\mathbf{p}^2$

$$\mathbf{p}^2 = \left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) \quad (r \neq 0), \tag{2.43}$$

which is valid everywhere *except in the origin.*

Problem 2.2 *Show that* p_r *is Hermitian for square-integrable functions* $\psi(\mathrm{r})$ *only if they are regular at the origin, i.e.* $\lim_{\mathrm{r}\to 0} \mathrm{r}\psi(\mathrm{r}) = 0$*.*

Solution: For p_r to be Hermitian we require the following expression to be zero:

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

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 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. *Note*: p_r is not an observable. To be an observable it must be Hermitian. This is only the case for square-integrable eigenfunctions $\psi(r)$ that are *regular* at the origin. However, the square-integrable eigenfunctions of p_r can also be *irregular* at the origin and have complex eigenvalues, *e.g.*

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

---

[8] In the Einstein notation the contraction of the Levi-Civita tensor is given by $\varepsilon_{ijk}\varepsilon_{ilm} = \delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}$.

2.3 Schrödinger equation

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

$$\left[\frac{1}{2\mu}\left(p_r^2+\frac{\mathbf{L}^2}{r^2}\right)+\mathcal{V}(r)\right]\psi(r,\theta,\phi)=E\psi(r,\theta,\phi). \tag{2.44}$$

Because the operators $\mathbf{L}^2$ and L_z commute with the hamiltonian they share a complete set of eigenstates with the hamiltonian; *i.e.,* the joint eigenfunctions $\psi(r,\theta,\phi)$ must be the form[9]

$$\psi=R(r,\theta,\phi)Y_{lm}(\theta,\phi), \tag{2.45}$$

where in view of Eq.(2.27) we require $\mathbf{L}^2R(r,\theta,\phi)=0$. This can only be satisfied for arbitrary value of r if the radial variable separates from the angular variables, $R(r,\theta,\phi)=R(r)X(\theta,\phi)$. In turn this requires $\mathbf{L}^2X(\theta,\phi)=0$, which in general can only be satisfied if $X(\theta,\phi)$ is independent of θ and ϕ. In other words $X(\theta,\phi)$ has to be a constant and without loss of generality we may presume $X(\theta,\phi)=1$ and write $R(r,\theta,\phi)=R(r)$. Hence, using Eq. (2.27) and substituting Eqs. (2.40) and (2.45) into Eq. (2.44) we obtain

$$\left[\frac{\hbar^2}{2\mu}\left(-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{l(l+1)}{r^2}\right)+\mathcal{V}(r)\right]R(r)Y_{lm}(\theta,\phi)=ER(r)Y_{lm}(\theta,\phi). \tag{2.46}$$

Here the term

$$\mathcal{V}_{\mathrm{rot}}(r)\equiv\frac{l(l+1)\hbar^2}{2\mu r^2} \tag{2.47}$$

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. (3.1) is independent of θ and ϕ we can eliminate the functions $Y_{lm}(\theta,\phi)$ from this equation. The remaining equation takes the form of the *radial wave equation.*

$$\left[\frac{\hbar^2}{2\mu}\left(-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{l(l+1)}{r^2}\right)+\mathcal{V}(r)\right]R_l(r)=ER_l(r), \tag{2.48}$$

where the solutions $R_l(r)$ must depend on l but be independent of θ and ϕ. Note that the solutions do not depend on m because the hamiltonian does not depend L_z. This is a property of central potentials. Eq. (2.48) is the starting point for the description of the relative radial motion of any particle in a central potential field.

Note that 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). The corresponding quantum numbers l and m_l are called *good quantum numbers* within the context of the hamiltonian considered. As p_r^2 does not commute with the hamiltonian it is not an *observable.*[10]

2.4 One-dimensional Schrödinger equation

The Eq. (2.40) suggests to introduce functions

$$\chi_l(r)=rR_l(r), \tag{2.49}$$

which allows us to bring the radial wave equation (2.48) in the form of a one-dimensional Schrödinger equation

$$\chi_l''+\left[\frac{2\mu}{\hbar^2}(E-V)-\frac{l(l+1)}{r^2}\right]\chi_l=0. \tag{2.50}$$

---

[9] Note that L_z commutes with $\mathbf{L}^2$ (see section 2.2.6); L_z and $\mathbf{L}^2$ commute with r and p_r (see section 2.2.7).

[10] Note that p_r does not commute with r (see section 2.2.7).

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

$$\chi'' + F(r)\chi = 0. \tag{2.51}$$

Equations of this type satisfy some very general properties. These are related to the Wronskian theorem, which is derived and discussed in appendix B.12.

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

$$\int r^2 \left|R(r)\right|^2 dr = \int \left|\chi(r)\right|^2 dr = \mathcal{N}, \tag{2.52}$$

where $\mathcal{N}$ is a finite number. However, there is an additional requirement. Because the separation in radial and angular motion as expressed by Eq. (2.43) is only valid outside the origin ($r > 0$) the solutions of the radial wave equation are not necessarily valid *in* 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 2.3 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. (2.48) and (2.50) can be valid solutions for all values of r, *including the origin.*

Problem 2.3 *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 because the kinetic energy diverges.*

Solution: We first use the Gauss theorem to demonstrate that $\Delta\left(1/r\right) = -4\pi\delta\left(\mathbf{r}\right)$. For this we integrate this expression on both sides over a small sphere V of radius ϵ around the origin,

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

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

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

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 remains normalizable. The divergent wavefunction $R_l(r)$ is defined everywhere except in the origin. This is more than simply a technical problem because it implies that the Schrödinger equation is not satisfied in the origin:

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

Note that in this expression, without separation of the radial and angular motion, the hamiltonian is valid throughout space, *i.e.*, *also in the origin.* Physically, irregular solutions must be rejected because the kinetic energy diverges: writing $R_0(r) = (\chi_0(r)/r)$ with $\lim_{r\to 0}\chi_0(r) = \chi_0 \neq 0$ the kinetic energy is given by

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

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 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 with the aid of the thermal wavelength as $\Lambda \gg r_0$, which is equivalent to $kr_0 \ll 1$, where $k \sim 1/\Lambda$ is the wavenumber of the relative motion of free atoms and r_0 the range of the interaction potential.

Importantly, as the Van der Waals interaction is an elastic interaction the energy of the relative motion is a conserved quantity. Because the relative energy is purely kinetic at large interatomic separation it can be expressed as $E = \hbar^2 k^2/2\mu$, which implies that also the wavenumbers for the relative motion before and after the collision must be the same. This shows that far from the scattering center the collision can only affect the phase of the wavefunction and not its wavelength. Apparently, the appearance of a phase shift relative to free atomic motion is the key parameter for the quantum mechanical description of elastic collisions.

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 potential. The range r_0 was already introduced in Chapter 1 as the distance beyond which the interaction may be neglected in the limit $k \to 0$. The second characteristic length, the s-wave scattering length a, is the effective *hard sphere diameter*. It is a measure for the *interaction strength* and determines the *collisional cross section* in the limit $k \to 0$ as will be shown in Chapter 4. It is the central parameter for the theoretical description of all bosonic quantum gases, determining both the *interaction energy* and the *kinetic properties* of the gas. The third characteristic length, the effective range r_e expresses how the potential affects the energy dependence of the cross section. The condition $k^2 a r_e \ll 1$ indicates when the $k \to 0$ limit is reached.

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 we specialize to the case of low-energy collisions. First, the basic phenomenology is introduced and analyzed for simple model potentials like the hard sphere and the square well. Then we show that this phenomenology holds for arbitrary *short-range potentials*. In the last part of the section we have a close look at the underpinning of the short range concept and derive an expression for

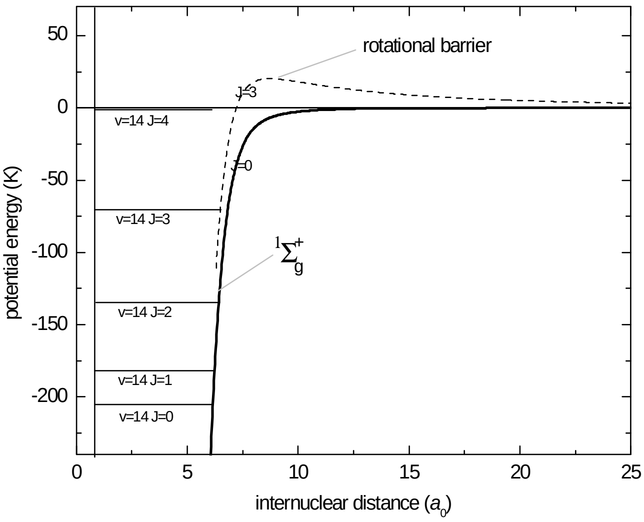

Figure 3.1: Example showing the high-lying bound states near the continuum of the singlet potential $^1\Sigma_g^+$ (the bonding potential) of the hydrogen molecule; v and J are the vibrational and rotational quantum numbers, respectively. The dashed line shows the effect of the $J = 3$ centrifugal barrier. The $M_S = -1$ branch of the triplet potential $^3\Sigma_u^+$ (the anti-bonding potential) is shifted downwards with respect to the singlet by 13.4 K in a magnetic field of 10 T.

the range r_0 of power-law potentials with special attention for the Van der Waals interaction. In the last section of this chapter (Section 3.4) we analyze how the energy of interaction between two atoms 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 (2.44),

$$\left[\frac{1}{2\mu}\left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) + \mathcal{V}(r)\right]\psi(r,\theta,\phi) = E\psi(r,\theta,\phi). \tag{3.1}$$

Here μ is the reduced mass of the atom pair and $\mathcal{V}(r)$ the interaction potential. As discussed in Section 2.3 the eigenfunctions $\psi(r,\theta,\phi)$ can be written as

$$\psi = R_l(r)Y_{lm}(\theta,\phi), \tag{3.2}$$

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

$$\left[\frac{\hbar^2}{2\mu}\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2}\right) + \mathcal{V}(r)\right]R_l(r) = ER_l(r). \tag{3.3}$$

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

$$\mathcal{V}_{\text{rot}}(r) = l(l+1)\frac{\hbar^2}{2\mu r^2}, \tag{3.4}$$

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.

To analyze the radial wave equation we introduce the quantities

$$\varepsilon = 2\mu E/\hbar^2 \quad \text{and} \quad U(r) = 2\mu\mathcal{V}(r)/\hbar^2, \tag{3.5}$$

which put Eq. (3.3) in the form

$$R_l'' + \frac{2}{r}R_l' + \left[\varepsilon - U(r) - \frac{l(l+1)}{r^2}\right] R_l = 0. \tag{3.6}$$

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

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

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

$$\chi_0'' + [\varepsilon - U(r)]\chi_0 = 0. \tag{3.8}$$

In this chapter we will introduce the *wave number* notation using $k = [2\mu E]^{1/2}/\hbar$ and $\varepsilon = k^2$ for $\varepsilon > 0$. Similarly, we will write $\varepsilon = -\kappa^2$ for $\varepsilon < 0$. Hence, for a bound state of energy $E_b < 0$ we have $\kappa = [-2\mu E_b]^{1/2}/\hbar = [2\mu\,|E_b|]^{1/2}/\hbar$.

3.2.2 Free particle motion

We first have a look at the case of free particles. In this case $\mathcal{V}(r) = 0$ and the radial wave equation (3.6) becomes

$$R_l'' + \frac{2}{r}R_l' + \left[k^2 - \frac{l(l+1)}{r^2}\right] R_l = 0, \tag{3.9}$$

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

$$R_l'' + \frac{2}{\varrho}R_l' + \left[1 - \frac{l(l+1)}{\varrho^2}\right] R_l = 0. \tag{3.10}$$

The general solution of Eq. (3.10) for angular momentum l is a linear combination of two particular solutions, a *regular* one $j_l(\varrho)$ (without divergencies), and an *irregular* one $n_l(\varrho)$ (cf. Appendix B.11.1):

$$R_l(\varrho) = Aj_l(\varrho) + Bn_l(\varrho). \tag{3.11}$$

To proceed we introduce a dimensionless number $\eta_l = \arctan B/A$ so that $A = C\cos\eta_l$ and $B = C\sin\eta_l$. Substituting this into Eq. (3.11) yields

$$R_l(\varrho) = C\left[\cos\eta_l\, j_l(\varrho) + \sin\eta_l\, n_l(\varrho)\right]. \tag{3.12}$$

For $\eta_l \to 0$ the general solution reduces to the regular one, $j_l(kr)$, which is the physical solution because it is well-behaved throughout space (including the origin). For $\varrho \to \infty$ the general solution assumes the following asymptotic form

$$R_l(\varrho) \underset{\varrho\to\infty}{\simeq} \frac{C}{\varrho}\{\cos\eta_l \sin(\varrho - \frac{1}{2}l\pi) + \sin\eta_l \cos(\varrho - \frac{1}{2}l\pi)\}, \tag{3.13}$$

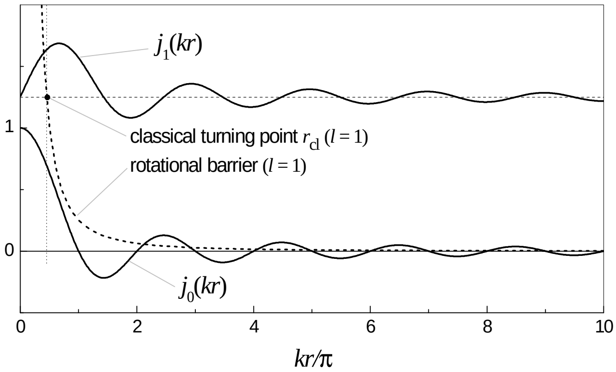

Figure 3.2: The lowest-order spherical Bessel functions $j_0(kr)$ and $j_1(kr)$, which are the $l = 0$ and $l = 1$ eigenfunctions of the radial wave equation in the absence of interactions (free atoms). Also shown is the $l = 1$ rotational barrier and the corresponding classical turning point for the radial motion for energy $E = \hbar^2k^2/2\mu$ of the eigenfunctions shown. The $j_1(kr)$ is shifted up by 1 for convenience of display. Note that $j_1(kr) \ll j_0(kr)$ for $kr \ll 1$.

which can be conveniently written for any finite value of k using the angle-addition formula for the sine

$$R_l(r) \underset{r\to\infty}{\simeq} \frac{c_l}{r}\sin(kr + \eta_l - \frac{1}{2}l\pi). \tag{3.14}$$

Hence, the constant $\eta_l(k)$ may be interpreted as an asymptotic phase shift, which for a given value of k completely fixes the general solution of the radial wavefunction $R_l(r)$ up to a (k and l dependent) normalization constant $c_l(k)$. Note that for free particles Eq. (3.12) 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. Further, it is instructive to rewrite Eq. (3.14) in the form

$$R_l(r) \underset{r\to\infty}{\simeq} D_l\frac{e^{ikr}}{r} + D_l^*\frac{e^{-ikr}}{r}, \tag{3.15}$$

where $D_l = (c_l/2i)\exp[i(\eta_l - \frac{1}{2}l\pi)]$ is a k-dependent coefficient. This expression shows that for $r \to \infty$ the stationary solution $R_l(r)$ can be regarded as an 'outgoing' spherical wave e^{ikr}/r interfering with an 'incoming' spherical wave e^{-ikr}/r. We return to these aspects when discussing collisions in Chapter 4.

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

The solution of the radial Schrödinger equation is particularly simple for the case $l = 0$. Writing the radial wave equation in the form of the 1D-Schrödinger equation (3.8) we have for free particles

$$\chi_0'' + k^2\chi_0 = 0, \tag{3.16}$$

with general solution $\chi_0(k,r) = C\sin(kr + \eta_0)$. Thus the case $l = 0$ is seen to be special because Eq. (3.14) is a good solution not only asymptotically but for all values $r > 0$,

$$R_0(k,r) = \frac{C}{kr}\sin(kr + \eta_0). \tag{3.17}$$

Note that this also follows from Eq. (B.72a). Again we require $\eta_0 = 0$ for the case of free particles to assure Eq. (3.17) to be 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. 3.2.

For two atoms with relative angular momentum $l > 0$ there exists a distance r_{cl}, the *classical turning point*, under which the rotational energy exceeds the total energy E. In this *classically inaccessible* region of space the radial wavefunction is exponentially suppressed. For the case $l = 1$ this is illustrated in Fig. 3.2.

3.2.4 Significance of the phase shifts

To introduce the collisional phase shifts we write the radial wave equation in the form of the 1D-Schrödinger equation (3.8)

$$\chi_l'' + [k^2 - \frac{l(l+1)}{r^2} - U(r)]\chi_l = 0. \tag{3.18}$$

For sufficiently large r the potential may be neglected in Eq. (3.18)

$$|U(r)| \ll k^2 \quad \text{for } r > r_k, \tag{3.19}$$

where r_k is defined by[1]

$$|U(r_k)| = k^2. \tag{3.20}$$

Thus we find that for $r \gg r_k$ Eq. (3.18) reduces to the free-particle Schrödinger equation, which implies that asymptotically the solution of Eq. (3.18) is given by

$$\lim_{r\to\infty} \chi_l(r) = \sin(kr + \eta_l - \frac{1}{2}l\pi). \tag{3.21}$$

Whereas in the case of free particles the phase shifts must all vanish as discussed in the previous section, in the presence of the interaction a finite phase shift allows to obtain the proper asymptotic form (3.21) for the *distorted wave* $R_l(k, r) = \chi_l(r)/kr$, which correctly describes the wavefunction near the scattering center. Thus we conclude that the non-zero phase shift is a purely collisional effect.

3.2.5 Integral representation for the phase shift

An exact integral expression for the phase shift can be obtained by applying the Wronskian Theorem. To derive this result we compare the *distorted wave* solutions $\chi_l = krR_l(r)$ with the *regular* solutions $y_l = krj_l(kr)$ of the 1D Schrödinger equation

$$y_l'' + [k^2 - \frac{l(l+1)}{r^2}]y_l = 0 \tag{3.22}$$

in which the potential is neglected. Comparing the solutions of Eq. (3.18) with Eq. (3.22) at the same value $\varepsilon = k^2$ we can use the Wronskian Theorem in the form (B.104)

$$W(\chi_l, y_l)|_a^b = -\int_a^b U(r)\chi_l(r)y_l(r)dr. \tag{3.23}$$

The Wronskian of χ_l and y_l is given by

$$W(\chi_l, y_l) = \chi_l(r)y_l'(r) - \chi_l'(r)y_l(r). \tag{3.24}$$

Because both χ_l and y_l should be regular at the origin, the Wronskian is zero in the origin. Asymptotically we find $y_l(r)$ with Eq. (B.73a) $\lim_{r\to\infty} y_l(r) = \sin(kr - \frac{1}{2}l\pi)$ and $\lim_{r\to\infty} y_l'(r) = k\cos(kr - \frac{1}{2}l\pi)$.

---

[1] Note that unlike the range r_0 the value r_k diverges for $k \to 0$.

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

$$\lim_{r\to\infty} W(\chi_l, y_l) = k\sin\eta_l. \tag{3.25}$$

With the Wronskian theorem (3.23) we obtain the following integral expression for the phase shift,

$$\sin\eta_l = -\frac{2\mu}{\hbar^2}\int_0^\infty \mathcal{V}(r)\chi_l(k,r)j_l(kr)rdr. \tag{3.26}$$

Problem 3.1 *Show that the integral expression for the phase shift only holds for potentials that tend asymptotically to zero faster than $1/r$, i.e. for non-Coulomb fields.*

Solution: Using the asymptotic expressions for $\mathcal{V}(r)$, $\chi_l(r)$ and $y_l(r)$ the integrand of Eq. (3.26) takes the asymptotic form

$$\begin{aligned}\mathcal{V}(r)\chi_l(k,r)j_l(kr)r &\underset{r\to\infty}{\sim} \frac{C_s^*}{kr^s}\left\{\sin(kr - \frac{1}{2}l\pi)\cos\eta_l + \cos(kr - \frac{1}{2}l\pi)\sin\eta_l\right\}\sin(kr - \frac{1}{2}l\pi)\\ &\underset{r\to\infty}{\sim} \frac{C_s}{kr^s}\left\{\cos\eta_l\left[1-\cos(2kr - l\pi)\right] + \sin(2kr - l\pi)\sin\eta_l\right\}\\ &\underset{r\to\infty}{\sim} \frac{C_s^*}{2kr^s}\left[\cos\eta_l - \cos(2kr - l\pi + \eta_l)\right].\end{aligned}$$

The oscillatory term is 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 $s > 1$. ▶

3.3 Motion in the low-energy limit

In this section we specialize to the case of low-energy collisions ($kr_0 \ll 1$). We first derive analytical expressions for the phase shift in the $k \to 0$ limit for the cases of hard sphere potentials (Sections 3.3.1 and 3.3.2) and spherical square wells (Sections 3.3.3 - 3.3.6). Specializing in this context to the case $l = 0$ we introduce the concepts of the *scattering length* a, a measure for the strength of the interaction, and the *effective range* r_e, a measure for its energy dependence. Then we turn to arbitrary short range potentials (Section 3.3.9). For the case $l = 0$ we derive general expressions for the energy dependence of the s-wave phase shift, both in the absence (Sections 3.3.10) and in the presence (Section 3.3.11) of a weakly-bound s level. Asking for the existence of finite range r_0 in the case of the Van der Waals interaction, we introduce in Section 3.3.12 power-law potentials $\mathcal{V}(r) = Cr^{-s}$, showing that a finite range only exists for low angular momentum values $l < \frac{1}{2}(s-3)$. For $l \geq \frac{1}{2}(s-3)$ we can also derive an analytic expression for the phase shift in the $k \to 0$ limit (Section 3.3.14) provided the presence of an l-wave shape resonance can be excluded.

3.3.1 Hard-sphere potentials

We now turn to analytic 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 $k = [2\mu E]^{1/2}/\hbar$. Thus, for $r > a$ the general solution for the radial wave functions of angular momentum l is given by Eq. (3.12)

$$R_l(k,r) = C\left[\cos\eta_l j_l(kr) + \sin\eta_l n_l(kr)\right]. \tag{3.27}$$

To determine the phase shift we require as a boundary condition that $R_l(k,r)$ vanishes at the hard sphere (see Fig. 3.3),

$$R_l(k,a) = C\left[\cos\eta_l j_l(ka) + \sin\eta_l n_l(ka)\right] = 0. \tag{3.28}$$

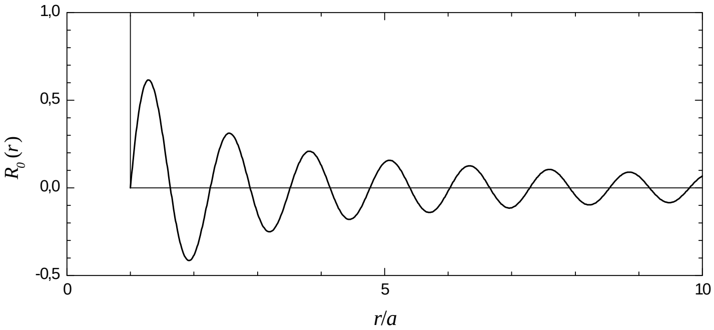

Figure 3.3: Radial wavefunction for the case of a hard sphere. The boudary condition is fixed by the requirement that the wavefunction vanishes at the edge of the hard sphere, $R_0(a) = 0$.

Hence, the phase shift follows from the expression

$$\tan \eta_l = -\frac{j_l(ka)}{n_l(ka)}, \tag{3.29}$$

or, in complex notation,[2]

$$e^{2i\eta_l} = -\frac{j_l(ka) - in_l(ka)}{j_l(ka) + in_l(ka)}. \tag{3.30}$$

For arbitrary l we analyze two limiting cases using the asymptotic expressions (B.73) and (B.74) for $j_l(ka)$ and $n_l(ka)$.

- For the case $ka \ll 1$ the phase shift can be written as[3]

$$\tan \eta_l \underset{k\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}(ka)^{2l+1} \Longrightarrow \eta_l \underset{k\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}(ka)^{2l+1}. \tag{3.31}$$

- Similarly we find for $ka \gg 1$

$$\tan \eta_l \underset{k\to\infty}{\simeq} -\tan(ka - \tfrac{1}{2}l\pi) \Longrightarrow \eta_l \underset{k\to\infty}{\simeq} -ka + \tfrac{1}{2}l\pi. \tag{3.32}$$

Substituting Eq. (3.32) for the asymptotic phase shift into Eq. (3.14) for the asymptotic radial wave function we obtain

$$R_l(r) \underset{r\to\infty}{\sim} \frac{1}{r}\sin[k(r-a)]. \tag{3.33}$$

Note that this expression is independent of l; *i.e.*, all wavefunctions are shifted by the diameter of the hard spheres. This is only the case for hard sphere potentials.

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[2] Here we use the logarithmic representation of the arctangent with a real argument α,

$$\tan^{-1}\alpha = \frac{i}{2}\ln\frac{1-i\alpha}{1+i\alpha}.$$

[3] The double factorial is defined as $n!! = n(n-2)(n-4)\cdots$.

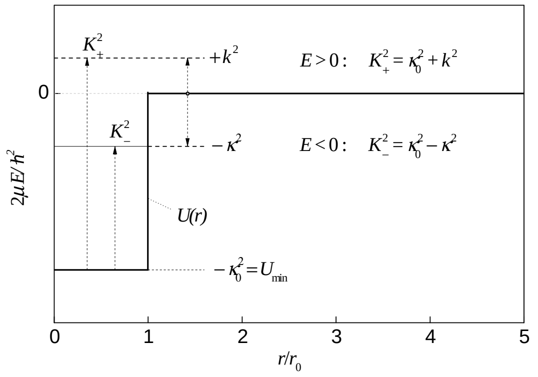

Figure 3.4: Plot of square well potential with related notation.

3.3.2 Hard-sphere potentials for the case $l = 0$

The case $l = 0$ is special because Eq. (3.33) for the radial wavefunction is valid for *all* values of k and not only asymptotically but for the *full* range of distances outside the sphere ($r \geq a$),

$$R_0(k,r) = \frac{C}{kr}\sin\left[k(r-a)\right]. \tag{3.34}$$

This follows directly from Eq. (3.27) with the aid of expression (B.72a) and the boundary condition $R_0(k,a) = 0$. Hence, the expression for the phase shift

$$\eta_0 = -ka \tag{3.35}$$

is exact for *any* value of k. Note that for $k \to 0$ the expression (3.34) behaves like

$$R_0(r) \underset{k\to 0}{\sim} \left(1 - \frac{a}{r}\right) \qquad (\text{for } 0 \leq r - a \ll 1/k). \tag{3.36}$$

This is an important result, showing that in the limit $k \to 0$ the wavefunction is essentially constant throughout space (up to a distance $1/k$), except for a small region of radius a around the potential center.

In preparation for comparison with the phase shift by other potentials and for the calculation of scattering amplitudes and collision cross sections (cf. Chapter 4) we rewrite Eq. (3.35) in the form of a series expansion of $k\cot\eta_0$ in powers of k^2,

$$k\cot\eta_0(k) = -\frac{1}{a} + \frac{1}{3}ak^2 + \frac{1}{45}a^3k^4 + \cdots. \tag{3.37}$$

This expansion is known as an *effective range expansion* of the phase shift. Note that whereas Eq. (3.35) is exact for *any* value of k this effective range expansion is only valid for $ka \ll 1$.

3.3.3 Spherical square wells

The second model potential to consider is the spherical square well with range r_0 as sketched in Fig. 3.4,

$$U(r) = \begin{cases} 2\mu E_{\rm min}/\hbar^2 = U_{\rm min} = -\kappa_0^2 & \text{for } r < r_0 \\ 0 & \text{for } r > r_0. \end{cases} \tag{3.38}$$

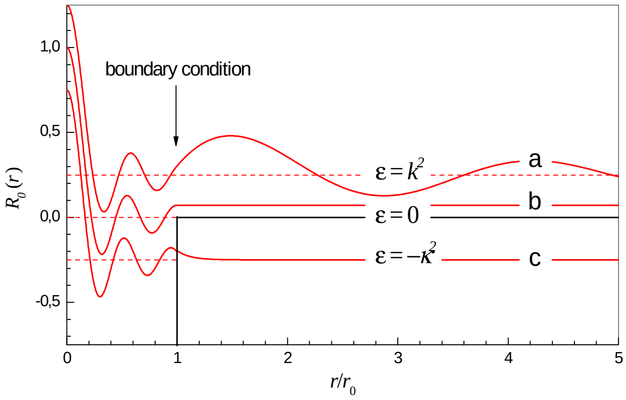

Figure 3.5: Radial wavefunctions for square wells: a.) continuum state ($\varepsilon = k^2 > 0$); b.) Zero energy state ($\varepsilon = k^2 = 0$) in the presence of an asymptotically bound level ($\varepsilon = -\kappa^2 = 0$); c.) bound state ($\varepsilon = -\kappa^2 < 0$). Note the continuity of $R_0(r)$ and $R_0'(r)$ at $r = r_0$.

Here $|U_{\min}| = \kappa_0^2$, corresponds to the *well depth*. The energy of the continuum states is given by $\varepsilon = k^2$. In analogy, the energy of the bound states is written as

$$\varepsilon_b = -\kappa^2. \tag{3.39}$$

With the spherical square well potential (3.38) the radial wave equation (3.6) takes the form

$$R_l'' + \frac{2}{r}R_l' + \left[(\varepsilon - U_{\min}) - \frac{l(l+1)}{r^2}\right] R_l = 0 \quad \text{for } r < r_0 \tag{3.40a}$$

$$R_l'' + \frac{2}{r}R_l' + \left[\varepsilon - \frac{l(l+1)}{r^2}\right] R_l = 0 \quad \text{for } r > r_0. \tag{3.40b}$$

Since the potential is constant inside the well ($r < r_0$) the wavefunction has to be free-particle like with the wave number given by $K_+ = [2\mu(E - E_{\min})]^{1/2}/\hbar = [\kappa_0^2 + k^2]^{1/2}$. As the wavefunction has to be regular in the origin, inside the well it is given by

$$R_l(r) = A j_l(K_+ r) \quad (\text{for } r < r_0), \tag{3.41}$$

where A is a normalization constant. This expression holds for $E > E_{\min}$ (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 wave vector $k = [2\mu E]^{1/2}/\hbar$. Thus, for $r \geq r_0$ the general solution for the radial wave functions of angular momentum l is given by the free atom expression (3.12),

$$R_l(k,r) = C[\cos\eta_l\, j_l(kr) + \sin\eta_l\, n_l(kr)] \quad (\text{for } r > r_0). \tag{3.42}$$

The full solution (see Fig. 3.5) is obtained by the *continuity condition* for $R_l(r)$ and $R_l'(r)$ at the boundary $r = r_0$. This is equivalent to continuity of the *logarithmic derivative* with respect to r

$$\frac{K_+ j_l'(K_+ r_0)}{j_l(K_+ r_0)} = k\frac{\cos\eta_l\, j_l'(kr_0) + \sin\eta_l\, n_l'(kr_0)}{\cos\eta_l\, j_l(kr_0) + \sin\eta_l\, n_l(kr_0)}. \tag{3.43}$$

This is an important result. It shows that the *asymptotic phase shift* η_l can take *any* value depending on the depth of the well.

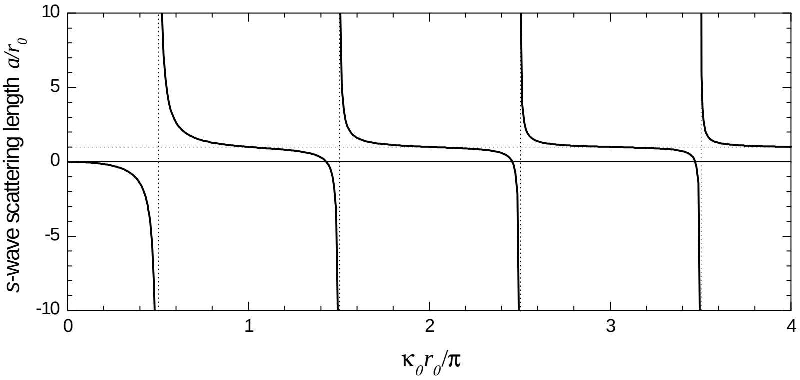

Figure 3.6: The s-wave scattering length a normalized on r_0 as a function of the depth of a square potential well. Note that, typically, $a \simeq r_0$, except near the resonances at $\kappa_0 r_0 = (n + \frac{1}{2})\pi$ with n being an integer.

3.3.4 Spherical square wells for the case $l = 0$ - scattering length

The analysis of square well potentials becomes particularly simple for the case $l = 0$. Let us first look at the case $E > 0$, where the radial wave equation can be written as a 1D-Schrödinger equation (3.8) of the form

$$\chi_0'' + [k^2 - U(r)]\chi_0 = 0. \tag{3.44}$$

The solution is

$$\chi_0(k,r) = \begin{cases} A\sin(K_+ r) & \text{for } r \le r_0 \\ C\sin(kr + \eta_0) & \text{for } r \ge r_0. \end{cases} \tag{3.45}$$

with the boundary condition of continuity of χ_0'/χ_0 at $r = r_0$ given by

$$k\cot(kr_0 + \eta_0) = K_+ \cot K_+ r_0. \tag{3.46}$$

Note that this expression coincides with the general result given by Eq. (3.43); *i.e.*, the boundary condition of continuity for χ_0'/χ_0 coincides with that for R_0'/R_0. As to be expected, for vanishing potential ($\kappa_0 \to 0$) we have $K_+ \cot K_+ r_0 \to k\cot kr_0$ and the boundary condition yields zero phase shift ($\eta_0 = 0$).

Introducing the *effective hard sphere diameter* a by the definition $\eta_0 \equiv -ka$; *i.e.*, in analogy with Eq. (3.35), the boundary condition becomes in the limit $k \to 0$, $K_+ = [\kappa_0^2 + k^2]^{1/2} \to \kappa_0$

$$\frac{1}{r_0 - a} = \kappa_0 \cot \kappa_0 r_0. \tag{3.47}$$

Eliminating a we obtain

$$a = r_0\left(1 - \frac{\tan \kappa_0 r_0}{\kappa_0 r_0}\right). \tag{3.48}$$

As shown in Fig. 3.6 the value of a can be positive, *negative* or zero depending on the depth κ_0^2. Therefore, the more general name *scattering length* is used for a. We identify the scattering length a as a new characteristic length, which expresses the strength of the interaction potential. It is typically of the same size as the range of the potential ($a \simeq r_0$) with the exception of very shallow potentials (where a vanishes) or near the *resonances* at $\kappa_0 r_0 = (n + \frac{1}{2})\pi$ with n being an integer. The scattering length is positive except for the narrow range of values where $\kappa_0 r_0 < \tan(\kappa_0 r_0)$. Note that this region becomes narrower with increasing well-depth. This is a property of the square well potential; in Section 3.3.15 we will see that this is not the case for Van der Waals potentials.

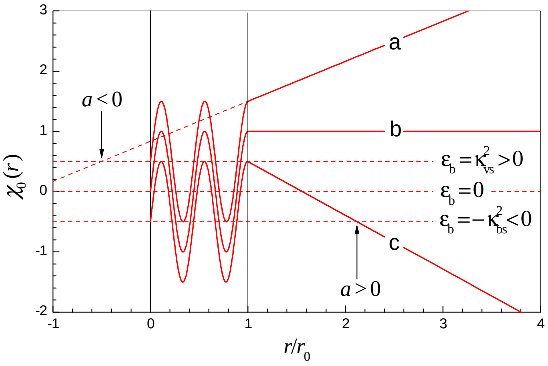

Figure 3.7: Radial wavefunctions $\chi_0(r) = rR_0(r)$ in the $k \downarrow 0$ limit for increasing well depth near the resonance value $\kappa_0 r_0 = (n+\frac{1}{2})\pi$ in the presence of: a.) an almost bound state ($\kappa = i\kappa_{vb}$); b.) resonantly bound state ($\kappa = 0$); c. bound state ($\kappa = \kappa_{bs}$). For $r > r_0$ the wavefunction is given by $\chi_0(r) = 1 - a/r$, hence the value of a is given by the intercept with the horizontal axis. Note that the curves are shifted relative to each other only for reasons of visibility.

For $r \geq r_0$ the radial wavefunction $R_0(r) = \chi_0(r)/r$ corresponding to (3.45) with $\eta_0 = -ka$ has the form

$$R_0(k,r) = \frac{C}{kr}\sin\left[k(r-a)\right] \tag{3.49}$$

and for $k \to 0$ this expression behaves like

$$R_0(r) \underset{k\to 0}{\sim} C\left(1 - \frac{a}{r}\right) \quad \text{for } r \geq r_0. \tag{3.50}$$

These expressions coincide indeed with the hard sphere results (3.34) and (3.36). However, in the present case they are valid for distances $r \geq r_0$ and a may be both positive and negative.

3.3.5 Spherical square wells for the case $l = 0$ - bound states

Turning to the case $E < 0$ we will show that the scattering resonances coincide with the appearance of new bound s levels in the well. The 1D Schrödinger equation takes the form

$$\chi_0'' + \left[-\kappa^2 - U(r)\right]\chi_0 = 0. \tag{3.51}$$

The solutions are of the type

$$\chi_0(\kappa,r) = \begin{cases} C\sin\left(K_- r\right) & \text{for } \ r \leq r_0 \\ Ae^{-\kappa r} & \text{for } \ r \geq r_0. \end{cases} \tag{3.52}$$

The corresponding asymptotic radial wavefunction is

$$R_0(r) = Ae^{-\kappa r}/r \quad (\text{for } r > r_0), \tag{3.53}$$

where $\kappa > 0$ and A is a normalization constant (see Fig. 3.7). The boundary condition connecting the inner part of the wavefunction to the outer part is given again by the continuity of the logarithmic derivative χ_0'/χ_0 at $r = r_0$,

$$-\kappa = K_- \cot K_- r_0, \tag{3.54}$$

where $K_- = [2\mu(E - E_{\min})]^{1/2}/\hbar = [\kappa_0^2 - \kappa^2]^{1/2}$. The appearance of a new bound state corresponds to $\kappa \to 0$, $K_- \to \kappa_0$. For this case Eq. (3.54) reduces to $\kappa_0 \cot \kappa_0 r_0 = 0$ and new bound states are seen to appear for $\kappa_0 r_0 = (n+\frac{1}{2})\pi$, as mentioned above.

Weakly bound s level - halo states

For a weakly bound s level ($\kappa \to 0$) we may approximate $-\kappa = K_{-} \cot K_{-} r_0 \simeq \kappa_0 \cot \kappa_0 r_0$ and substituting this relation into Eq. (3.48) we obtain

$$a = r_0 \left[1 - (1/\kappa_0 r_0) \tan(\kappa_0 r_0)\right] \simeq 1/\kappa \qquad (0 < \kappa r_0 \ll 1). \tag{3.55}$$

We note that in the presence of a weakly bound s-level the scattering length is *large and positive,* $a \gg r_0$. The relation (3.55) may be rewritten with Eq. (3.39) as a convenient relation between the binding energy of the most weakly bound state and the scattering length

$$E_b = -\frac{\hbar^2 \kappa^2}{2\mu} \underset{\kappa \to 0}{\simeq} -\frac{\hbar^2}{2\mu a^2}. \tag{3.56}$$

In Section 3.3.11 this relation is shown to hold for arbitrary short-range potentials. The weakly-bound state is referred to as a *halo state* because for $\kappa r_0 \ll 1$ most of the probability of the bound state is found *outside* the potential well, thus surrounding the scattering center like a halo.

3.3.6 Spherical square wells for the case $l = 0$ - effective range

To obtain the energy dependence of the phase shift we rewrite the boundary condition (3.46) in the form

$$\eta_0 = \eta_{bg} + \eta_{\mathrm{res}} = -kr_0 + \tan^{-1}\left(\frac{kr_0}{K_{+} r_0 \cot K_{+} r_0}\right), \tag{3.57}$$

where $\eta_{bg} = -kr_0$ is called the *background* contribution and $\eta_{\mathrm{res}} = \tan^{-1}\left[kr_0/\left(K_{+} r_0 \cot K_{+} r_0\right)\right]$ the *resonance* contribution to the phase shift. The background contribution give rise to the same linear phase development as obtained for hard spheres. For wells with many bound levels ($\kappa_0 r_0 \gg 1$) the resonance contribution is small for most values of k because $K_{+} r_0 = [\kappa_0^2 + k^2]^{1/2} r_0 > \kappa_0 r_0 \gg 1$. However, for $\cot K_{+} r_0$ crossing through zero; *i.e.,* around $K_{+} r_0 = (n + \frac{1}{2})\pi \equiv K_{\mathrm{res}} r_0$ (with $n = 0, 1, 2, \cdots$), the phase shifts over π, with $\eta_{\mathrm{res}} = \pi/2$ at the center of the resonance.

The leading energy dependence of the phase shift is obtained by applying the angle-addition formula to the tangent of the r.h.s. of Eq. (3.57). Expanding $\tan kr_0$ in (odd) powers of k, we find for $kr_0 \cot \eta_0$ an expression containing only even powers of k,

$$kr_0 \cot \eta_0 = \frac{K_{+} r_0 \cot K_{+} r_0 + k^2 r_0^2 + \cdots}{1 - \left(1 + \frac{1}{3} k^2 r_0^2 + \cdots\right) K_{+} r_0 \cot K_{+} r_0}, \tag{3.58}$$

Since $K_{+} r_0 = [\kappa_0^2 + k^2]^{1/2} r_0 \simeq \kappa_0 r_0 + \frac{1}{2} k^2 r_0^2/\kappa_0 r_0$, for $k \ll \kappa_0$ we can expand $K_{+} r_0 \cot K_{+} r_0$ in to leading order in k^2 using the angle-addition formula for the cotangent,

$$K_{+} r_0 \cot K_{+} r_0 = \gamma \cot \gamma - \tfrac{1}{2} k^2 r_0^2 \left[1 + (1 - \tan\gamma/\gamma) \cot^2 \gamma\right] + \cdots. \tag{3.59}$$

Here we introduced the dimensionless well parameter $\gamma \equiv \kappa_0 r_0$. Substituting Eq. (3.59) into Eq. (3.58) and retaining again only the terms to leading order in k^2 we arrive after some calculus at an expansion in even powers of k

$$kr_0 \cot \eta_0 = -\frac{1}{1 - \tan\gamma/\gamma} + \tfrac{1}{2} k^2 r_0^2 \left(1 - \frac{3\,(1 - \tan\gamma/\gamma) + \gamma^2}{3\gamma^2\,(1 - \tan\gamma/\gamma)^2}\right) + \cdots. \tag{3.60}$$

In the limit $k \to 0$ we regain the expression (3.48) for the scattering length: $a = r_0\,(1 - \tan\gamma/\gamma)$. Divided by r_0, the expansion is called the *effective range expansion*,

$$k \cot \eta_0 = -\frac{1}{a} + \tfrac{1}{2} k^2 r_e + \cdots. \tag{3.61}$$

where

$$r_e = r_0 \left(1 - \frac{3ar_0 + \gamma^2 r_0^2}{3\gamma^2 a^2}\right) \tag{3.62}$$

is called the *effective range*.

Note that the effective-range expansion breaks down for $1 - \tan\gamma/\gamma = 0$, *i.e.*, for vanishing scattering length ($a = 0$). For $|a| \ll r_0$ this break down emerges as a divergence of the effective range,

$$r_e \simeq \begin{cases} -\frac{1}{3} r_0 \left(r_0/a\right)^2 & (a \to 0 \text{ and } \gamma > 0) \\ r_0 \left(r_0/a\right) & (\gamma \to 0) \end{cases} . \tag{3.63}$$

To find the energy dependence of the phase shift for this case, we recall the relation $\kappa_0 \cot \kappa_0 r_0 = 1/(r_0 - a)$. Hence, for $a = 0$ Eq. (3.59) reduces to $K_+ r_0 \cot K_+ r_0 = 1 - \frac{1}{2}k^2 r_0^2 + \cdots$, the phase shift is given by $\eta_0 \simeq -kr_0 + \tan^{-1}\left[kr_0/(1 - \frac{1}{2}k^2 r_0^2)\right] \simeq \frac{5}{6}k^3 r_0^3$ and the leading term in the expansion of $k \cot \eta_0$ becomes

$$k \cot \eta_0 = \frac{6/5}{k^2 r_0^3} + \cdots \qquad (a = 0)\,. \tag{3.64}$$

Another case of interest is the case $a = r_0$. For this special case we find with the aid of Eq. (3.62)

$$r_e = r_0 \left(2/3 - 1/\gamma^2\right) \simeq \tfrac{2}{3} r_0. \tag{3.65}$$

Hence, for $\gamma \to \infty$ this result coincides with that of the hard sphere, $r_e = \frac{2}{3} r_0$. Since $\gamma \geq \pi$ for all instances of $a = r_0$, the hard-sphere expression is found to provide an excellent approximation for essentially all instances.

3.3.7 Spherical square wells for the case $l = 0$ - scattering resonances

It is instructive to write Eq. (3.61) in the form of an effective (k-dependent) scattering length,

$$a(k) \equiv -\frac{1}{k \cot \eta_0} = \frac{a(0)}{1 - \frac{1}{2}k^2 r_e a(0)}. \tag{3.66}$$

Hence, the k^2 term becomes important for $k^2 \gtrsim 1/|ar_e|$. The effective range r_e represents a new characteristic length providing information on the range of k values for which the scattering length approximation is valid; *i.e.*, for which $a(k) \simeq a(0)$. In view of its importance in the context of quantum gases we elaborate a bit on Eq. (3.66). We exclude for simplicity shallow potential wells, presuming $\kappa_0 r_0 \gg 1$. First we consider the case of a typical, not resonantly-enhanced scattering length $a = 2r_0$ and calculate with Eq. (**??**) $r_e \simeq r_0$. For the special case $a = r_0$ we found $r_e \simeq \frac{2}{3} r_0$. Hence, in such cases the k^2 term becomes important only for $kr_0 \gtrsim 1$, showing that in ordinary quantum gases, where $kr_0 \ll 1$, the effective range term may be neglected. However, this conclusion is only valid as long as $|a|$ is not too large. For $a \gg r_0$ the effective range expression yields $r_e \simeq r_0$ and the k^2 term is important for $kr_0 \gtrsim (r_0/a)^{1/2}$; *i.e.*, in the limit $|a| \to \infty$ even for the lowest values of k.

Example: resonant enhancement by a weakly-bound s level

Resonant enhancement of the scattering length is further explored in two examples. Here we investigate as a first example a potential well ($\kappa_0 r_0 \gg 1$) with n bound levels with binding energies $\varepsilon = -\kappa_n^2$ of which the last one, $\kappa_n = \kappa$, is a weakly-bound s level ($\kappa r_0 \ll 1$). Hence, in view of Eq. (3.55), the scattering length is large and positive, $a = 1/\kappa$. Substituting this value into Eq. (3.66) we obtain

$$a(k) \equiv -\frac{1}{k \cot \eta_0} = \frac{1}{\kappa - \frac{1}{2}k^2 r_e}. \tag{3.67}$$

In this case the scattering length is said to be resonantly enhanced by the presence of a weakly-bound s level A compact expression for the phase shift is obtained starting from Eq. (3.57). Since $K_- \simeq \kappa_0 \simeq K_+$ we can use the boundary condition (3.54) of the bound state, $-\kappa = K_- \cot K_- r_0$, to evaluate Eq. (3.57). Simply replacing K_+ by K_- we immediately obtain

$$\eta_0 \simeq -kr_0 - \tan^{-1}\frac{k}{\kappa}, \tag{3.68}$$

or, in complex notation

$$e^{2i\eta_0} = e^{-2ikr_0}\frac{k+i\kappa}{k-i\kappa}. \tag{3.69}$$

Eq. (3.68) represents the leading terms in the expansion in powers of k (cf. Problem 3.2). The phase shift appears as the sum of two contributions,

$$\eta_0 \simeq -k[r_0 + a_{\mathrm{res}}(k)], \tag{3.70}$$

where r_0 is the *background* contribution and $a_{\mathrm{res}}(k) = (1/k)\tan^{-1}(k/\kappa) \simeq 1/\kappa$ (for $k^2 \ll \kappa/r_0$) the *resonance* contribution to the scattering length. Eq. (3.67) shows that the presence (or absence) of the resonance can be established by measuring the k-dependence of $a(k)$ and to obtain $a = 1/\kappa$ and r_e with a fitting procedure. In practice this is done by studying elastic scattering (cf. Chapter 4). The most famous example of a system with a weakly-bound s level is the *deuteron*, the weakly-bound state of a proton and a neutron with parallel spin. When scattering slow neutrons from protons (with parallel spin) the scattering length increases with decreasing energy in accordance with Eq. (3.67). The fitting procedure yields $a = 5.41 \times 10^{-15}$ m and $r_e = 1.75 \times 10^{-15}$ m ($\kappa r_e = 0.31$).[4] Among the quantum gases the famous example of a system with a weakly-bound s level is doubly spin-polarized ^{133}Cs, where $a \approx 2400\, a_0$ and $r_0 \approx 101\, a_0$ ($\kappa r_0 \approx 0.042$).[5]

Example: resonant enhancement by a virtual s level

Interestingly, Eq. (3.66) is also valid for large *negative* scattering lengths. Therefore, we consider in this second example the presence of an 'almost-bound state', $a = -1/\kappa_{vs}$. Such states are called *virtual bound states* and in this case Eq. (3.66) can be written in the form

$$a(k) \equiv -\frac{1}{k\cot\eta_0} = \frac{1}{-\kappa_{vs} - \frac{1}{2}k^2 r_e}. \tag{3.71}$$

The phase shift can be written as

$$\eta_0 \simeq -kr_0 + \tan^{-1}\frac{k}{\kappa_{vs}}, \tag{3.72}$$

or, in complex notation

$$e^{2i\eta_0} = e^{-2ikr_0}\frac{k-i\kappa_{vs}}{k+i\kappa_{vs}}. \tag{3.73}$$

Eq. (3.72) may be derived along the same lines as Eq. (3.68) by using for the virtual bound state the boundary condition $\kappa_{vs} = K_- \cot K_- r_0$. A virtual bound state is observed in low-energy collisions between a neutron and a proton with opposite spins, $a = -2.38 \times 10^{-14}$ m and $r_e = 2.67 \times 10^{-15}$ m ($-\kappa_{vs} r_e = 0.11$).[6] An example of a virtual bound state in the quantum gases is doubly-polarized ^{85}Rb, where $a \approx -369\, a_0$ and $r_0 \approx 83\, a_0$ ($-\kappa_{vs} r_0 \approx 0.22$).[7]

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[4] N.F. Mott and H.S.W. Massey, *The theory of atomic collisions,* Clarendon Press, Oxford 1965.

[5] M. Arndt, M. Ben Dahan, D. Guéry-Odelin, M.W. Reynolds, and J. Dalibard, Phys. Rev. Let., **79**, 625 (1997); P.J. Leo, C.J. Williams, and P.S. Julienne, Phys. Rev. Let. **85**, 2721 (2000).

[6] N.F. Mott and H.S.W. Massey, *loc. cit.*.

[7] J.L. Roberts, N.R. Claussen, J.P. Burke, C.H. Greene, E.A. Cornell, and C.E. Wieman, Phys. Rev. Lett. **81**, 5109 (1998).

Problem 3.2 *Show that in the presence of a weakly-bound s level and for $kr_0 \ll 1$ the following expansion holds for a not shallow ($K_- r_0 > 1$) square well potential*

$$\frac{k}{K_+ \cot K_+ r_0} = -k a_{\text{res}} + \mathcal{O}(k^3).$$

Solution: In wavenumber notation the bound state is represented by $K_- = [\kappa_0^2 - \kappa^2]^{1/2}$. Since $K_- \simeq \kappa_0 \simeq K_+$ we can use the boundary condition (3.54) of the bound state, $-\kappa = K_- \cot K_- r_0$, to evaluate Eq. (3.57). Simply replacing K_+ by K_- we immediately obtain Eq. (3.68). Higher order terms are obtained by expanding $K_+ = [\kappa_0^2 - \kappa^2 + k^2 + \kappa^2]^{1/2} = K_-[1 + \left(k^2 + \kappa^2\right)/K_-^2]^{1/2}$ in powers of $\left(k^2 + \kappa^2\right)/K_-^2$ we obtain to first order $K_+ r_0 \simeq K_- r_0 + (k^2 + \kappa^2) r_0 / 2K_-$. As the cotangent appears in the denominator of Eq. (3.57) we have

$$\frac{k}{K_+ \cot K_+ r_0} \simeq k \frac{[1 - \left(k^2 + \kappa^2\right)/2K_-^2]}{K_-} \frac{\tan K_- r_0 + \tan[(k^2 + \kappa^2) r_0 / 2K_-]}{1 - \tan K_- r_0 \tan[(k^2 + \kappa^2) r_0 / 2K_-]}.$$

Using the boundary condition (3.54) and expanding the tangents we obtain

$$\frac{k}{K_+ \cot K_+ r_0} \simeq k[1 - \left(k^2 + \kappa^2\right)/2K_-^2] \frac{-1/\kappa + (k^2 + \kappa^2) r_0 / 2K_-^2}{1 + (k^2 + \kappa^2) r_0 / 2\kappa}.$$

Retaining only the terms of order $-k/\kappa$ in the numerator and expanding the denominator we obtain

$$\frac{k}{K_+ \cot K_+ r_0} \simeq -\frac{k}{\kappa} \left[1 - \kappa r_0/2 - k r_0 \left(k r_0/2\right)\right] = -k a_{\text{res}} + \mathcal{O}(k^3),$$

where $a_{\text{res}} \simeq (1 - \kappa r_0/2)/\kappa \simeq 1/\kappa$. ▶

The Breit-Wigner formula

We can expand $K_+ \cot K_+ r_0$ around the points of zero crossing. Writing $K_+ = [\kappa_0^2 + (k_{\text{res}} + \delta k)^2]^{1/2}$, where $\delta k = k - k_{\text{res}}$, we have for $|\delta k| k_{\text{res}} \ll K_{\text{res}}^2 \equiv \kappa_0^2 + k_{\text{res}}^2$

$$K_+ \simeq [\kappa_0^2 + k_{\text{res}}^2 + 2\delta k\, k_{\text{res}}]^{1/2} \simeq K_{\text{res}} + \delta k\, k_{\text{res}}/K_{\text{res}}. \tag{3.74}$$

Hence, close to the zero crossings $\left(|\delta k| k_{\text{res}} \ll K_{\text{res}}^2\right)$ we may approximate $K_+ \simeq K_{\text{res}}$ and obtain

$$\frac{k}{K_+ \cot K_+ r_0} \simeq -\frac{1}{\delta k\, r_0} \simeq \frac{-\left(k + k_{\text{res}}\right)}{(k^2 - k_{\text{res}}^2) r_0}. \tag{3.75}$$

Using this expression the resonant phase shift can be written as a function of the collision energy $E = \hbar^2 k^2 / 2\mu$

$$\tan \eta_{\text{res}} = \frac{-\Gamma/2}{E - E_{\text{res}}}, \tag{3.76}$$

where $\Gamma(k) = \hbar^2 \left(k + k_{\text{res}}\right)/\mu r_0$ is called the *width* and $E_{\text{res}} = \hbar^2 k_{\text{res}}^2 / 2\mu$ the *position* of the resonance. Knowing the tangent we readily obtain the sine and Eq. (3.76 can be reexpressed in the form of the *Breit-Wigner distribution*

$$\sin^2 \eta_{\text{res}} = \frac{(\Gamma/2)^2}{(E - E_{\text{res}})^2 + (\Gamma/2)^2}. \tag{3.77}$$

For optical resonances this from is known as the *Lorentz lineshape.* Note that Γ corresponds to the full-width-at-half-maximum (FWHM) of this line shape.

Narrow versus wide resonances

Eq.(3.76) shows that the resonant phase shift changes only substantially for energies in the range $|E-E_{\mathrm{res}}| \lesssim \Gamma/2$. If $\Gamma/2 \ll E_{\mathrm{res}}$ the resonance is called *narrow* because it only contributes in a narrow band of energies to the phase shift. In this case we may approximate $k \simeq k_{\mathrm{res}}$ and the resonance width is to good approximation energy independent. For $\Gamma(k)/2 \gtrsim E_{\mathrm{res}}$ the resonance is called *wide* because it contributes for any collision energy in the range $0 \leq E \lesssim 2E_{\mathrm{res}}$ to the phase shift. Adopting this convention the s-wave resonances of the spherical square well (when located within the s-wave band of energies, $k_{\mathrm{res}}r_0 \lesssim 1$) are of the broad type, $\Gamma(k) > \hbar^2 k_{\mathrm{res}}/\mu r_0 = 2(k_{\mathrm{res}}r_0)^{-1}\hbar^2 k_{\mathrm{res}}^2/2\mu > E_{\mathrm{res}}$.

3.3.8 Spherical square wells for the case $l = 0$ - zero range limit

An important model potential is obtained by considering a spherical square well in the zero-range limit $r_0 \to 0$. For $E > 0$ and given value of r_0 the boundary condition is given for $k \to 0$ by Eq. (3.47), which we write in the form

$$\frac{1}{K_+}\frac{1}{r_0 - a} = \cot K_+ r_0. \tag{3.78}$$

Reducing the radius r_0 the same scattering length can be obtained by adapting the well depth κ_0^2. In the limit $r_0 \to 0$ the well depth should diverge in accordance with

$$K_+ = \sqrt{\kappa_0^2 + k^2} = (n + \frac{1}{2})\frac{\pi}{r_0}. \tag{3.79}$$

With this choice $\cot K_+ r_0 = 0$ and also the l.h.s. of Eq. (3.78) is zero because $K_+ \to \infty$ for $r_0 \to 0$. In the zero-range limit the radial wavefunction for $k \to 0$ is given by

$$R_0(k,r) = \frac{C}{kr}\sin[k(r-a)] \quad (\text{for } r > 0), \tag{3.80}$$

which implies $R_0(k,r) \simeq 1 - a/r$ for $0 < r \ll 1/k$.

Similarly, for $E < 0$ we see from the boundary condition (3.54) that bound states are obtained whenever

$$-\frac{\kappa}{K_-} = \cot K_- r_0. \tag{3.81}$$

Reducing the radius r_0 the same binding energy can be obtained by adapting the well depth κ_0^2. In the limit $r_0 \to 0$ the well depth should diverge in accordance with

$$K_- = \sqrt{\kappa_0^2 - \kappa^2} = (n + \frac{1}{2})\frac{\pi}{r_0}. \tag{3.82}$$

With this choice $\cot K_- r_0 = 0$ and also the l.h.s. of Eq. (3.81) is zero because $K_- \to \infty$ for $r_0 \to 0$. In the zero size limit the bound-state wavefunction is given by

$$R_0(r) = Ae^{-\kappa r}/r \quad (\text{for } r > 0) \tag{3.83}$$

and unit normalization, $\int 4\pi r^2 R_0^2(r)dr = 1$, is obtained for $A = \sqrt{\kappa/2\pi}$.

Bethe-Peierls boundary condition

Note that Eq. (3.83) is the solution for $E < 0$ of the 1D-Schrödinger equation in the zero-range approximation

$$\chi_0'' - \kappa^2\chi_0 = 0 \quad (r > 0), \tag{3.84}$$

under the boundary condition

$$\chi_0'/\chi_0|_{r\to 0} = -\kappa. \tag{3.85}$$

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*.[8] It shows that for weakly-bound states the wavefunction has the *universal form* of a *halo state*, which only depends on the binding energy, $\varepsilon_b = -\kappa^2$.

For $E > 0$ the 1D-Schrödinger equation in the zero-range approximation is given by

$$\chi_0'' + k^2\chi_0 = 0 \quad (r > 0). \tag{3.86}$$

The general solution is $\chi_0(k,r) = C\sin[kr + \eta_0]$. Using the Bethe-Peierls boundary condition we obtain

$$k\cot\eta_0(k) = -\kappa, \tag{3.87}$$

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 level, $\varepsilon_b = -\kappa^2 = -1/a^2$.

3.3.9 Arbitrary short-range potentials

The results obtained above for rectangular potentials 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. Heuristically, an interaction potential may be neglected for distances $r \gg r_0$ when the kinetic energy of confinement within a volume of radius r (*i.e.* the zero-point energy $\sim \hbar^2/\mu r^2$) dominates over the potential energy $|\mathcal{V}(r)|$ outside the sphere. Estimating r_0 as the distance where the two contributions are equal,

$$|\mathcal{V}(r_0)| = \hbar^2/\mu r_0^2, \tag{3.88}$$

it is obvious that $\mathcal{V}(r)$ has to fall off faster than $1/r^2$ to be negligible at long distance. More careful analysis shows 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. Section 3.3.13). Inversely, for given power s the finite range *only exists for low angular momentum values*, *e.g.* for the Van der Waals interaction ($s = 6$) it only applies for s-wave and p-wave collisions.

For short-range potentials and distances $r \gg r_0$ the radial wave equation (3.6) reduces to the spherical Bessel differential equation

$$R_l'' + \frac{2}{r}R_l' + \left[k^2 - \frac{l(l+1)}{r^2}\right]R_l = 0. \tag{3.89}$$

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. (3.12),

$$R_l(k,r) = C[\cos\eta_l\, j_l(kr) + \sin\eta_l\, n_l(kr)]. \tag{3.90}$$

For any finite value of k this expression has the asymptotic form

$$R_l(r) \underset{r\to\infty}{\sim} \frac{1}{r}\sin(kr + \eta_l - \frac{1}{2}l\pi), \tag{3.91}$$

thus regaining the appearance of a phase shift like in the previous sections.

For $kr \ll 1$ equation (3.90) reduces with Eq. (B.74) to

$$R_l(kr) \underset{kr\to 0}{\simeq} A\frac{(kr)^l}{(2l+1)!!} + B\frac{(2l+1)!!}{2l+1}\left(\frac{1}{kr}\right)^{l+1}. \tag{3.92}$$

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[8] H. Bethe and R. Peierls, Proc. Roy. Soc. A **148**, 146 (1935).

To determine the coefficients $A = C\cos\eta_l$ and $B = C\sin\eta_l$ 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 reduces in this case to

$$R_l'' + \frac{2}{r}R_l' = \frac{l(l+1)}{r^2}R_l. \tag{3.93}$$

The general solution of this equation is

$$R_l(r) = c_{1l}\, r^l + c_{2l}/r^{l+1}. \tag{3.94}$$

Comparing Eqs. (3.92) and (3.94) we find

$$A = C\cos\eta_l \underset{kr\to 0}{\simeq} c_{1l}(2l+1)!!k^{-l}; \quad B = C\sin\eta_l \underset{kr\to 0}{\simeq} c_{2l}\frac{2l+1}{(2l+1)!!}k^{l+1}.$$

Writing $a_l^{2l+1} = -c_{2l}/c_{1l}$ we find

$$\tan\eta_l \underset{kr\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}\,(ka_l)^{2l+1}. \tag{3.95}$$

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. (3.95) we have regained the form of Eq. (3.31). This is not surprising because a hard sphere potential is of course a short-range potential. By comparing Eqs. (3.95) and (3.31) we see that for hard spheres all scattering lengths are equal to the diameter of the sphere, $a_l = a$. Eq. (3.95) also holds for other short-range potentials like the spherical square well and for potentials exponentially decaying with increasing interatomic distance.

In particular, for the s-wave phase shift ($l = 0$) we find with Eq. (3.95)

$$\tan\eta_0 \underset{k\to 0}{\simeq} -ka \;\Leftrightarrow\; k\cot\eta_0 \underset{k\to 0}{\simeq} -\frac{1}{a}, \tag{3.96}$$

and since $\tan\eta_0 \to \eta_0$ for $k \to 0$ this result coincides with the hard-sphere result (3.35), $\eta_0 = -ka$. For any finite value of k the radial wavefunction (3.91) has the asymptotic form

$$R_0(r) \underset{r\to\infty}{\sim} \frac{1}{r}\sin(kr+\eta_0) \simeq \frac{1}{r}\sin\left[k(r-a)\right]. \tag{3.97}$$

As follows from Eq. (3.94), for the range of distances $r_0 \ll r \ll 1/k$ the radial wavefunction takes the form

$$R_0(r) \underset{k\to 0}{\simeq} C\left(1-\frac{a}{r}\right) \qquad (\text{for } r_0 \ll r \ll 1/k). \tag{3.98}$$

This is a very important result. Exactly as in the case of hard spheres or spherical square-well potentials the wavefunction of an arbitrary 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 the p-wave phase shift ($l = 1$) we find in the limit $k \to 0$

$$\tan\eta_1 \underset{k\to 0}{\simeq} -\frac{1}{3}\,(ka_1)^3 \Leftrightarrow k\cot\eta_1 \underset{k\to 0}{\simeq} -\frac{3}{a_1^3k^2}. \tag{3.99}$$

3.3.10 Energy dependence of the s-wave phase shift - effective range

In the previous section we restricted ourselves to the $k \to 0$ limit by using Eq. (3.93) to put a boundary condition on the general solution (3.90) 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,

$$\chi_0'' + [k^2 - U(r)]\chi_0 = 0 \quad \text{and} \quad y_0'' + k^2 y_0 = 0. \tag{3.100}$$

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 ($C = 1$) we turn to the normalization $C = 1/\sin\eta_0(k)$,

$$y_0(k,r) = \cot\eta_0(k)\sin(kr) + \cos(kr) \underset{r\gg r_0}{\simeq} \chi_0(k,r). \tag{3.101}$$

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 $y_0(k_2,r)$,

$$W[y_0(k_1,r), y_0(k_2,r)]\,|_{r=0} = k_2\cot\eta_0(k_2) - k_1\cot\eta_0(k_1).$$

Then we specialize to the case $k_1 = k$ and obtain using Eq. (3.96) in the limit $k_2 \to 0$

$$W[y_0(k_1,r), y_0(k_2,r)]\,|_{r=0} \simeq -1/a - k\cot\eta_0(k). \tag{3.102}$$

To employ this Wronskian we apply the Wronskian Theorem twice in the form (B.103) with $k_1 = k$ and $k_2 = 0$,

$$W[y_0(k,r), y_0(0,r)]\,|_0^b = k^2\textstyle\int_0^b y_0(k,r)y_0(0,r)dr \tag{3.103}$$

$$W[\chi_0(k,r), \chi_0(0,r)]\,|_0^b = k^2\textstyle\int_0^b \chi_0(k,r)\chi_0(0,r)dr. \tag{3.104}$$

Since $\chi_0(k,0) = 0$ we have $W[\chi_0(k_1,r), \chi_0(k_2,r)]\,|_{r=0} = 0$. Further, 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. (3.104) from Eq. (3.103) we obtain the Bethe formula[9]

$$1/a + k\cot\eta_0(k) = k^2\textstyle\int_0^b [y_0(k,r)y_0(0,r) - \chi_0(k,r)\chi_0(0,r)]\,dr \equiv \frac{1}{2}r_e(k)k^2. \tag{3.105}$$

In view of Eq. (3.101) 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 known as *the effective range* of the interaction. Replacing $r_e(k)$ by its $k \to 0$ limit,

$$r_e = 2\textstyle\int_0^\infty \left[y_0^2(0,r) - \chi_0^2(0,r)\right]dr, \tag{3.106}$$

where $y_0(0,r) = 1 - r/a$, and the phase shift may be expressed as

$$k\cot\eta_0(k) \underset{k\to 0}{=} -\frac{1}{a} + \frac{1}{2}r_e k^2 + \cdots . \tag{3.107}$$

Comparing the first two terms in Eq. (3.107) we find that the $k \to 0$ limit is reached for

$$k^2 a r_e \ll 1. \tag{3.108}$$

Comparing Eq. (3.107) with the effective range expansion (3.37) for hard spheres we find $r_e = 2a/3$. Thus we see that for hard spheres $r_0 \equiv a \simeq r_e$. This close proximity of the characteristic lengths r_0, a and r_e is a coincidence. A counter example 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*.[10] In this case r_0 is not well-defined because of the

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[9] H.A. Bethe, Phys. Rev. **76**, 38 (1949).

[10] M. J. Jamieson, A. Dalgarno and M. Kimura, Phys. Rev. A **51**, 2626 (1995).

importance of the exchange interaction.

It is good to remember that the range r_0, the scattering length a and the effective range r_e express quite different aspects of the interaction potential within the context of low energy collisions. The range is the distance beyond which the potential may be neglected, the scattering length expresses how the potential affects the phase shift in the $k \to 0$ limit and the effective range expresses how the potential affects the energy dependence of the phase shift at low but finite energy.

Problem 3.3 *Show that the effective range of a spherical square well of depth* $-\kappa_0^2$ *and radius* r_0 *is given by*

$$r_e = 2r_0 \left[1 - \frac{r_0}{a} + \frac{1}{3}\left(\frac{r_0}{a}\right)^2 + \frac{1}{2}\left(\frac{\cot \kappa_0 r_0}{\kappa_0 r_0} - \frac{1}{\sin^2 \kappa_0 r_0}\right)\left(1 - \frac{r_0}{a}\right)^2 \right]. \tag{3.109}$$

Note that this equation can be rewritten in the form (3.62).

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. (3.106) 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 in Eq. (3.109), which coincides exactly with Eq. (**??**). ▶

3.3.11 Phase shifts in the presence of a weakly-bound s state (s-wave resonance)

The analysis of the previous section can be refined in the presence of a weakly-bound s level with binding energy $E_b = -\hbar^2\kappa^2/2\mu$. In this case four 1D Schrödinger equations are relevant to calculate the phase shift:

$$\begin{array}{ll} \chi_0'' + [k^2 - U(r)]\chi_0 = 0 & \qquad y_0'' + k^2 y_0 = 0 \\ B_0'' - [\kappa^2 + U(r)]B_0 = 0 & \qquad B_a'' - \kappa^2 B_a = 0. \end{array}$$

The first two equations are the same as the ones in the previous section and yield the continuum solutions (3.101). The second couple of equations deal with the bound state. Like the continuum solutions they can be made to overlap asymptotically, $B_a(r) = e^{-\kappa r} \underset{r \gg r_0}{\simeq} B_0(r)$. Hence, we have

$$\begin{array}{ll} B_a(0) = 1 & \qquad B_a'(0) = -\kappa \\ y_0(k,0) = 1 & \qquad y_0'(k,0) = k \cot \eta_0(k). \end{array}$$

As in the previous section we apply the Wronskian Theorem in the form (B.103) to the cases with and without potential.

$$W[B_0(r), \chi_0(k,r)]\,|_0^b = -\left(\kappa^2 + k^2\right)\int_0^b B_0(r)\chi_0(k,r)dr$$

$$W[B_a(r), y_0(k,r)]\,|_0^b = -\left(\kappa^2 + k^2\right)\int_0^b B_a(r)y_0(k,r)dr.$$

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

$$W[B_a(r), y_0(k,r)]\,|_{r=0} = \left(\kappa^2 + k^2\right)\int_0^b [B_a(r)y_0(k,r) - B_0(r)\chi_0(k,r)]\,dr.$$

With $W[B_a(r), y_0(k,r)]\,|_{r=0} = k\cot \eta_0(k) + \kappa$ we obtain in the limit $k \to 0$

$$k \cot \eta_0(k) \simeq -\kappa + \frac{1}{2}\left(\kappa^2 + k^2\right) r_e, \tag{3.110}$$

where

$$r_e = 2\int_0^b \left[B_a(r)y_0(0,r) - B_0(r)\chi_0(0,r)\right] dr \tag{3.111}$$

is the effective range for this case. Comparing Eq. (3.110) with Eq. (3.107) we find that the scattering length can be written as

$$-\frac{1}{a} = -\kappa + \frac{1}{2}\kappa^2 r_e \Leftrightarrow \kappa = \frac{1}{a}\frac{1}{1-\kappa r_e/2}. \tag{3.112}$$

For the special case $\kappa r_e \ll 1$; *i.e.*, for very weakly-bound s levels, the scattering length has the *positive* value $a \simeq 1/\kappa \gg r_e$ and the binding energy can be expressed in terms of the scattering length and the effective range as

$$E_b \simeq -\frac{\hbar^2}{2\mu}\frac{1}{(a-r_e/2)^2} \simeq -\frac{\hbar^2}{2\mu a^2}. \tag{3.113}$$

For the case of a square well potential this result was obtained in Section 3.3.4.

3.3.12 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 3.3.9. 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.[11] For this purpose we consider potentials of the power-law type,

$$\mathcal{V}(r) = -\frac{C_s}{r^s}, \tag{3.114}$$

where $C_s = \mathcal{V}_0 r_c^s$ is the Power-law coefficient, with $\mathcal{V}_0 \equiv |\mathcal{V}(r_c)|$ the well depth.These potentials are also important from the general physics point of view because they capture major features of interparticle interactions.

For power-law potentials, the radial wave equation (3.6) is of the form

$$R_l'' + \frac{2}{r}R_l' + \left[k^2 + \frac{U_0 r_c^s}{r^s} - \frac{l(l+1)}{r^2}\right] R_l = 0, \tag{3.115}$$

where $U_0 = 2\mu\mathcal{V}_0/\hbar^2$. Because Eq. (3.115) 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. (3.115) 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

$$G_l(x) = r^{-\nu} R_l(r), \tag{3.116}$$

where the coefficient ν is to be selected in a later stage. Turning to the variable $x = \beta r^{(2-s)/2}$ with $\beta = U_0^{1/2} r_c^{s/2}[2/(s-2)]$ (*i.e.* excluding the case $s = 2$) the radial wave equation (3.115) can be written as (cf. Problem 3.4)

$$G_l'' + \frac{(2-s/2+2\nu)}{(1-s/2)\,x}G_l' + \left[\frac{k^2}{U_0}\frac{r^s}{r_c^s} + 1 - \frac{[l(l+1)-\nu(\nu+1)]}{(1-s/2)^2}\frac{1}{x^2}\right] G_l = 0. \tag{3.117}$$

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[11] See, N.F. Mott and H.S.W. Massey, *The theory of atomic collisions,* Clarendon Press, Oxford 1965.

Choosing $\nu = -\frac{1}{2}$ we obtain for $r \ll r_k = r_c \left(U_0/k^2\right)^{1/s} \Leftrightarrow x \gg x_k = kr_c \left(U_0/k^2\right)^{1/s}$ the Bessel differential equation (B.77),

$$G_n'' + \frac{1}{x}G_n' + \left(1 - \frac{n^2}{x^2}\right) G_n = 0, \tag{3.118}$$

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. (B.78a). Substituting the general solution into Eq. (3.116) with $\nu = -1/2$, the general solution for the radial wave equation of a power-law potential in the $k \to 0$ limit is given by

$$R_l(r) = r^{-1/2}\left[AJ_n(x) + BJ_{-n}(x)\right], \tag{3.119}$$

where the coefficients A and B are to be fixed by a boundary condition and the normalization.

Problem 3.4 *Show that the radial wave equation (3.115) can be written in the form*

$$G_l'' + \frac{(2 - s/2 + 2\nu)}{(1-s/2)\,x} G_l' + \left[\frac{k^2}{U_0}\frac{r^s}{r_c^s} + 1 - \frac{[l(l+1) - \nu\,(\nu+1)]}{(1-s/2)^2}\frac{1}{x^2}\right] G_l = 0,$$

where $x = rU_0^{1/2}(r_c/r)^{s/2}[2/\,(s-2)]$ *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 (3.115) 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 $\gamma^2\beta^2 = U_0 r_c^s$. Replacing twice βr^γ by x the radial wave equation (3.115) can be expressed in terms of $G(x)$ and its derivatives,

$$G_l'' + \frac{(1+\gamma+2\nu)}{\gamma x} G_l' + \frac{\nu\,(\nu+1)}{\gamma^2 x^2} G_l + \left[\frac{k^2}{U_0} + \left(1 - \frac{l(l+1)(\beta^2/x^2)^{(1-s/2)/\gamma}}{U_0 r_c^s}\right)\frac{r_c^s}{r^s}\right]\frac{r^s}{r_c^s} G_l = 0.$$

Collecting the terms proportional to $G(x)$, substituting the expression for β^2 and choosing $\gamma = 1 - s/2$ (*i.e.* excluding the case $s = 2$) we obtain the requested form, with $x = [U_0^{1/2} r_c^{s/2}/\gamma] r^\gamma = rU_0^{1/2}(r_c/r)^{s/2}[2/\,(s-2)]$. ►

3.3.13 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

$$R_l(r) = c_{1l}\, r^l + c_{2l}/r^{l+1}. \tag{3.120}$$

as was discussed in Section 3.3.9. The asymptotic behavior of $R_l(r)$ follows from the general solution (3.119) by using the expansion in powers of $(x/2)^2$ given by Eq. (B.79),

$$R_l(r) \sim r^{-1/2}\left[Ax^n(1-\frac{x^2}{4(1+n)}+\cdots)+Bx^{-n}(1-\frac{x^2}{4(1-n)}+\cdots)\right], \tag{3.121}$$

where $n=(2l+1)/(s-2)$. Substituting the definition $x=\beta r^{(2-s)/2}=\beta r^{(2l+1)/2n}$ with $\beta = U_0^{1/2}r_c^{s/2}[2/(s-2)]$ we find for $r\to\infty$

$$R_l(r)\sim Ar^l(1-a_1r^{2-s}+\cdots)+Br^{-l-1}(1-b_1r^{2-s}+\cdots), \tag{3.122}$$

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 and B depend on boundary condition and normalization. From Eq. (3.122) 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 (leaving aside the value of the coefficients A and B). If further the first-order term of the left expansion may be neglected in comparison with the zero-order 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 (3.120). This is the case for $l+2-s<-l-1$. Thus we have obtained that the potential may be neglected for

$$l<\frac{1}{2}(s-3)\quad\text{provided}\ \frac{x^2}{4(1\pm n)}\ll 1. \tag{3.123}$$

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 $l\geq 2$.

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 not a bad approximation even for $s=4$. With this presumption the inequality (3.123) may be rewritten in a form enabling the definition of the range r_0,

$$r^{2-s}\ll r_c^{2-s}(s-2)^2/\left(U_0r_c^2\right)=r_0^{2-s}\Leftrightarrow r_0=r_c\left[U_0r_c^2/(s-2)^2\right]^{1/(s-2)} \tag{3.124}$$

In terms of the range r_0 the variable x is defined as

$$x=2\left(r_0/r\right)^{(s-2)/2}. \tag{3.125}$$

For $1/r^6$ potentials we obtain $r_0=r_c\left[U_0r_c^2/16\right]^{1/4}$. Note that this value agrees within a factor of 2 with the heuristic estimate $r_0=r_c\left[U_0r_c^2/2\right]^{1/4}$ obtained with Eq. (3.88).

3.3.14 Phase shifts for power-law potentials

To obtain an expression for the phase shift by a power-law potential of the type (3.114) 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,

$$\tan\eta_l \underset{kr\to 0}{\simeq} -\frac{2l+1}{[(2l+1)!!]^2}\left(ka_l\right)^{2l+1} \tag{3.126}$$

For $l\geq\frac{1}{2}(s-3)$ 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

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

in the limit $k \to 0$ by replacing $\chi_l(k,r)$ with $krj_l(kr)$ in the integral expression (3.26) 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 (3.114)

$$\sin\eta_l \simeq \frac{\pi}{2}\int_0^\infty \frac{U_0 r_c^s}{r^s}\left[J_{l+1/2}(kr)\right]^2 r dr. \tag{3.127}$$

Here we turned to Bessel functions of half-integer order using Eq. (B.75). To evaluate the integral we use Eq. (B.89) 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 $l > \frac{1}{2}(s-3)$,

$$\sin\eta_l \underset{k\to 0}{\simeq} U_0 r_c^2 \frac{3\pi(2l+3-s)!!}{(2l+5)!!}(kr_c)^{s-2}. \tag{3.128}$$

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.

3.3.15 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 1.4.4. It may be modeled by a potential consisting of a hard core and a $-1/r^6$ long-range tail (see Fig. 1.4),

$$\mathcal{V}(r) = \begin{cases} \infty & \text{for } r \le r_c \\ -C_6/r^6 & \text{for } r > r_c. \end{cases} \tag{3.129}$$

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. For this model potential the radial wavefunctions $R_l(r)$ are given by the general solution (3.119) for power-law potentials in the $k \to 0$ limit for the case $s=6$. Choosing $l=0$ we find for radial s-waves,

$$R_0(r) = r^{-1/2}\left[AJ_{1/4}(x) + BJ_{-1/4}(x)\right], \tag{3.130}$$

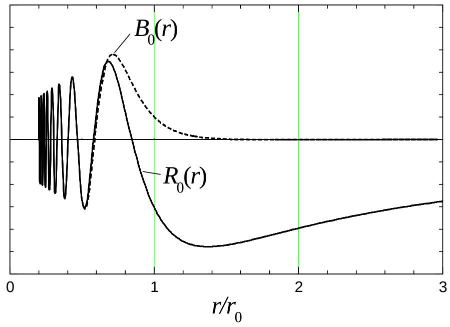

Figure 3.8: The radial wavefunction $R_0(r)$ of a $-1/r^6$ power-law potential for the case of a resonant bound state (diverging scattering length). The corresponding first regular bound state $B_0(r)$ is also shown. It has a classical outer turning point close to the last node of $R_0(r)$. The sign of the wavefunction is determined by the normalization. Note the $1/r$ long-range behavior typical for resonant bound states.

where we used $n = (2l+1)/(s-2) = 1/4$ and $x = 2(r_0/r)^2$. Here $r_0 = r_c\left[U_0 r_c^2/16\right]^{1/4}$ is the range of the Van der Waals potential as defined by Eq. (3.124). In Table 3.1 some values for C_6 and r_0 are listed for hydrogen and the alkali atoms[12].

Imposing the boundary condition $R_0(r_c) = 0$ with $r_c \ll r_0$ (*i.e.* $x_c = 2(r_0/r_c)^2 \gg 1$) we calculate for the ratio of coefficients

$$\frac{A}{B} = -\frac{J_{-1/4}(x_c)}{J_{1/4}(x_c)} \underset{x_c\to\infty}{\simeq} -\frac{\cos(x_c - 3\pi/8 + \pi/4)}{\cos(x_c - 3\pi/8)} = -2^{-1/2}\left[1 - \tan(x_c - 3\pi/8)\right]. \tag{3.131}$$

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 (B.82) for the Bessel function. Choosing $B = r_0^{1/2}\Gamma(3/4)$ the zero-energy radial wavefunction is asymptotically normalized to unity and of the form (3.98),

$$R_0(r) \underset{x\ll 1}{\simeq} Br^{-1/2}\left[\frac{A}{B}\frac{(x/2)^{1/4}}{\Gamma(5/4)} + \frac{(x/2)^{-1/4}}{\Gamma(3/4)}\right] = 1 - \frac{a}{r}. \tag{3.132}$$

where

$$a = \bar{a}\left[1 - \tan(x_c - 3\pi/8)\right], \tag{3.133}$$

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.*[13]

It is interesting to note the similarities between Eq. (3.133) and the result obtained for square well potentials given by Eq. (3.48). 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 only 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.

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[12] The C_6 coefficients are from A. Derevianko, J.F. Babb, and A. Dalgarno, PRA **63** 052704 (2001). The hydrogen value is from K.T. Tang, J.M. Norbeck and P.R. Certain, J. Chem. Phys. **64**, 3063 (1976).

[13] See G.F. Gribakin and V.V. Flambaum, Phys. Rev. A **48**, 546 (1993).

3.3.16 Asymptotic bound states in Van der Waals potentials

Asymptotic bound states are bound states with a classical turning point at distances where the potential may be neglected; *i.e.*, $r = r_{cl} \gg r_0$. In the limit of zero binding energy they become *resonant bound states.* In Fig. 3.8 we sketched 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 (3.129). Because for such states the scattering length diverges the radial wavefunction (3.130) must be of the form

$$R_0(r) \sim r^{-1/2} J_{1/4}(x). \tag{3.134}$$

The uppermost $l = 0$ regular bound state $B_0^*(r)$ for the same value of $x_c \Leftrightarrow r_c$ (obtained by numerical integration of the Schrödinger equation from r_c outward) is also shown in Fig. 3.8. The binding energy of this state corresponds to the largest binding energy ε_b^* the last bound state can have and may be estimated by calculating the potential energy at the position $r = r_{cl}^*$ of the classical outer turning point, $E_b^* = -C_6/r_{cl}^{*6}$. For the numerical solution $B_0^*(r)$ we find $r_{cl}^* = 0.860\, r_0$. Thus the largest possible *dissociation energy* $D^* = -E_b^*$ of the uppermost $l = 0$ bound state are readily calculated when C_6 and r_0 are known,

$$D^* \simeq 2.474\, C_6/r_0^6. \tag{3.135}$$

These energies 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. Because $r_{cl}^* \simeq r_0$ asymptotic bound states necessarily have a dissociation energy $D \lll D^*$.

The value for D^* was obtained above by imposing 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 $r_c \ll r \ll r_\phi \equiv |C_6/E|^{1/6}$, where $|E| \ll C_6/r_\phi^6$ the phase development is fully determined by the interaction potential. Note in Fig. 3.1 that the value $r_{cl}^* = 0.860\, r_0$ 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 $J_{1/4}(x^*) = 0$, where $x^* \approx 2.778$ is the lowest non-zero node of the Bessel function $J_{1/4}(x)$. Thus, the subsequent nodes of $J_{1/4}(x)$ may be used to quickly estimate the turning points of the next bound states in the Van der Waals potential and their binding energies. The expression (3.135) for D^* holds for all potentials with a long-range Van der Waals tail provided 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 *accumulated phase* is at the basis of semi-emperical precision descriptions of collisional phenomena in ultracold gases.[14] In a semi-classical approximation the turning points a and b of the p-th bound state are defined by the phase condition

$$\phi = (p + 1/2)\,\pi = \textstyle\int_a^b k dr, \tag{3.136}$$

where $k = [2\mu[E - \mathcal{V}(r)]]^{1/2}/\hbar$.

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 (3.106),

$$r_e = 2\textstyle\int_0^\infty \left[y_0^2(r) - \chi_0^2(r)\right] dr, \tag{3.137}$$

where $y_0(r) = 1 - r/a$. The wavefunction $\chi_0(r)$ is given by Eq. (3.130), normalized to the asymptotic form $\chi_0(r) \simeq 1 - r/a$. Using Eqs. (3.133) and (3.131) and turning to the dimensionless variable $\rho = r/r_0$ the function $\chi_0(r)$ takes the form

$$\chi_0(\rho) = \rho^{1/2}\left[\Gamma\left(5/4\right) J_{1/4}(2/\rho^2) - (r_0/a)\,\Gamma\left(3/4\right) J_{-1/4}(2/\rho^2)\right]. \tag{3.138}$$

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[14] A.J. Moerdijk and B.J. Verhaar, Phys. Rev. Lett. **73**, 518 (1994).

Substituting this expression into Eq. (3.137) we obtain for the effective range[15]

$$r_e/2r_0 = I_0 - 2\left(r_0/a\right) I_1 + I_2\left(r_0/a\right)^2 \tag{3.139}$$

$$= \frac{16}{3\pi}\left[\left[\Gamma\left(5/4\right)\right]^2 - \frac{\pi}{2}\left(r_0/a\right) + \left[\Gamma\left(3/4\right)\right]^2\left(r_0/a\right)^2\right]. \tag{3.140}$$

Substituting numerical values the expression (3.107) for the s-wave phase shift becomes

$$k\cot\eta_0 = -\frac{1}{a} + \frac{1}{2}r_0k^2 \times 2.789\left[1 - 1.912\left(r_0/a\right) + 1.828\left(r_0/a\right)^2\right]. \tag{3.141}$$

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 square well.

3.3.17 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. The existence of such pseudo potentials is not surprising in view of the zero-range square well solutions discussed in Section 3.3.8.

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

$$\left(\Delta + k^2\right)\psi_k\left(\mathbf{r}\right) = 0, \tag{3.142}$$

where $k = [2\mu E]^{1/2}/\hbar$ is the wave number for the relative motion (cf. Section 2.3). The general solution of this homogeneous equation can be expressed in terms of the complete set of eigenfunctions $R_l(k,r)Y_l^m(\hat{\mathbf{r}})$,

$$\psi_k(\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} c_{lm}R_l(k,r)Y_l^m(\hat{\mathbf{r}}). \tag{3.143}$$

In this section we restrict ourselves to the s-wave limit (*i.e.* choosing $c_{lm} = 0$ for $l \geq 1$) where $\eta_0 = -ka$.[16] We are looking for a pseudo potential that will yield a solution of the type (3.97) *throughout* space,

$$\psi_k(\mathbf{r}) = \frac{C}{kr}\sin(kr + \eta_0), \tag{3.144}$$

where the contribution of the spherical harmonic $Y_0^0(\hat{\mathbf{r}}) = (4\pi)^{-1/2}$ is absorbed into the proportionality constant. The difficulty of this expression is that it is irregular in the origin. We claim that the operator

$$-\frac{4\pi}{k\cot\eta_0}\delta\left(\mathbf{r}\right)\frac{\partial}{\partial r}r \tag{3.145}$$

---

[15] Here we use the following definite integrals:

$$I_2 = \int_0^\infty \varrho^2\left[1 - \left[\Gamma\left(3/4\right)J_{-1/4}(x)\right]^2/\varrho\right]d\varrho = \left[\Gamma\left(3/4\right)\right]^2 16/3\pi$$

$$I_1 = \int_0^\infty \varrho\left[1 - \Gamma\left(3/4\right)J_{-1/4}(x)\Gamma\left(5/4\right)J_{1/4}(x)\right]d\varrho = 4/3$$

$$I_0 = \int_0^\infty\left[1 - \varrho\left[\Gamma\left(5/4\right)J_{1/4}(x)\right]^2\right]d\varrho = \left[\Gamma\left(5/4\right)\right]^2 16/3\pi.$$

[16] For the case of arbitrary l see K. Huang, *Statistical Mechanics*, John Wiley and sons, Inc., New York 1963.

is the s-wave pseudo potential $U(\mathbf{r})$ that has the desired properties; *i.e.*,

$$\left(\Delta + k^2 + \frac{4\pi}{k\cot\eta_0}\delta\left(\mathbf{r}\right)\frac{\partial}{\partial r}r\right)\psi_k\left(\mathbf{r}\right) = 0. \tag{3.146}$$

The presence of the delta function makes the pseudo potential act as a boundary condition at $r = 0$,

$$\frac{4\pi\delta\left(\mathbf{r}\right)}{k\cot\eta_0}\left[\frac{\partial}{\partial r}r\psi_k\left(\mathbf{r}\right)\right]_{r=0} = 4\pi\delta\left(\mathbf{r}\right)\frac{C}{k}\sin\eta_0 = -4\pi\delta\left(\mathbf{r}\right)\frac{C}{k}\sin(ka) \underset{k\to 0}{\simeq} -4\pi aC\delta\left(\mathbf{r}\right), \tag{3.147}$$

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. (3.146) we obtain the inhomogeneous equation

$$\left(\Delta + k^2\right)\psi_k\left(\mathbf{r}\right) \underset{k\to 0}{\simeq} 4\pi aC\delta\left(\mathbf{r}\right). \tag{3.148}$$

This inhomogeneous equation has the solution (3.144) as demonstrated in problem 3.5.

For functions $f\left(\mathbf{r}\right)$ with regular behavior in the origin we have

$$\left[\frac{\partial}{\partial r}rf\left(\mathbf{r}\right)\right]_{r=0} = f\left(\mathbf{r}\right) + \left[r\frac{\partial}{\partial r}f\left(\mathbf{r}\right)\right]_{r=0} = f\left(\mathbf{r}\right) \tag{3.149}$$

and the pseudo potential takes the form of a *delta function potential*[17]

$$U(\mathbf{r}) = -\frac{4\pi}{k\cot\eta_0}\delta\left(\mathbf{r}\right) \underset{k\to 0}{\simeq} 4\pi a\,\delta\left(\mathbf{r}\right) \tag{3.150}$$

or, equivalently, restoring the dimensions

$$\mathcal{V}\left(\mathbf{r}\right) = g\,\delta\left(\mathbf{r}\right) \quad \text{with } g = \left(2\pi\hbar^2/\mu\right)a. \tag{3.151}$$

This expression, valid in the zero energy limit, is very convenient to calculate the interaction energy but is accurate only as long as we can *restrict ourselves to first order in perturbation theory.* For instance, with the delta function potential (3.150) we can readily regain the interaction energy Eq. (3.156) for the boundary condition (3.154) using first-order perturbation theory. More importantly, as shown in the next section, the delta function potential enables us to calculate with first-order perturbation theory the interaction energy for a pair of atoms starting from the usual free-atom wavefunctions.

Problem 3.5 *Verify that*

$$\left(\Delta + k^2\right)\psi_k\left(\mathbf{r}\right) = 4\pi\delta\left(\mathbf{r}\right)\frac{1}{k}\sin\eta_0 \tag{3.152}$$

by direct substitution of the solution (3.144) setting $C = 1$.

Solution: Integrating Eq. (3.148) by over a small sphere V of radius ϵ around the origin we have

$$\int_V \left(\Delta + k^2\right)\frac{1}{kr}\sin(kr + \eta_0)d\mathbf{r} = -\frac{4\pi}{k}\sin\eta_0 \tag{3.153}$$

Here we used $\int_V \delta\left(\mathbf{r}\right)d\mathbf{r} = 1$ for an arbitrarily small sphere around the origin. The second term on the l.h.s. of Eq. (3.153) vanishes,

$$4\pi k\lim_{\epsilon\to 0}\int_0^\epsilon r\sin(kr + \eta_0)dr = 4\pi k\sin(\eta_0)\lim_{\epsilon\to 0}\epsilon = 0.$$

---

[17] 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, $\int \delta\left(\mathbf{r}\right)d\mathbf{r} = 1$. Pseudo potentials do not carry physical significance but are mathematical constructions that can chosen such that they provide wavefunctions with the proper phase shift.

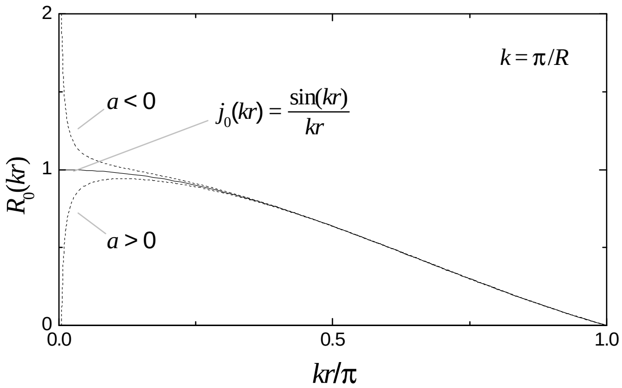

Figure 3.9: Radial wavefunctions satisfying the boundary condition of zero amplitude at the surface of a spherical quantization volume of radius R. In this example $|a/R| = 0.1$. Note that for positive scattering length the wavefunction is suppressed for distances $r \lesssim a$ as expected for repulsive 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).

The first term follows with the divergence theorem (Gauss theorem)

$$\begin{aligned}\lim_{\epsilon\to 0}\int_V \Delta\frac{1}{kr}\sin(kr+\eta_0)d\mathbf{r} &= \lim_{\epsilon\to 0}\oint_S d\mathbf{S}\cdot\boldsymbol{\nabla}\frac{1}{kr}\sin(kr+\eta_0)\\ &= \lim_{\epsilon\to 0}4\pi\epsilon^2\left(\frac{1}{k\epsilon}\cos(k\varepsilon+\eta_0)-\frac{1}{k\epsilon^2}\sin\eta_0\right)\\ &= -\frac{4\pi}{k}\sin\eta_0.\ \blacktriangleright\end{aligned}$$

3.4 Energy of interaction between two atoms

3.4.1 Energy shift due to interaction

To further analyze the effect of the interaction we ask ourselves how much the total energy changes due to the presence of the interaction. This can be established by analyzing the boundary condition. Putting the reduced mass inside a spherical box of radius $R \gg |a|$ around the potential center, the wavefunction should vanish at the surface of the sphere (see Fig. 3.9). For free atoms this corresponds to the condition

$$R_0(R) = \frac{c_0}{R}\sin(kR) = 0 \Leftrightarrow k = n\frac{\pi}{R} \quad \text{with } n \in \{1, 2, \cdots\}. \tag{3.154}$$

In the presence of the interactions we have asymptotically; *i.e.*, near surface of the sphere

$$R_0(R) \underset{r\to\infty}{\sim} \frac{1}{R}\sin\left[k'(R-a)\right] = 0 \Leftrightarrow k' = n\frac{\pi}{(R-a)} \quad \text{with } n \in \{1, 2, \cdots\}. \tag{3.155}$$

As there is no preference for any particular value of n as long as $|a| \ll R$, we choose for the boundary condition $n = 1$ and the change in total energy as a result of the interaction is given by

$$\begin{aligned}\delta E &= \frac{\hbar^2}{2\mu}\left(k'^2 - k^2\right) = \frac{\hbar^2}{2\mu}\left(\frac{\pi^2}{(R-a)^2} - \frac{\pi^2}{R^2}\right)\\ &= \frac{\hbar^2}{2\mu}\frac{\pi^2}{R^2}\left[1 + 2\frac{a}{R} + \cdots - 1\right] \underset{a\ll R}{\simeq} \frac{\hbar^2}{\mu}\frac{\pi^2}{R^3}a\,.\end{aligned} \tag{3.156}$$

Note that for $a > 0$ the total energy of the pair of atoms is seen to increase due to the interaction (*effective repulsion*). Likewise, for $a < 0$ the total energy of the pair of atoms is seen to decrease due to the interaction (*effective attraction*). The energy shift δE is known as the *interaction energy* of the pair. Apart from the s-wave scattering length it depends on the reduced 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_0. 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.

3.4.2 Energy shift obtained with pseudo potentials

The method used above to calculate the interaction energy δE of the reduced mass μ 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 atom 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 3.3.17 provide this boundary condition.

For free atoms the relative motion is described by the unperturbed relative wavefunction

$$\varphi_k(\mathbf{r}) = CY_0^0(\hat{\mathbf{r}})j_0(kr)$$

where $Y_0^0(\hat{\mathbf{r}}) = (4\pi)^{-1/2}$ is the lowest order spherical harmonic with $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$ the unit vector in the radial direction (θ, ϕ). The normalization condition is $1 = \langle\varphi_k|\varphi_k\rangle = \int_V [CY_0^0(\hat{\mathbf{r}})j_0(kr)]^2 d\mathbf{r}$ with $kR = \pi$. Rewriting the integral in terms of the variable $\varrho \equiv kr$ we find after integration and setting $k = \pi/R$ we obtain

$$\frac{1}{C^2} = \frac{1}{k^2}\int_0^R \sin^2(kr)dr = \frac{1}{k^3}\int_0^\pi \sin^2(\varrho)d\varrho = \frac{R^3}{\pi^3}\frac{\pi}{2}.$$

Then, to first order in perturbation theory the interaction energy is given by

$$\delta E = \frac{\langle\varphi_k|\,\mathcal{V}(r)\,|\varphi_k\rangle}{\langle\varphi_k|\varphi_k\rangle} \underset{k\to 0}{\simeq} \frac{\hbar^2}{2\mu}\int 4\pi a\,\delta(\mathbf{r})\,\varphi_k^2(\mathbf{r})d\mathbf{r} = \frac{\hbar^2}{2\mu}aC^2\left[\frac{\sin^2(kr)}{k^2r^2}\right]_{r\to 0} = \frac{\hbar^2}{\mu}\frac{\pi^2}{R^3}a\,, \tag{3.157}$$

which is seen to coincide with Eq. (3.156).

3.4.3 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[18]

$$\mathcal{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + \mathcal{V}(r). \tag{3.158}$$

In the absence of the interaction the pair wavefunction of the two atoms is given by the product wavefunction (7.5),

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V}e^{-i\mathbf{k}_1\cdot\mathbf{r}_1}e^{-i\mathbf{k}_2\cdot\mathbf{r}_2}$$

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 $\mathbf{r} = |\mathbf{r}_1 - \mathbf{r}_2|$,

$$\delta E = \frac{\langle\mathbf{k}_1,\mathbf{k}_2|\,\mathcal{V}(\mathbf{r})\,|\mathbf{k}_1,\mathbf{k}_2\rangle}{\langle\mathbf{k}_1,\mathbf{k}_2|\mathbf{k}_1,\mathbf{k}_2\rangle} = \frac{g}{V}. \tag{3.159}$$

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[18] In this description we leave out the internal states of the atoms (including spin).

This result follows in two steps. With Eq. (7.5) the norm is given by

$$\begin{aligned}\langle \mathbf{k}_1, \mathbf{k}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle &= \iint_V \left| \psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{V^2} \int_V |\mathrm{e}^{-i\mathbf{k}_1\cdot\mathbf{r}_1}|^2 d\mathbf{r}_1 \int_V |\mathrm{e}^{-i\mathbf{k}_2\cdot\mathbf{r}_2}|^2 d\mathbf{r}_2 = 1, \end{aligned} \tag{3.160}$$

because $\left|\mathrm{e}^{-i\alpha}\right|^2 = 1$. As the plane waves are regular in the origin we can indeed use the delta function potential (3.151) to approximate the interaction

$$\begin{aligned}\langle \mathbf{k}_1, \mathbf{k}_2 | \, \mathcal{V}(r) \, | \mathbf{k}_1, \mathbf{k}_2 \rangle &= \frac{g}{V^2} \iint_V \delta(\mathbf{r}_1 - \mathbf{r}_2) \left| \mathrm{e}^{-i\mathbf{k}_1\cdot\mathbf{r}_1} \mathrm{e}^{-i\mathbf{k}_2\cdot\mathbf{r}_2} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \qquad (3.161) \\ &= \frac{g}{V^2} \int_V |\mathrm{e}^{-i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_1}|^2 d\mathbf{r}_1 = g/V. \end{aligned}$$

Like in Eq. (3.156) the interaction energy depends on the reduced mass of the atoms and scales inversely proportional to the quantization volume.

3.4.4 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 3.4.3 we will use first-order perturbation theory and the delta function potential

$$\mathcal{V}(r) = g\,\delta(\mathbf{r}) \quad \text{with } g = \left(4\pi\hbar^2/m\right) a\,, \tag{3.162}$$

where m is the atomic mass (the reduced mass equals $\mu = m/2$ 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 Eq. (7.11) 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

$$\begin{aligned}\delta E = g \, \langle \mathbf{k}, \mathbf{k} | \, \delta(\mathbf{r}) \, | \mathbf{k}, \mathbf{k} \rangle &= \frac{g}{V^2} \iint_V \delta(\mathbf{r}_1 - \mathbf{r}_2) \left| \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}_1} \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}_2} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{g}{V^2} \int_V \left| \mathrm{e}^{-i2\mathbf{k}\cdot\mathbf{r}_1} \right|^2 d\mathbf{r}_1 = g/V. \end{aligned} \tag{3.163}$$

We notice that we have obtained exactly the same result as in Section 3.4.3.

For $\mathbf{k}_1 \neq \mathbf{k}_2$ the situation is different. The pair wavefunction is given by Eq. (7.9) 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

$$\begin{aligned}\delta E &= g \, \langle \mathbf{k}_1, \mathbf{k}_2 | \, \delta(\mathbf{r}) \, | \mathbf{k}_1, \mathbf{k}_2 \rangle \\ &= \frac{1}{2} \frac{g}{V^2} \iint_V \delta(\mathbf{r}_1 - \mathbf{r}_2) \left| \mathrm{e}^{-i\mathbf{k}_1\cdot\mathbf{r}_1} \mathrm{e}^{-i\mathbf{k}_2\cdot\mathbf{r}_2} + \mathrm{e}^{-i\mathbf{k}_2\cdot\mathbf{r}_1} \mathrm{e}^{-i\mathbf{k}_1\cdot\mathbf{r}_2} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} \frac{g}{V^2} \int_V [|\mathrm{e}^{-i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_1}|^2 + |\mathrm{e}^{-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_1}|^2 + |\mathrm{e}^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_1}|^2 + |\mathrm{e}^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_1}|^2] d\mathbf{r}_1 \\ &= 2g/V. \end{aligned} \tag{3.164}$$

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 kinetic 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 *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 cases considered expressions for 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 4.5 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.

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[1] N.F. Mott, *Proc. Roy. Soc.* A**126**, 259 (1930).

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 atomic species. These atoms are called *distinguishable* because they have a different composition of elementary particles and consequently lack a prescribed overall exchange symmetry, *i.e.* the pair wavefunction can be symmetric or antisymmetric (or any linear combination of the two) under exchange of the two atoms. Before discussing the actual collision we first consider two non-interacting atoms moving freely in space. Since the atoms are distinguishable it is possible to label them 1 and 2 and to define the relative momentum as $\mathbf{p} = \mu(\mathbf{v}_1 - \mathbf{v}_2) = \mu\mathbf{v} = \hbar\mathbf{k}$ in the center-of-mass-fixed coordinate frame (see Appendix A.1). Let us choose, purely for mathematical convenience, the direction of $\mathbf{p}$ along the positive z-axis, *i.e.* the reduced mass μ moves in the positive z direction (the same holds for the motion of atom 1 relative to atom 2). Experimentally, this can be arranged by providing the colliding atoms in opposing atomic beams. For free atoms the relative motion may be described by the plane wave

$$\psi_{in}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikz}, \tag{4.1}$$

where $\mathbf{k}\cdot\mathbf{r} = kr\cos\theta_i = kz$ for $\theta_i = 0$, with θ_i representing the angle of incidence with respect to the positive z-axis. The relative kinetic energy of the atoms is given by

$$E = \hbar^2 k^2/2\mu. \tag{4.2}$$

If the atoms can *scatter elastically* under the influence of a *central* potential $\mathcal{V}(r)$ the wavefunction for the relative motion must contain a term representing the scattered wave. In view of the central symmetry the variables for the radial and angular motion separate (see Section 2) and at large distance from the scattering center the radial dependence of this term must be of the form

$$\psi_{out}(r) \underset{r\to\infty}{\sim} e^{ikr}/r. \tag{4.3}$$

Note that the intensity of the scattered wave falls off like $1/r^2$ and that the modulus of the relative wave vector $k = |\mathbf{k}|$ is conserved as required for elastic collisions. Combining Eqs. (4.1) and (4.3) we obtain a general expression for the wavefunction describing the relative motion of the pair far from the scattering center at position $\mathbf{r} \equiv (r, \theta, \phi)$,

$$\psi_k(\mathbf{r}) \underset{r\to\infty}{\sim} \psi_{in} + f(\theta,\phi)\,\psi_{out}. \tag{4.4}$$

Here the quantity $f(\theta,\phi)$ represents the probability amplitude for scattering of the reduced mass in the direction (θ,ϕ). Because the potential $\mathcal{V}(r)$ has central symmetry $f(\theta,\phi)$ is independent of the azimuthal scattering angle ϕ. Hence, the wave function for the overall relative motion will be an axially symmetric solution of the Schrödinger equation (2.44) of the following asymptotic type:

$$\psi_k(r,\theta) \underset{r\to\infty}{\sim} e^{ikz} + f(\theta)e^{ikr}/r. \tag{4.5}$$

Here we omitted the explicit normalization factor. The quantity $f(\theta)$ is called the *scattering amplitude* and θ is the *scattering angle* of the reduced mass, defined with respect to the positive z-axis. The scattering behavior of the reduced mass in the center-of-mass-fixed frame is illustrated in Fig. 4.1. When observing this collision experimentally in the center-of-mass frame, 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 complementary direction $(\pi-\theta, \pi-\phi)$. A pair of mass spectrometers in the directions θ and $\pi-\theta$ would be an appropriate (atom selective) detector in this case.

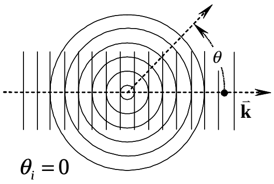

Figure 4.1: Schematic drawing of the scattering of a matter wave at a spherically symmetric scattering center in the center-of-mass coordinate system. Indicated are the wavevector $\mathbf{k}$ of the incident wave representing the reduced mass μ moving in the positive z-direction ($\theta_i = 0$) as well as the scattering angle θ.

Knowing the angular and radial eigenfunctions, the general solution for a particle in a central potential field $\mathcal{V}(r)$ can be expressed in terms of the complete set of eigenfunctions $R_l(k,r)Y_l^m(\theta,\phi)$,

$$\psi_k(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm} R_l(k,r) Y_l^m(\theta,\phi), \tag{4.6}$$

where $\mathbf{r} \equiv (r,\theta,\phi)$ is the position vector. This important expression is known as the *partial-wave expansion.* The coefficients c_l depend on the particular choice of coordinate axes. Our interest concerns in particular the wave functions with axial symmetry along the z-axis. These are ϕ independent. Hence, all coefficients c_l with $m \neq 0$ should be zero. Accordingly, for axial symmetry along the z-axis the partial wave expansion (4.6) reduces to

$$\psi_k(r,\theta) = \sum_{l=0}^{\infty} c_l R_l(k,r) P_l(\cos\theta), \tag{4.7}$$

where the $P_l(\cos\theta)$ are Legendre polynomials and the $R_l(r)$ satisfy the radial wave equation (3.6). The coefficients c_l must be chosen such that at large distances the partial-wave expansion has the asymptotic form (4.5). For short-range potentials, the asymptotic form should satisfy the spherical Bessel equation (3.9), hence satisfy the form (3.14):

$$\begin{aligned} R_l(k,r) \underset{r\to\infty}{\sim} \frac{1}{kr}\sin(kr+\eta_l-\frac{1}{2}l\pi) &= \frac{1}{2ikr}\left[i^{-l}e^{ikr}e^{i\eta_l} - i^{l}e^{-ikr}e^{-i\eta_l}\right] \\ &= \frac{i^{-l}e^{-i\eta_l}}{2ikr}\left[e^{ikr} + (e^{2i\eta_l}-1)e^{ikr} + (-1)^{l+1}e^{-ikr}\right]. \end{aligned} \tag{4.8}$$

Substituting this into the partial-wave expansion (4.7) we obtain

$$\psi(r,\theta) \underset{r\to\infty}{\sim} \frac{1}{2ikr}\sum_{l=0}^{\infty} c_l P_l(\cos\theta) i^{-l}e^{-i\eta_l}\left[e^{ikr} + (e^{2i\eta_l}-1)e^{ikr} + (-1)^{l+1}e^{-ikr}\right]. \tag{4.9}$$

Similarly, using the asymptotic relation Eq. (B.73a), the partial-wave expansion of the plane wave e^{ikz} given by Eq. (4.12) becomes

$$e^{ikz} \underset{r\to\infty}{\sim} \frac{1}{2ikr}\sum_{l=0}^{\infty}(2l+1)i^l P_l(\cos\theta) i^{-l}\left[e^{ikr} + (-1)^{l+1}e^{-ikr}\right]. \tag{4.10}$$

Comparing the terms of order l in Eqs. (4.9) and (4.10) we find that by choosing $c_l = i^l(2l+1)e^{i\eta_l}$ for the expansion coefficients, the partial-wave expansion (4.9) takes the asymptotic form (4.5). Thus, subtracting the plane wave expansion (4.10) from the partial-wave expansion (4.9) we obtain the scattering amplitude as the coefficient of the e^{ikr}/r term,

$$f(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)(e^{2i\eta_l}-1)P_l(\cos\theta). \tag{4.11}$$

Problem 4.1 *Show that the plane wave* e^{ikz}*, describing the motion of a free particle in the positive* z *direction, can be expanded in partial waves as*

$$e^{ikz} = \sum_{l=0}^{\infty}(2l+1)i^l j_l(kr)P_l(\cos\theta). \tag{4.12}$$

Solution: The only regular solutions of the spherical Bessel equation are the spherical Bessel functions (see Section B.11.1). So we set $R_l(kr) = j_l(kr)$ in the partial-wave expansion (4.7) and our task is to determine the coefficients c_l. Expanding the l.h.s. in powers of $kr\cos\theta$ we find

$$e^{ikz} = \sum_{l=0}^{\infty}\frac{(ikr\cos\theta)^l}{l!}. \tag{4.13}$$

Turning to the r.h.s. of Eq. (4.7) we obtain

$$\sum_{l=0}^{\infty}c_l j_l(kr)P_l(\cos\theta) \underset{r\to 0}{\sim} \sum_{l=0}^{\infty}c_l\frac{(kr)^l}{(2l+1)!!}\frac{1}{2^l l!}\frac{(2l)!}{l!}(\cos\theta)^l. \tag{4.14}$$

Here we used the expansion of the Bessel function $j_l(kr)$ in powers $(kr)^l$ as given by Eq. (B.73b),

$$j_l(kr) \underset{r\to 0}{\sim} \frac{(kr)^l}{(2l+1)!!}(1+\cdots),$$

and used Eq. (B.23) formula (with $u \equiv \cos\theta$) to find the term of order $(\cos\theta)^l$ in the expansion of $P_l(\cos\theta)$,

$$P_l(u) = \frac{1}{2^l l!}\frac{d^l}{du^l}(u^2-1)^l = \frac{1}{2^l l!}\frac{d^l}{du^l}\left(u^{2l}+\cdots\right) = \frac{1}{2^l l!}\frac{(2l)!}{l!}(u^l+\cdots).$$

Thus, equating the terms of order $(kr\cos\theta)^l$ in Eqs. (4.13) and (4.14), we obtain for the coefficients[2]

$$c_l = i^l(2l+1)!!\frac{2^l l!}{(2l)!} = i^l(2l+1), \tag{4.15}$$

which leads to the desired result after substitution into Eq. (4.7). ▶

Problem 4.2 *Calculate the current density of a plane wave* e^{ikz} *running in the positive* z *direction.*

Solution: We only have to calculate the z component of the current density vector,

$$\begin{aligned}\boldsymbol{j}_z &= \frac{i\hbar}{2\mu}\left(\psi\nabla_z\psi^* - \psi^*\nabla_z\psi\right)\\ &= \mathbf{1}_z\frac{i\hbar}{2\mu}(-2ik)\\ &= \frac{\hbar\mathbf{k}_z}{\mu} = \mathbf{v}_z,\end{aligned} \tag{4.16}$$

where $\mathbf{v}$ is the velocity of the reduced mass along the positive z direction. ▶

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[2] Note that $(2n)!/(2n-1)!! = (2n)!! = 2^n n!$

4.2.1 Partial-wave scattering amplitudes and forward scattering

Eq. (4.11) can be rewritten as

$$f(\theta) = \sum_{l=0}^{\infty}(2l+1)f_l P_l(\cos\theta), \tag{4.17}$$

where the contribution f_l of the partial wave with angular momentum l can be written in several equivalent forms

$$\begin{aligned} f_l &= \frac{1}{2ik}(e^{2i\eta_l}-1) && (4.18a)\\ &= k^{-1}e^{i\eta_l}\sin\eta_l && (4.18b)\\ &= \frac{1}{k\cot\eta_l - ik} && (4.18c)\\ &= k^{-1}\left(\sin\eta_l\cos\eta_l + i\sin^2\eta_l\right). && (4.18d) \end{aligned}$$

Each of these expressions has its specific advantage. In particular we draw the attention to:

- Eq. (4.18a) can be written in the form

  $$S_l \equiv e^{2i\eta_l} = 1 + 2ikf_l, \tag{4.19}$$

  which is called the S matrix. This relation between the scattering amplitudes f_l and the S matrix is one of the fundamental relations of scattering theory because the S matrix makes is possible to factorize different contributions to the phase shift

  $$S_l = e^{2i\eta_l} = e^{2i\eta_l^0}e^{2i\eta_l^{res}} \equiv S_{bg}S_{res} \tag{4.20}$$

  and to approximate these separately.

- Eq. (4.18d) shows that the imaginary part of the scattering amplitude f_l is given by

  $$\operatorname{Im} f_l = \frac{1}{k}\sin^2\eta_l. \tag{4.21}$$

  Specializing this equation 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.

  $$\operatorname{Im} f(0) = \sum_{l=0}^{\infty}(2l+1)\operatorname{Im} f_l\, P_l(1) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\sin^2\eta_l, \tag{4.22}$$

  again a fundamental relation of scattering theory.

4.2.2 The S matrix

The S-matrix

$$S_l \equiv e^{2i\eta_l} \tag{4.23}$$

is an important quantity in the formal theory of scattering. The name is somewhat confusing because in the present context of a single elastic scattering channel it is no more than an l-dependent complex function of k with modulus equal to unity, $S_l^* S_l = 1$. The S-matrix is interesting in the vicinity of resonances where it suits to factorize different contributions to the phase shift. For instance, in the case of two contributions to the phase shift, $\eta_l = \eta_l^0 + \eta_l^{res}$, we have

$$S_l = e^{2i\eta_l^0}e^{2i\eta_l^{res}} \equiv S_{bg}S_{res}. \tag{4.24}$$

Applying this to the resonance structure analyzed in Section 3.3.3 and writing Eq. (3.76) in the form

$$\eta_{\rm res} = -\tan^{-1}[(\Gamma/2)\,/\,(E - E_{\rm res})], \tag{4.25}$$

the S-matrix becomes[3].

$$S_{res} = \frac{E - E_{\rm res} - i\Gamma/2}{E - E_{\rm res} + i\Gamma/2} = 1 - \frac{i\Gamma}{E - E_{\rm res} + i\Gamma/2}. \tag{4.26}$$

Importantly, the same expression may be obtained *without* the approximating expansion (3.74) around the zero crossing. For this we recall that in the presence of a weakly-bound ($\kappa = \kappa_b$) or virtually-bound ($\kappa = -\kappa_{vb}$) s-level the phase shift is given by

$$\eta_0 = -kr_0 - \tan^{-1}\frac{k}{\kappa}. \tag{4.27}$$

Thus the resonance contribution to the S-matrix is given by

$$S_{res} = \frac{k + i\kappa}{k - i\kappa}. \tag{4.28}$$

4.2.3 Differential and total cross section

To obtain the *partial cross-section* for scattering over an angle between θ and $\theta + d\theta$ we have to compare the probability current density of the scattered wave with that of the incident wave. For the scattered wave in Eq. (4.5), $\psi_{sc} = f(\theta)e^{ikr}/r$, the probability current density is given by

$$\boldsymbol{j}_r(r) = \frac{i\hbar}{2\mu}\left(\psi_{sc}\nabla_r\psi_{sc}^* - \psi_{sc}^*\nabla_r\psi_{sc}\right) = \mathbf{1}_r\,|f(\theta)|^2\,\frac{\hbar k}{\mu r^2} = \mathbf{1}_r\,|f(\theta)|^2\,\frac{v}{r^2}. \tag{4.29}$$

Hence, the probability current (*i.e.* probability per unit time) $dI = \boldsymbol{j}_r(r)\cdot d\mathbf{S}$ of atoms (reduced masses) scattering through a surface element $d\mathbf{S} = r^2 d\boldsymbol{\Omega}$ in the direction $\boldsymbol{\Omega} \equiv (\theta, \phi)$ is given by $dI(\boldsymbol{\Omega}) = j_r(r)dS = v\,|f(\theta)|^2\,d\Omega$. Its ratio to the current density (4.16) of the incident wave is

$$d\sigma(\boldsymbol{\Omega}) = \frac{dI(\boldsymbol{\Omega})}{j_z} = |f(\theta)|^2\,d\Omega, \tag{4.30}$$

with $d\Omega = \sin\theta d\theta d\phi$. The probability per unit solid angle to scatter in the direction $\boldsymbol{\Omega}$ is given by

$$\frac{d\sigma(\boldsymbol{\Omega})}{d\Omega} = |f(\theta)|^2, \tag{4.31}$$

This quantity is called the *differential cross section.* The partial cross section for scattering over an angle between θ and $\theta + d\theta$ is

$$d\sigma(\theta) = 2\pi\sin\theta\,|f(\theta)|^2\,d\theta. \tag{4.32}$$

For pure d-wave scattering this is illustrated in Fig. 4.2.

The total cross section is obtained by integration over all scattering angles,

$$\sigma = \int_0^\pi 2\pi\sin\theta\,|f(\theta)|^2\,d\theta. \tag{4.33}$$

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[3] Here we use the logarithmic representation of the arctangent with a real argument α,

$$\tan^{-1}\alpha = \frac{i}{2}\ln\frac{1 - i\alpha}{1 + i\alpha}.$$

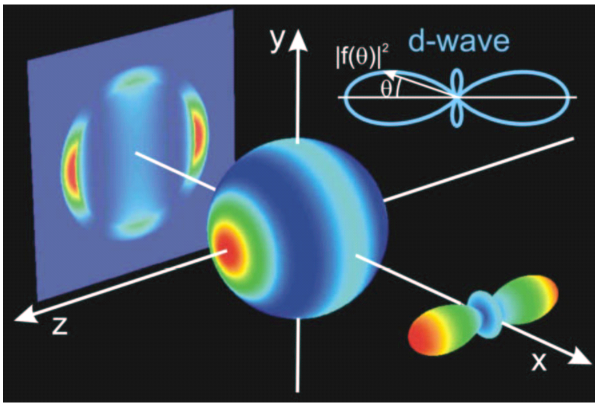

Figure 4.2: Schematic plot of a pure d-wave sphere emerging from a scattering center and its projection as can be observed with absorption imaging after collision of two ultracold clouds. Also shown are 2D and 3D angular plots of $|f(\theta)|^2$ where the length of the radius vector represents the probability 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.

Substituting Eq. (4.18a) for the scattering amplitude we find for the cross-section

$$\sigma = 2\pi \sum_{l,l'=0}^{\infty} (2l'+1)(2l+1) f_{l'}^* f_l \int_0^{\pi} P_{l'}(\cos\theta) P_l(\cos\theta) \sin\theta d\theta. \tag{4.34}$$

The cross terms drop due to the orthogonality of the Legendre polynomials,

$$\sigma = 2\pi \sum_{l=0}^{\infty} (2l+1)^2 |f_l|^2 \int_0^{\pi} [P_l(\cos\theta)]^2 \sin\theta d\theta, \tag{4.35}$$

which reduces with Eq. (B.28) to

$$\sigma = 4\pi \sum_{l=0}^{\infty} (2l+1)|f_l|^2 \equiv \sum_{l=0}^{\infty} \sigma_l. \tag{4.36}$$

Here

$$\sigma_l = 4\pi(2l+1)|f_l|^2 \tag{4.37}$$

is called the partial cross section for l-wave scattering. The squared moduli of the partial-wave scattering amplitudes are usually written in one of three equivalent forms

$$|f_l|^2 = \frac{1}{4k^2}|e^{2i\eta_l} - 1|^2 \tag{4.38a}$$

$$= \frac{1}{k^2}\sin^2\eta_l \tag{4.38b}$$

$$= \frac{1}{k^2\cot^2\eta_l + k^2}. \tag{4.38c}$$

Optical theorem and unitarity limit

Using Eq. (4.38b) the cross section takes the well-known form

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2\eta_l. \tag{4.39}$$

Substituting Eq. (4.22) into Eq. (4.39) we obtain

$$\sigma = \frac{4\pi}{k} \operatorname{Im} f(0). \tag{4.40}$$

This expression is known as the *optical theorem.* 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. (4.39) as $\sigma = \sum_{l=0}^{\infty} \sigma_l$, we note that the l-wave contribution to the cross section has an upper limit given by

$$\sigma_l \leq \frac{4\pi}{k^2}(2l+1). \tag{4.41}$$

This limit is called the *unitarity limit*.

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.

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 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. This is a complicating factor and will be discussed in Section 4.4.

4.3.1 Identical atoms in the same internal state

Let us start again with two non-interacting atoms moving freely in space in opposite directions along the z-axis. For identical atoms it is impossible to determine which atom is moving in the positive direction (to the right) and which in the negative direction (to the left). Therefore, also the direction of the reduced mass is unknown and the wavefunction for the relative motion has to be symmetrized. In this section we consider the case where the atoms are in the same internal state. Therefore, the spin state is symmetric under exchange of two complete atoms. In accordance, the wavefunction for the relative motion must be symmetric (+) in the case of bosonic atoms and anti-symmetric (−) in the case of fermionic atoms,

$$\psi_{in}(\mathbf{r}) = e^{ikz} \pm e^{-ikz}. \tag{4.42}$$

What happens in the presence of scattering? When an atom is detected after scattering in the *direction* θ it may be an atom coming from the left after scattering over the angle $\vartheta = \theta$ into the detector. Equally well it may be an atom coming from the right after scattering over the complementary angle, $\vartheta = \pi - \theta$. Since we cannot distinguish between these two processes the corresponding waves interfere and we have to add their amplitudes.

Let us analyze how this works. Because the scattering is elastic the atoms stay in the same internal state and we only have to consider the orbital part of the motion. Adding to the incident wave a scattered part, the wavefunction for the relative motion of the pair takes the following general form,

$$\psi(\mathbf{r}) \underset{r\to\infty}{\sim} (e^{ikz} \pm e^{-ikz}) + f_{\pm}(\theta)e^{ikr}/r \qquad (0 \le \theta \le \pi/2)\,. \tag{4.43}$$

Here the first term expresses that *one* of the atoms is initially moving from left to right. Similarly, $f_{\pm}(\theta)$ expresses the probability amplitude that *one* of the two atoms is scattered in the direction θ. The substitution $\theta \to \pi - \theta$ amounts to interchanging the scattered atoms, $f_{\pm}(\pi - \theta) = \pm f_{\pm}(\theta)$, and because this does not represent a different scattering process (in both cases *one* of the atoms scatters in the direction θ) the angle θ is restricted to the interval $0 \le \theta \le \pi/2$. As any relative motion can be expanded it its partial waves, the amplitudes $f_{\pm}(\theta)$ can be obtained by term-by-term comparison of the partial wave expansion (4.9) with the asymptotic expansions of $(e^{ikz} \pm e^{-ikz})$,

$$(e^{ikz} \pm e^{-ikz}) \underset{r\to\infty}{\sim} \frac{1}{2ikr}\sum_{l=0}^{\infty}(2l+1)[1 \pm (-1)^l]P_l(\cos\theta)\left[e^{ikr} + (-1)^{l+1}e^{-ikr}\right]. \tag{4.44}$$

The expansion of e^{ikz} is given by Eq. (4.10). The expansion for e^{-ikz} is also obtained from this equation by the substitution $\theta \to \pi - \theta$ $(\cos\theta \to -\cos\theta)$ and use of the *parity rule* for the Legendre polynomials, $P_l(-u) = (-1)^l P_l(u)$ (cf. Section **??**). Comparing the terms of order l in Eqs. (4.9) and (4.44) we find for the expansion coefficients $c_l = i^l(2l+1)[1 \pm (-1)^l]e^{i\eta_l}$. Subtracting the plane wave expansion (4.44) from the expansion (4.9) we obtain for the scattered wave

$$f_{\pm}(\theta)e^{ikr}/r = \frac{e^{ikr}}{kr}\sum_l (2l+1)[1 \pm (-1)^l]e^{i\eta_l}P_l(\cos\theta)\sin\eta_l \qquad (0 \le \theta \le \pi/2)\,. \tag{4.45}$$

This implies $f_{\pm}(\theta) = f(\theta) \pm f(\pi - \theta)$ as follows with Eq. (4.17). Rewriting Eq. (4.45) we find that the scattering amplitude is represented by sum over the even (bosonic atoms) or odd (fermionic atoms) partial waves,

$$f_{\pm}(\theta) = \begin{cases} f(\theta) + f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\mathrm{even}} (2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & \text{(bosons)} \\ f(\theta) - f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\mathrm{odd}} (2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & \text{(fermions),} \end{cases} \tag{4.46}$$

with $0 \le \theta \le \pi/2$. In view of the parity of the Legendre polynomials we note that the even terms have even parity and the odd terms odd parity. Therefore, the parity of the orbital wavefunction is conserved in the collision.

4.3.2 Differential and total section

For identical atoms in the same state the scattered wave is given by

$$\psi_{sc} = |f(\theta) \pm f(\pi - \theta)|^2\, e^{ikr}/r \tag{4.47}$$

and its current density is

$$\boldsymbol{j}_r(r) = \frac{i\hbar}{2\mu} = \frac{i\hbar}{2\mu}\left(\psi_{sc}\nabla_r\psi_{sc}^* - \psi_{sc}^*\nabla_r\psi_{sc}\right) = |f(\theta) \pm f(\pi - \theta)|^2\,\frac{\mathbf{v}_r}{r^2}. \tag{4.48}$$

Throughout this section the scattering angle is restricted to the interval $0 \le \theta \le \pi/2$. Hence, the probability current $dI(\boldsymbol{\Omega}) = \boldsymbol{j}_r(r)\cdot d\mathbf{S}$ that *one* of the colliding atoms scatters through a surface element $d\mathbf{S} = r^2 d\boldsymbol{\Omega}$ in the direction $\boldsymbol{\Omega} \equiv (\theta, \phi)$ is given by $dI(\boldsymbol{\Omega}) = j_r(r)dS = v\,|f(\theta) \pm f(\pi - \theta)|^2\, d\Omega$.

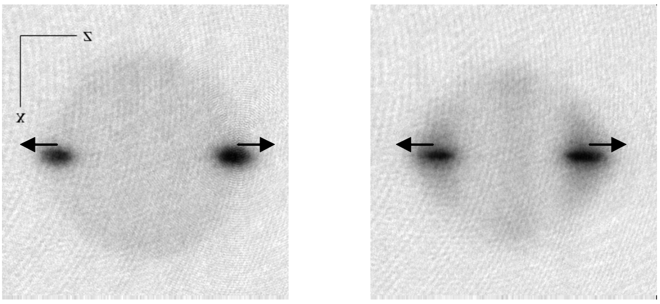

Figure 4.3: Absorption images of collision halo's of two ultracold clouds of ^{87}Rb atoms just after their collision. Left: collision energy $E/k_B = 138(4)\,\mu$K (mostly s-wave scattering), measured 2.4 ms after the collision (this corresponds to the $k \to 0$ limit discussed in this course); Right: 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).

Note that an atom observed in the direction $\mathbf{\Omega}$ must originate *either* from the incident wave e^{ikz} *or* form the incident wave e^{-ikz}. Therefore, the partial cross section for *one* of the atoms to scatter in the direction $\mathbf{\Omega}$ is given by

$$d\sigma_{\pm}(\mathbf{\Omega}) = \frac{dI(\mathbf{\Omega})}{j_z} = |f(\theta) \pm f(\pi - \theta)|^2 \, d\Omega, \tag{4.49}$$

where j_z is the current density given by Eq. (4.16), *i.e.* the current density of *one* of the incident waves. The total cross section is defined as

$$\sigma_{\pm} = \int |f(\theta) \pm f(\pi - \theta)|^2 \, d\Omega = \int_0^{\pi/2} 2\pi \sin\theta \, |f(\theta) \pm f(\pi - \theta)|^2 \, d\theta, \tag{4.50}$$

where we used $d\Omega = 2\pi \sin\theta d\theta$. After substitution of the scattering amplitude (4.46), the cross section is given by

$$\sigma_{\pm} = \frac{8\pi}{k^2} \sum_{l,l'=\text{even/odd}} (2l'+1)(2l+1) e^{i(\eta_l - \eta_{l'})} \sin\eta_{l'} \sin\eta_l \int_0^{\pi/2} P_{l'}(\cos\theta) P_l(\cos\theta) \sin\theta d\theta. \tag{4.51}$$

For the case of almost pure s-wave scattering and d-wave scattering the probability for scattering over an angle between θ and $\theta + d\theta$, $d\sigma_{\pm}(\theta) = 2\pi \sin\theta \, |f(\theta) \pm f(\pi - \theta)|^2 \, d\theta$, is illustrated in Fig. 4.3. Using the orthogonality of the Legendre polynomials Eq. (4.51) becomes

$$\sigma_{\pm} = \frac{8\pi}{k^2} \sum_{l=\text{even/odd}} (2l+1)^2 \sin^2\eta_l \int_0^{\pi/2} [P_l(\cos\theta)]^2 \sin\theta d\theta. \tag{4.52}$$

Evaluating the integral using Eq. (B.28) we obtain

$$\sigma_{\pm} = \frac{8\pi}{k^2} \sum_{l=\text{even/odd}} (2l+1) \sin^2\eta_l \quad \text{(bosons/fermions)}. \tag{4.53}$$

For a given partial wave the total cross-section is found to be either zero or twice as large as for distinguishable atoms.

4.4 Identical atoms in different internal states

Arguably more subtle situations occur 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. Interestingly, for atoms in different spin *eigenstates* the same expression for the elastic cross section is obtained as was found in Section 4.2.3 for distinguishable atoms. First we show this for the important case of spin-1/2 atoms (Section 4.4.1). In Section 4.4.2 it is generalized to the case of arbitrary half-integer nuclear spin.

4.4.1 Fermionic ${}^1S_0$ atoms with nuclear spin 1/2

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'. 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 must be anti-symmetric under exchange of complete atoms,[4]

$$\psi_{in} \underset{r\to\infty}{\sim} e^{ikz}|\Uparrow\Downarrow) - e^{-ikz}|\Downarrow\Uparrow). \tag{4.54}$$

To better reveal the relevant symmetries this expression can be rewritten in the form

$$\psi_{in} \underset{r\to\infty}{\sim} \tfrac{1}{\sqrt{2}}\left(e^{ikz} + e^{-ikz}\right)|0,0\rangle + \tfrac{1}{\sqrt{2}}\left(e^{ikz} - e^{-ikz}\right)|1,0\rangle, \tag{4.55}$$

where the state $|I, m_I\rangle$ represents the total nuclear spin state of the pair, with Clebsch-Gordan decomposition

$$|0,0\rangle = \tfrac{1}{\sqrt{2}}[|\Uparrow\Downarrow) - |\Downarrow\Uparrow)]; \qquad |1,0\rangle = \tfrac{1}{\sqrt{2}}[|\Uparrow\Downarrow) + |\Downarrow\Uparrow)]. \tag{4.56}$$

Note that 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 $i_1 = i_2 = 1/2$ 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 used in Section 4.3.1 we find for the corresponding scattering amplitudes

$$f_{\pm}(\theta) = \begin{cases} f(\theta) + f(\pi - \theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{even}} (2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I=0) \\ f(\theta) - f(\pi - \theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{odd}} (2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I=1)\,. \end{cases} \tag{4.57}$$

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[4] The curved brackets $|s_1, \cdots, s_N)$ are used for unsymmetrized many-body states with the convention of refering always in the same order to the states of particle $1, \cdots, N$. With the symbol $\Uparrow$ we refer to a nuclear spin 1/2.

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 $I = 1$, $|\uparrow\uparrow\rangle = |1,1\rangle$ and $|\downarrow\downarrow\rangle = |1,-1\rangle$, which implies that these atoms also scatter through the triplet channel.

Differential and total cross section

In view of the modern *quantum theory of measurement* the concepts of singlet- and triplet-channel must be handled with caution. The spin states (4.56) are examples of *maximally entangled states*, also known as *Bell states.*[5] By *repeated* measurement with spin-selective detectors only the probability of observing a singlet or a triplet state can determined. For ^{3}He atoms in different spin eigenstates the pair-wavefunction for the scattered wave is asymptotically given by

$$\psi_{sc} \underset{r\to\infty}{\sim} \sum_{I=0,1} \tfrac{1}{\sqrt{2}}[f(\theta) + (-1)^I f(\pi-\theta)]|I,0\rangle e^{ikr}/r \qquad (0 \le \theta \le \pi/2)\,. \tag{4.58}$$

For the same reasons as presented in Section 4.3.1 the scattering angle is restricted to the interval $0 \le \theta \le \pi/2$. The probability current density of the scattered wave is

$$\boldsymbol{j}_r(r) = \frac{i\hbar}{2\mu}\left(\psi_{sc}\nabla_r\psi_{sc}^* - \psi_{sc}^*\nabla_r\psi_{sc}\right) = \frac{1}{2}\sum_{I=0,1}\left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 |I,0\rangle\frac{\mathbf{v}_r}{r^2}. \tag{4.59}$$

The singlet-triplet cross terms drop due to the orthogonality of the singlet and triplet wavefunctions. The probability current that *one* of the colliding atoms scatters through a surface element $d\mathbf{S} = r^2 d\boldsymbol{\Omega}$ in the direction $\boldsymbol{\Omega} = (\theta,\phi)$ is given by

$$dI(\boldsymbol{\Omega}) = j_r(r)dS = \frac{1}{2}\sum_{I=0,1} v\left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 d\Omega.$$

Note that any atom observed in the direction $\boldsymbol{\Omega}$ must originate *either* from the incident wave $e^{ikz}|\uparrow\downarrow\rangle$ *or* form the incident wave $e^{-ikz}|\downarrow\uparrow\rangle$. Therefore, the partial cross sections for scattering in the direction $\boldsymbol{\Omega}$ is given by

$$d\sigma_{\uparrow\downarrow}(\Omega) = \frac{dI(\boldsymbol{\Omega})}{j_z} = \frac{1}{2}\sum_{I=0,1}\left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 d\Omega, \tag{4.60}$$

where j_z is the current density given by Eq. (4.16), *i.e.* the current density of *one* of the incident waves. The total cross section is given by

$$\sigma_{\uparrow\downarrow} = \frac{1}{2}\sum_{I=0,1}\sigma_I, \text{ where } \sigma_I = \int_0^{\pi/2} 2\pi\sin\theta\left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 d\theta. \tag{4.61}$$

Evaluating the integral like in Section 4.3.1 we obtain

$$\sigma_I = \begin{cases} \sigma_+ = \dfrac{8\pi}{k^2}\displaystyle\sum_{l=\text{even}}(2l+1)\sin^2\eta_l \quad (I=0) \\[2ex] \sigma_- = \dfrac{8\pi}{k^2}\displaystyle\sum_{l=\text{odd}}(2l+1)\sin^2\eta_l \quad (I=1)\,. \end{cases} \tag{4.62}$$

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[5] J.S. Bell, Physics **1**, 195 (1964).

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. (4.57) where we point out that two ^{3}He atoms in the same spin state also carry total spin $I = 1$. Substituting Eq. (4.62) into Eq. (4.61) we establish that the cross section is given by the average of the even (σ_+) and odd (σ_-) parity contributions,

$$\sigma_{⇡⇣} = \frac{1}{2}\left(\sigma_+ + \sigma_-\right) = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\eta_l. \tag{4.63}$$

Note that this expression coincides with the result obtained for distinguishable atoms.

To conclude this section we discuss the consequences of the above analysis for the collisions in an unpolarized gas of spin 1/2 fermionic atoms. In this case we identify four possibilities for the initial spin configurations, $|⇡⇡\rangle, |⇡⇣), |⇣⇡)$ and $|⇣⇣\rangle$, each with equal probability. Therefore, the effective cross section required to calculate for instance the thermalization rate of the gas is given by the statistical average,

$$\sigma = \tfrac{1}{4}\left(\sigma_+ + 3\sigma_-\right). \tag{4.64}$$

4.4.2 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 with arbitrary half-integer spin.[6] Aside from the spin-1/2 systems ^{3}He, ^{111}Cd and ^{113}Cd, ^{199}Hg and ^{171}Yb this class includes the spin-3/2 systems ^{9}Be, ^{21}Ne, ^{135}Ba, ^{137}Ba and ^{201}Hg, , the spin-5/2 systems ^{25}Mg,^{67}Zn and ^{173}Yb, the spin-7/2 system ^{43}Ca, and the spin-9/2 systems ^{83}Kr and ^{87}Sr. As we are dealing with fermions the pair wavefunction must be anti-symmetric under exchange of complete atoms,[7]

$$\psi_{in} \underset{r\to\infty}{\sim} e^{ikz}|m_1m_2) - e^{-ikz}|m_2m_1), \tag{4.65}$$

which can be rewritten in the form

$$\psi_{in} \underset{r\to\infty}{\sim} \tfrac{1}{2}\left(e^{ikz} + e^{-ikz}\right)\left[|m_1m_2) - |m_2m_1)\right] + \tfrac{1}{2}\left(e^{ikz} - e^{-ikz}\right)\left[|m_1m_2) + |m_2m_1)\right] \tag{4.66}$$

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 4.3)

$$\begin{aligned}\psi_{in} \underset{r\to\infty}{\sim} \left(e^{ikz} + e^{-ikz}\right)\sum_{I=\text{even}}^{I_{\max}}\sum_{M=-I}^{I}|IM\rangle\langle IM|i_1i_1m_1m_2)\\ + \left(e^{ikz} - e^{-ikz}\right)\sum_{I=\text{odd}}^{I_{\max}}\sum_{M=-I}^{I}|IM\rangle\langle IM|i_1i_1m_1m_2).\end{aligned} \tag{4.67}$$

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

$$f_\pm(\theta) = \begin{cases} f(\theta) + f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{even}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I = \text{even})\\ f(\theta) - f(\pi-\theta) = \dfrac{2}{k}\displaystyle\sum_{l=\text{odd}}(2l+1)e^{i\eta_l}P_l(\cos\theta)\sin\eta_l & (I = \text{odd}). \end{cases} \tag{4.68}$$

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[6] All stable bosonic isotopes with $^1S_0$ electronic ground state have nuclear spin $I = 0$.

[7] The curved brackets $|s_1, \cdots, s_N)$ are used for unsymmetrized many-body states with the convention of refering always in the same order to the states of particle $1, \cdots, N$. With the symbol ⇡ we refer to a nuclear spin 1/2.

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.

Differential and total cross section

The pair-wavefunction for the scattered wave is asymptotically given by

$$\psi_{sc} \underset{r\to\infty}{\sim} \sum_{I}^{I_{\max}} \sum_{M=-I}^{I} \langle IM|i_1 i_1 m_1 m_2)[f(\theta) + (-1)^I f(\pi-\theta)]|I, M\rangle e^{ikr}/r, \tag{4.69}$$

where the scattering angle is restricted to the interval $0 \leq \theta \leq \pi/2$. The probability current density of the scattered wave is

$$\begin{aligned} \boldsymbol{j}_r(r) &= \frac{i\hbar}{2\mu}\left(\psi_{sc}\nabla_r\psi_{sc}^* - \psi_{sc}^*\nabla_r\psi_{sc}\right) \\ &= \sum_{I}^{I_{\max}} \sum_{M=-I}^{I} |(i_1 i_1 m_1 m_2|IM\rangle|^2 \left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 |I, M\rangle \frac{\mathbf{v}_r}{r^2}. \end{aligned} \tag{4.70}$$

Here we used the orthogonality of the singlet and triplet wavefunctions. The probability current that *one* of the colliding atoms scatters through a surface element $d\mathbf{S} = r^2 d\boldsymbol{\Omega}$ in the direction $\boldsymbol{\Omega} = (\theta, \phi)$ is given by

$$dI(\boldsymbol{\Omega}) = j_r(r)dS = \sum_{I}^{I_{\max}} \sum_{M=-I}^{I} |(i_1 i_1 m_1 m_2|IM\rangle|^2 v \left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 d\Omega.$$

Note that any atom observed in the direction $\boldsymbol{\Omega}$ must originate *either* from the incident wave $e^{ikz}|\uparrow\downarrow)$ *or* form the incident wave $e^{-ikz}|m_1 m_2)$. Therefore, the partial cross sections for scattering in the direction $\boldsymbol{\Omega}$ is given by

$$d\sigma_{m_1 m_2}(\Omega) = \frac{dI(\boldsymbol{\Omega})}{j_z} = \sum_{I}^{I_{\max}} \sum_{M=-I}^{I} |(i_1 i_1 m_1 m_2|IM\rangle|^2 \left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 d\Omega, \tag{4.71}$$

where j_z is the current density given by Eq. (4.16), *i.e.* the current density of *one* of the incident waves. The total cross section is given by

$$\sigma_{m_1 m_2} = \sum_{I}^{I_{\max}} \sum_{M=-I}^{I} |(i_1 i_1 m_1 m_2|IM\rangle|^2 \sigma_I, \text{ where } \sigma_I = \int_0^{\pi/2} 2\pi \sin\theta \left|f(\theta) + (-1)^I f(\pi-\theta)\right|^2 d\theta. \tag{4.72}$$

Evaluating the integral like in Section 4.3.1 we obtain

$$\sigma_I = \begin{cases} \sigma_+ = \dfrac{8\pi}{k^2} \displaystyle\sum_{l=\text{even}} (2l+1)\sin^2\eta_l & (I = \text{even}) \\ \sigma_- = \dfrac{8\pi}{k^2} \displaystyle\sum_{l=\text{odd}} (2l+1)\sin^2\eta_l & (I = \text{odd}) \,. \end{cases} \tag{4.73}$$

Thus the expressions for the cross sections with $I =$ 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. (4.73) into Eq. (4.72) we establish that the cross section is given by the average of the even (σ_+) and odd (σ_-) parity contributions,

$$\sigma_{m_1 m_2} = \sum_{I=\text{even}}^{I_{\max}} \sum_{M=-I}^{I} |(i_1 i_1 m_1 m_2|IM\rangle|^2 \sigma_- + \sum_{I=\text{odd}}^{I_{\max}} \sum_{M=-I}^{I} |(i_1 i_1 m_1 m_2|IM\rangle|^2 \sigma_+. \tag{4.74}$$

The summations both yield 1/2, see Eq. (C.8), therefore Eq. (4.74) reduces to

$$\sigma_{m_1 m_2} = \frac{1}{2}\left(\sigma_- + \sigma_+\right) = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\eta_l \qquad \text{for } m_1 \neq m_2, \tag{4.75}$$

which coincides with Eq. (4.63) 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 $\{|i_1 i_1 m_1 m_2)\}$. From these possibilities we have $(2i_1+1)$ cases with $m_1 = m_2$ and cross section $\sigma_{m_1 m_1} = \sigma_-$. 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 $\sigma_{m_1 m_2} = \frac{1}{2}\left(\sigma_- + \sigma_+\right)$. Therefore, the effective elastic cross section is given by

$$\sigma = \frac{1}{(2i_1+1)^2}\sum_{m_1,m_2}\sigma_{m_1 m_2} = \frac{1}{(2i_1+1)}\left[i_1\sigma_+ + (i_1+1)\,\sigma_-\right]. \tag{4.76}$$

Problem 4.3 *Derive the following relation*

$$\tfrac{1}{2}\left[|i_1 i_1 m_1 m_2) \pm |i_1 i_1 m_2 m_1)\right] = \sum_{I=\text{even/odd}}^{2i_1}\ \sum_{M=-I}^{I}|IM\rangle\langle IM|i_1 i_1 m_1 m_2).$$

Solution: Using a Clebsch-Gordan decomposition we have

$$\begin{aligned}\tfrac{1}{2}\left[|i_1 i_1 m_1 m_2) \pm |i_1 i_1 m_2 m_1)\right] &= \frac{1}{2}\sum_{I=0}^{2i_1}\sum_{M=-I}^{I}|IM\rangle\left[\langle IM|i_1 i_1 m_1 m_2) \pm \langle IM|i_1 i_1 m_2 m_1)\right] \\ &= \frac{1}{2}\sum_{I=0}^{2i_1}\sum_{M=-I}^{I}\left[1 \pm (-1)^I\right]|IM\rangle\langle IM|i_1 i_1 m_1 m_2).\end{aligned}$$

Here we used the property $\langle IM|i_1 i_1 m_2 m_1) = -\langle IM|i_1 i_1 m_1 m_2)$. The latter summation can be rewritten as the requested expression. ▶

4.5 Scattering at low energy

4.5.1 s-wave scattering

In this section we apply the general scattering formalism to the case of cold atoms under conditions typical for quantum gases. As discussed in Section 1.5 the classical description of gases has to be replaced by a quantum mechanical description when the thermal wavelength Λ exceeds the radius of action r_0 of the interaction potential. Note that the condition $\Lambda \gg r_0$ is equivalent with the condition $kr_0 \ll 1$ for which we derived in Section 3.3.9 an expression for the phase shifts in the presence of an arbitrary short-range potential,

$$\tan\eta_l \underset{k\to 0}{\simeq} -\frac{2l+1}{\left[(2l+1)!!\right]^2}\left(ka_l\right)^{2l+1}. \tag{4.77}$$

Knowing these phase shifts we can calculate the scattering amplitudes using Eq. (4.18c),

$$f_l = \frac{1}{k}\frac{\tan\eta_l}{1 - i\tan\eta_l} \underset{k\to 0}{\simeq} -a_l\frac{2l+1}{\left[(2l+1)!!\right]^2}\left(ka_l\right)^{2l}. \tag{4.78}$$

We see that for $kr_0 \ll 1$ all partial-wave amplitudes f_l with $l \neq 0$ are small in comparison to the s-wave scattering amplitude f_0, showing that in the low-energy limit only s-waves contribute to the scattering of atoms. This may be traced back to the presence of the rotational barrier for all scattering processes with $l > 0$ (see Section 3.2.1). Under these conditions the gas is said to be in the s-wave scattering regime.

Depending on the symmetry under permutation of the scattering partners Eq. (4.78) leads to the following expressions for the total scattering amplitudes in the s-wave regime:

$$\text{unlike atoms:} \quad f(\theta) \simeq f_0 \simeq -a \tag{4.79a}$$

$$\text{identical bosons:} \quad f(\theta) + f(\pi - \theta) \simeq 2f_0 \simeq -2a \tag{4.79b}$$

$$\text{identical fermions:} \quad f(\theta) - f(\pi - \theta) \simeq 6f_1 \cos\theta \simeq -2a_1 \left(ka_1\right)^2 \cos\theta. \tag{4.79c}$$

We notice that for bosons the scattering amplitude is closely related to the s-wave scattering length a, which is the *effective hard sphere diameter* of the atoms introduced in Section 3.3.4. For fermions the lowest non-zero partial wave is the p-wave ($l = 1$), which turns out to vanish in the limit $k \to 0$. In practice this means that *fermionic quantum gases do not thermalize.*

4.5.2 Existence of the finite range r_0

In this section we derive a criterion for the existence of a finite range r_0 for potentials with long-range power-law behavior

$$\mathcal{V}(r) \underset{r\to\infty}{\simeq} -\frac{C_s}{r^s}, \tag{4.80}$$

where $C_s = \mathcal{V}_0 r_c^s$ is the Power-law coefficient, with $\mathcal{V}_0 \equiv |\mathcal{V}\left(r_c\right)|$ the 'well depth'. We start by combining Eqs. (4.18b) and (3.26) to obtain the integral expression for the s-wave scattering amplitude,

$$f_0 = k^{-1} e^{i\eta_0} \sin\eta_0 = -k^{-1} e^{i\eta_0} \frac{2\mu}{\hbar^2} \int_0^\infty \mathcal{V}(r)\chi_0(kr) j_0(kr) r dr. \tag{4.81}$$

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. (3.101) into Eq. (4.81) this contribution can be written as

$$\begin{aligned} \Delta f_0 &= k^{-1} \left(kr_c\right)^s e^{i\eta_0} \left(U_0/k^2\right) \int_{kr_0}^\infty \frac{1}{\varrho^s} \left[\sin\eta_0 \cos\varrho + \cos\eta_0 \sin\varrho\right] \sin\varrho d\varrho \\ &= k^{s-3} e^{i\eta_0} U_0 r_c^s \int_{kr_0}^\infty \frac{1}{\varrho^s} \left[\cos\eta_0 - \cos(2\varrho + \eta_0)\right] d\varrho. \end{aligned} \tag{4.82}$$

where $U_0 = 2\mu\mathcal{V}_0/\hbar^2$. Because the integral in Eq. (4.82) 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 $s > 3$.

4.5.3 Energy dependence of the s-wave scattering amplitude

To analyze the k-dependence for scattering in the s-wave regime we use expression (4.18c) to write the s-wave scattering amplitude in the form

$$f_0 = \frac{1}{k\cot\eta_0 - ik}. \tag{4.83}$$

Let us first look at the case of *hard spheres* of diameter a, where $\eta_0 = -ka$ for all collision energies (see Eq. (3.35)). Substituting this phase shift into Eq. (4.83) yields with the expansion (3.37) for the cotangent

$$f_0 = \frac{1}{k\cot(-ka) - ik} \underset{ka\ll 1}{\simeq} \frac{1}{-1/a + \frac{1}{3}ak^2 - ik}. \tag{4.84}$$

For arbitrary short-range potentials we have to substitute expression (3.107) for the s-wave phase shift into Eq. (4.83),

$$f_0 \underset{k\to 0}{\simeq} \frac{1}{-1/a + \frac{1}{2}r_e k^2 - ik}, \tag{4.85}$$

with r_e given by Eq. (3.106). This expression may be refined by taking into account the weakest bound level at energy $E_b = -\hbar^2\kappa^2/2\mu$. In this case the phase shift is given by Eq. (3.110) and

$$f_0 \underset{k\to 0}{\simeq} \frac{1}{-\kappa + \frac{1}{2}r_e\left(\kappa^2 + k^2\right) - ik} = -\frac{1}{\kappa}\frac{1}{1 - \frac{1}{2}r_e\kappa\left(1 + k^2/\kappa^2\right) + ik/\kappa} \tag{4.86}$$

Here r_e is the *effective range* defined by Eq. (3.111). For $k \ll \kappa$ we reach the $k \to 0$ limit for the scattering amplitude,

$$f_0 = -a = -\frac{1}{\kappa}\frac{1}{1 - \kappa r_e/2}. \tag{4.87}$$

In the limit *of a weakly-bound s-level* ($\kappa r_e \ll 1$) this expression simplifies to

$$f_0 \simeq -\frac{1}{\kappa} = -\sqrt{\frac{-\hbar^2}{2\mu E_b}}, \tag{4.88}$$

showing that the scattering amplitude diverges with vanishing binding energy of the bound level.

4.5.4 Expressions for the cross section in the s-wave regime

Using Eqs. (4.39) and (4.77) the cross-section for unlike atoms in the limit $k \to 0$ is found to be

$$\sigma = \frac{4\pi}{k^2}\sin^2\eta_0 \underset{k\to 0}{\approx} 4\pi a^2. \tag{4.89}$$

Similar we find, starting from Eq. (4.53), for the cross section of bosons in the $k \to 0$ limit

$$\sigma = \frac{8\pi}{k^2}\sin^2\eta_0 \underset{k\to 0}{\approx} 8\pi a^2. \tag{4.90}$$

For fermions we find

$$\sigma = \frac{8\pi}{k^2}3\sin^2\eta_1 \underset{k\to 0}{\approx} 8\pi a_1^2\left(ka_1\right)^4. \tag{4.91}$$

With Eqs. (4.89)-(4.91) we have obtained the quantum mechanical underpinning of Eq. (1.2) for the zero temperature limit ($k \to 0$). Importantly, although the interaction energy (and therefore the thermodynamics) differs dramatically depending on the sign of the scattering length a (see Section 3.4) this has no consequences for the kinetic aspects (such a the collision rate) because the cross section depends on the scattering length squared.

For the example of the spherical square well of Section 3.3.4 we have an explicit expression in the form of Eq. (3.48) for the s-wave scattering length as a function of the well depth. Substituting this expression into Eq. (4.89) the cross section can be expressed as

$$\sigma = 4\pi r_0^2\left(1 - \frac{\tan\kappa_0 r_0}{\kappa_0 r_0}\right)^2. \tag{4.92}$$

As shown in Fig. 4.4 this expression shows resonances which may be associated with the appearance of new bound states in the potential.

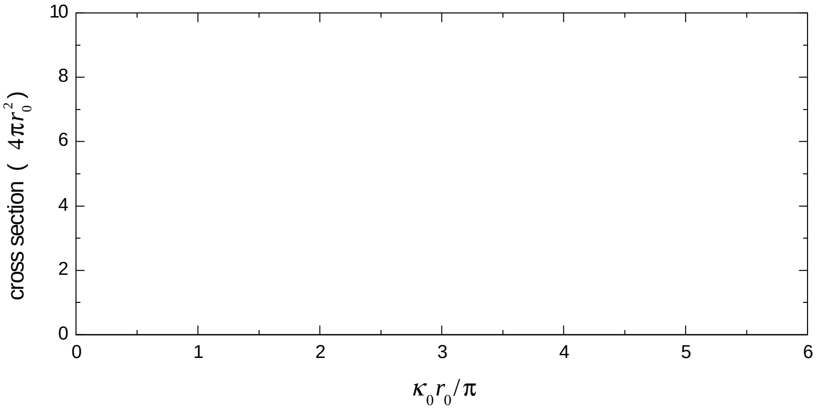

Figure 4.4: Cross section as a function of the depth of the square potential well of section 3.3.4 with the atoms treated as distinguishable. Note that the cross section equals $\sigma = 4\pi r_0^2$ except near the resonances at $\kappa_0 r_0 = (n + \frac{1}{2})\pi$ with n being an integer.

Problem 4.4 *Show that for bosons in the limit $k \to 0$ the k-dependence of the s-wave cross-section is given by*

$$\sigma \simeq \frac{8\pi a^2}{\left(1 - \frac{1}{2}k^2 a r_e\right)^2 + (ka)^2},$$

where a is the s-wave scattering length and r_e is the effective range of the interaction.
Solution: The s-wave cross section for bosons is given by

$$\sigma = \frac{8\pi}{k^2}\sin^2\eta_0 = \frac{8\pi}{k^2}\frac{1}{1+\cot^2\eta_0(k)}.$$

Substitution of the effective range result $\cot\eta_0(k) \simeq -1/ka + \frac{1}{2}kr_e$, see Eq. (3.107), directly yields the requested result. ►

4.5.5 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,

$$d\sigma(u) = \frac{8\pi}{k^2}\frac{25}{4}\sin^2\eta_2\ \left(3u^2-1\right)^2 du, \tag{4.93}$$

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

$$\sigma = \frac{8\pi}{k^2}5\sin^2\eta_2. \tag{4.94}$$

Problem 4.5 *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. (4.53). For hard-sphere bosons the low energy phase shifts are given by Eq. (3.31),

$$\eta_l \underset{k\to 0}{\sim} -(ka)^{2l+1}.$$

Hence, for $ka \ll 1$ all but the $l = 0$ phase shift vanish (to first order in ka) and

$$\sigma = \frac{8\pi}{k^2}\sin^2\eta_0 \underset{k\to 0}{\approx} 8\pi a^2. \tag{4.95}$$

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 4.6 *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 differential 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

$$f(\eta_0, \eta_2, u) = \frac{5}{2}\frac{\sin\eta_2}{\sin\eta_0}(3u^2 - 1).\ ▶$$

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 center 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 center, with or without excess energy.

In this chapter we discuss how the spin dependence of the interatomic interaction gives rise to both *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 a continuum of states. Within the *Feshbach-Fano partitioning theory* one separates the resonance due to the bound state from the background contribution of the continuum.[1] Such resonances are known in nuclear physics as Feshbach resonances and in atomic physics as Fano resonances. In molecular physics they give rise to *predissociation* of molecules in excited states or the inverse process.[2] In the context of ultracold gases they are of special importance as they allow *in situ* modification of the interactions between the atoms, in particular the scattering length.[3] The modification of the scattering length near a Feshbach resonance was pioneered by B.J. Verhaar and his group.[4]

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 internuclear distances ($\lesssim 15\ a_0$) the electrons redistribute themselves in the Coulomb field of the nuclei. As the electronic motion is fast as compared to the

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[1] H. Feshbach, Ann. Phys.(NY) **5** (1958) 357; U. Fano, *Physical Review* **124** (1961) 1866.

[2] W.C. Stwalley, *Physical Review Letters*, **37** (1976) 1628.

[3] C. Chin, R. Grimm, P. Julienne and E.Tiesinga, Rev. Mod. Phys., submitted.

[4] E. Tiesinga, B.J. Verhaar and H.T.C. Stoof, *Physical Review A*, **47** (1993) 4114.

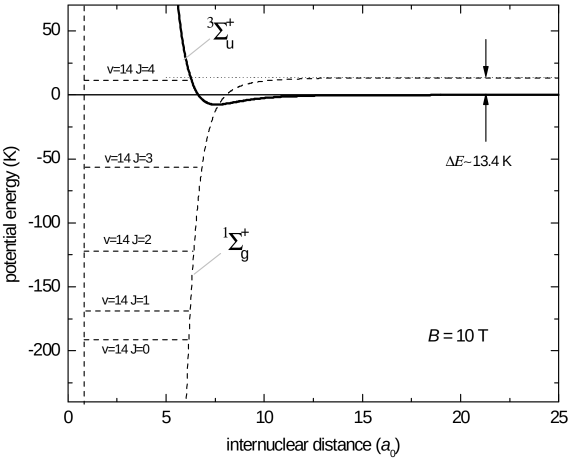

Figure 5.1: Example showing the $M_S = -1$ branch of the triplet potential $^3\Sigma_u^+$ (the 'anti-bonding' potential - solid line) which acts between two spin-polarized hydrogen atoms. Choosing the zero of energy corresponding to two spin-polarized atoms at large separation the singlet potential $^1\Sigma_g^+$ (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 inaccesible in low-temperature gases.

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 ($\Lambda = 0$).[5] 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.[6]

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. The exchange $J(r)$ may be parametrized with a function of the type[7]

$$J(r) = J_0 r^{\frac{7}{2\alpha}-1} e^{-2\alpha r}, \tag{5.2}$$

where $-\alpha^2/2$ is the atomic ionization energy and r both $\beta\alpha$ and r in atomic units. As this function decays exponentially with internuclear distance, beyond typically 15 a_0 the exchange interaction

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[5] 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.

[6] The superscript + refers to the symmetry of the orbital wavefunction under reflection with respect to a plane containing the symmetry axis.

[7] B.M. Smirnov and M.S. Chibisov, Sov. Phys. JETP **21**, 624 (1965).

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

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \tfrac{1}{2}\mathbf{S}^2 - \tfrac{3}{4} \tag{5.3}$$

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.

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 inaccesible 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.[8]

5.2.2 Radial motion in singlet and triplet potentials

To describe the relative motion in the presence of triplet and singlet potentials we follow the procedure of section 2.3, asking for eigenstates of the hamiltonian

$$\mathcal{H} = \frac{1}{2\mu}\left(p_r^2 + \frac{\mathbf{L}^2}{r^2}\right) + \mathcal{V}_S(r). \tag{5.6}$$

This hamiltonian is diagonal in the representation $\{\left|R_l^S, l, m_l\right\rangle |s_1, s_2, S, M_S\rangle\}$, where $\langle \mathbf{r}\left|R_l^S, l, m_l\right\rangle = R_l^S(r) Y_l^m(\theta, \phi)$. 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

$$\mathcal{H}_{\text{rel}} = \frac{p_r^2}{2\mu} + \frac{l\,(l+1)\,\hbar^2}{2\mu r^2} + V_s(r) + J(r)S \tag{5.7}$$

The corresponding Schrödinger equation is a radial wave equation as introduced in section 2.3, which for given values of s_1, s_2, S and l is given by

$$R''_{S,l} + \frac{2}{r}R'_{S,l} + \left[\varepsilon - U_{S,l}(r)\right] R_{S,l} = 0, \tag{5.8}$$

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[8] M.W. Reynolds, I. Shinkoda, R.W. Cline and W.N. Hardy, *Physical Review B*, **34** (1986) 4912.

with $U_{S,l}(r) = \left(2\mu/\hbar^2\right) \mathcal{V}_{S,l}(r)$ and

$$\mathcal{V}_{S,l}(r) = V_s(r) + J(r)S + \frac{l\,(l+1)\,\hbar^2}{2\mu r^2} \tag{5.9}$$

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 $R_{l,S}\,(k,r) = \langle r|R^S_{k,l}\rangle$ 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 $R_{v,l,S}\,(r) = \langle r|R^S_{v,l}\rangle$ corresponding to the bound states $|\psi^S_{v,l}\rangle$ of energy

$$\varepsilon^S_{v,l} = -\kappa^2_{v,S} + l\,(l+1)\,\mathcal{R}^S_{v,l}, \tag{5.11}$$

where $\mathcal{R}^S_{v,l} = \langle R^S_{v,l}|r^{-2}|R^S_{v,l}\rangle$ 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

$$\mathcal{H}^{\pm}_{\rm hf} = \left(a_{\rm hf1}/2\hbar^2\right)(\mathbf{s}_1 \pm \mathbf{s}_2)\cdot\mathbf{i}_1 \pm \left(a_{\rm hf2}/2\hbar^2\right)(\mathbf{s}_1 \pm \mathbf{s}_2)\cdot\mathbf{i}_2. \tag{5.15}$$

For $a_{\rm hf1} = a_{\rm hf2} = a_{\rm hf}$ these equations reduce to

$$\mathcal{H}^{\pm}_{\rm hf} = \left(a_{\rm hf}/2\hbar^2\right)(\mathbf{s}_1 \pm \mathbf{s}_2)\cdot(\mathbf{i}_1 \pm \mathbf{i}_2)\,. \tag{5.16}$$

Because $\mathcal{H}^+_{\rm hf}$ 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.* $\mathcal{H}^+_{\rm hf}$ does *not* couple singlet and triplet channels (see problem 5.1). On the other hand the term $\mathcal{H}^-_{\rm hf}$ does not conserve $\mathbf{S}$ but transforms triplet into singlet and *vice versa* (see problem 5.2).

Problem 5.1 *Show that $\mathcal{H}^+_{\rm hf}$ as defined in Eq.(5.15) does not induce singlet-triplet mixing.*

Solution: Because $\mathcal{H}_{\mathrm{hf}}^{+}$ depends on the total electronic spin $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$ we can use the inner product rule (2.32) to write Eq. (5.15) in the form

$$\mathcal{H}_{\mathrm{hf}}^{+} = \sum\nolimits_{\gamma} \left(a_{\mathrm{hf}\gamma}/2\hbar^2\right) \left\{S_Z i_{\gamma z} + \tfrac{1}{2}\left[S_+ i_{\gamma -} + S_- i_{\gamma +}\right]\right\}, \tag{5.17}$$

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.[9]

Problem 5.2 *Show that* $\mathcal{H}_{\mathrm{hf}}^{-}$ *as defined in Eq.(5.15) transforms singlet states into triplet states and vice versa.*

Solution: We first write Eq. (5.15) in the form

$$\mathcal{H}_{\mathrm{hf}}^{-} = \sum\nolimits_{\gamma} (-)^{\gamma-1} \left(a_{\mathrm{hf}\gamma}/2\hbar^2\right) \left\{(s_{1z} - s_{2z})\, i_{\gamma z} + \tfrac{1}{2}\left[(s_{1+} - s_{2+})\, i_{\gamma -} + (s_{1-} - s_{2-})\, i_{\gamma +}\right]\right\}. \tag{5.18}$$

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

$$(s_{1z} - s_{2z})\,|0,0\rangle = \hbar\,|1,0\rangle\,;\ (s_{1+} - s_{2+})\,|0,0\rangle = \hbar\,|1,1\rangle\,;\ (s_{1-} - s_{2-})\,|0,0\rangle = \hbar\,|1,-1\rangle \tag{5.19}$$

Acting on the triplet states non-zero results are obtained only in the cases

$$(s_{1z} - s_{2z})\,|1,0\rangle = (s_{1-} - s_{2-})\,|1,1\rangle = (s_{1+} - s_{2+})\,|1,-1\rangle = \hbar\,|0,0\rangle\,. \tag{5.20}$$

Hence, the $\mathcal{H}_{\mathrm{hf}}^{-}$ operator transforms triplet into singlet and *vice versa.*

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 $\left\{\left|R_l^S, l, m_l\right\rangle |s_1, s_2, S, M_S\rangle\, |i_1, i_2, m_1, m_2\rangle\right\}$ 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

$$\left|\langle S', M_S', m_1', m_2'|\langle R_l^{S'}|\mathcal{H} - E\left|R_l^S\right\rangle |S, M_S, m_1, m_2\rangle\right| = 0. \tag{5.23}$$

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 (possibly quasibound states) of the singlet $|R_{v,l}^0\rangle$

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[9] Note that $S_{\pm}\,|S, M_S\rangle = \hbar\sqrt{S\,(S+1) - M_S\,(M_S \pm 1)}\,|S, M_S \pm 1\rangle$.

potential with those of the triplet potentials, $|R^1_{v',l}\rangle$. Then, we can factor out the radial integral and using $\mathcal{H}_{\rm rel}|R^S_{v,l}\rangle = \varepsilon^S_{v,l}|R^S_{v,l}\rangle$ the secular equation becomes for given l

$$\left|{}_{l,v'}\langle S', M_S', m_1', m_2'|\mathcal{H}_Z + \mathcal{H}_{\rm hf}^+ + \langle R^{S'}_{v',l}|R^S_{v,l}\rangle\mathcal{H}_{\rm hf}^- + \varepsilon^S_{v,l} - E\,|S, M_S, m_1, m_2\rangle_{l,v}\right| = 0,$$

Note that $\langle R^{S'}_{v',l}|R^S_{v,l}\rangle\langle S'|\mathcal{H}_{\rm hf}^-|S\rangle = 0$ unless $S \neq S'$. The overlap integral $\langle R^{S'}_{v',l}|R^S_{v,l}\rangle$ is a so-called *Franck-Condon factor.*. For most combinations of vibrational levels these are small, $\langle R^0_{v',l}|R^1_{v,l}\rangle \ll 1$. 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. In such cases the singlet-triplet coupling may be neglected and the secular equation for given l reduces to the form

$$\left|{}_{l,v}\langle S, M_S', m_1', m_2'|\mathcal{H}_Z + \mathcal{H}_{\rm hf}^+ + \varepsilon^S_{v,l} - E|S, M_S, m_1, m_2\rangle_{l,v}\right| = 0. \tag{5.24}$$

This equation is solved by a diagonalization procedure. Note that Eq. (5.24) factorizes into a singlet and a triplet block. A good example of the absence of singlet-triplet coupling between bound states is the case of hydrogen, in the present context HD, because the triplet potential does not support bound states.

Asymptotic bound states

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 $|R^0_{v,l}\rangle$ is close to resonant with the binding energy of an asymptotically bound state in the triplet potential $|R^1_{v',l}\rangle$ the Franck-Condon factor of these states is close to unity, $\langle R^0_{v',l}|R^1_{v,l}\rangle \simeq 1$. In such cases the secular equation may be approximated by

$$\left|{}_{l,v'}\langle S', M_S', m_1', m_2'|\mathcal{H}_Z + \mathcal{H}_{\rm hf} + \varepsilon^S_{v,l} - E\,|S, M_S, m_1, m_2\rangle_{l,v}\right| = 0 \tag{5.25}$$

and the energy eigenvalues follow again by diagonalization. A good example of nearly complete Franck-Condon overlap is the case of ^{6}Li^{40}K.[10] 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 Pure singlet and triplet potentials modelled by spherical square wells

Let us model a two channel system with square well potentials like in section 3.3.4, with the triplet potential represented by a square well of range r_0 shown as the solid line in Fig. 5.3, with $V_t(r) = -\kappa_o^2$ for $r \leq r_0$ 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. 5.3, with $V_s(r) = -\kappa_c^2$ for $r \leq r_0$, *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.

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[10] E. Wille *et al.*, *Physical Review Letters* **100,** 053201 (2008).

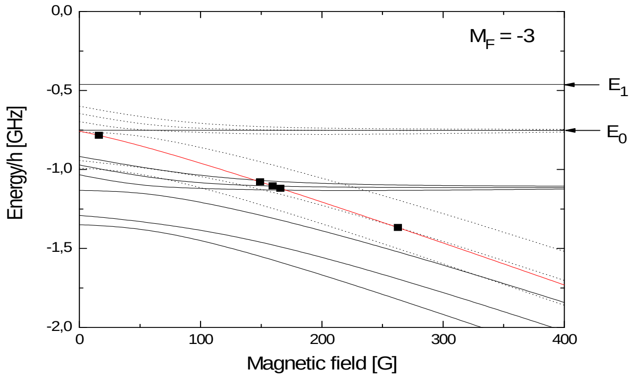

Figure 5.2: Energy levels of ^{6}Li^{40}K for the $l = 0$ (curved drawn lines) and $l = 1$ (curved dotted lines) molecular bound states as a function of magnetic field. The horizontal lines represent the highest bound states in the pure singlet (E_0) and triplet (E_1) potentials. The energy shift of the open channel of atoms in the $|^6\mathrm{Li}; 1/2, 1/2\rangle$ and $|^{40}\mathrm{P}; 9/2, -7/2\rangle$ states carry the experimental data points.

For the triplet potential the radial wave function is given by Eq. (3.45). The full radial wavefunction, including spin part, describing the motion in the open channel is written as

$$|\psi_o\rangle = \frac{\sin(kr + \eta_0)}{kr} |1, m_S\rangle \qquad \text{for } r \geq r_0 \tag{5.26a}$$

$$|\psi_o\rangle = \frac{\sin K_+ r}{K_+ r} |1, m_S\rangle \qquad \text{for } r < r_0 \tag{5.26b}$$

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[11]

$$|\psi_c\rangle = 0 \qquad \text{for } r \geq r_0 \tag{5.27a}$$

$$|\psi_c\rangle = \frac{\sin K_- r}{K_- r} |0, 0\rangle \qquad \text{for } r < r_0. \tag{5.27b}$$

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 at . 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. 5.3). 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.

5.3.2 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.[12] In the presence of this coupling the interaction operator of the previous section takes the form

$$U(r) = -\kappa_o^2 |1, m_S\rangle \langle 1, m_S| - \kappa_c^2 |0, 0\rangle \langle 0, 0| + \Omega \{|0, 0\rangle \langle 1, m_S| + |1, m_S\rangle \langle 0, 0|\} \quad \text{for } r < r_0 \tag{5.28}$$

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[11] Here we presume for simplicity $V_t(r) \to \infty$ for $r \geq r_0$.

[12] See Cheng Chin, *cond-mat*/0506313 (2005).

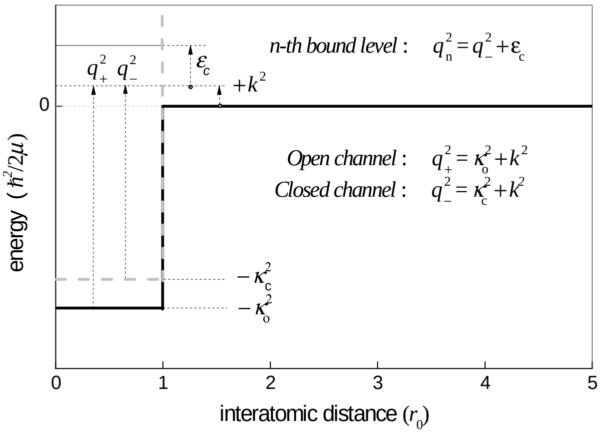

Figure 5.3: Plot of the potentials corresponding to the open (black solid line) and closed (gray dashed line) channel with related notation. The asymptote of the closed channel is presumed to be at a high positive energy and is not shown in this figure.

with $U(r) = 0$ for $r \geq r_0$. 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

$$\left[-\nabla_r^2 + U(r)\right] |\chi\rangle = \varepsilon\, |\chi\rangle \tag{5.29}$$

should be of the form

$$|\chi\rangle = A \sin qr \left\{\cos\theta\, |1, m_S\rangle + \sin\theta\, |0,0\rangle\right\} \qquad \text{for } r < r_0 \tag{5.30a}$$

$$|\chi\rangle = \sin(kr_0 + \eta_0)\, |1, m_S\rangle \qquad \text{for } r \geq r_0. \tag{5.30b}$$

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. (5.30a) into the 1D-Schrödinger equation we obtain two coupled equations

$$\langle 1, m_S| \left[-\nabla_r^2 + U(r) - k^2\right] |\chi\rangle = A \sin qr \left\{\left[q^2 - \kappa_o^2 - k^2\right] \cos\theta + \Omega \sin\theta\right\} = 0 \tag{5.31a}$$

$$\langle 0, 0| \left[-\nabla_r^2 + U(r) - k^2\right] |\chi\rangle = A \sin qr \left\{\Omega \cos\theta + \left[q^2 - \kappa_c^2 - k^2\right] \sin\theta\right\} = 0. \tag{5.31b}$$

The solutions are obtained by solving the secular equation

$$\begin{vmatrix} \left[q^2 - \kappa_o^2 - k^2\right] & \Omega \\ \Omega & \left[q^2 - \kappa_c^2 - k^2\right] \end{vmatrix} = 0, \tag{5.32}$$

which amounts to solving a quadratic equation in $\left(q^2 - k^2\right)$ and results in

$$q_\pm^2 = k^2 + \frac{1}{2}\left(\kappa_o^2 + \kappa_c^2\right) \pm \frac{1}{2}\sqrt{\left(\kappa_o^2 - \kappa_c^2\right)^2 + 4\Omega^2}. \tag{5.33}$$

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. 5.3 the two solutions can be expressed in terms of shifts with respect to the unperturbed wavenumbers

$$q_\pm^2 = K_\pm^2 \pm \frac{\Omega^2}{\left(\kappa_o^2 - \kappa_c^2\right)} + \cdots . \tag{5.34}$$

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

$$|\chi_\pm\rangle = A_\pm \sin q_\pm r \, |\pm\rangle \,, \tag{5.35}$$

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.(5.31) and notice that these equations should hold for arbitrary values of $r \leq r_0$. Using the upper equation to fix θ_+ and the lower equation to fix θ_- we find for the limit of weak coupling

$$\tan\theta_+ = \cot\theta_- = -\frac{q_\pm^2 - K_\pm^2}{\Omega} \simeq -\frac{\Omega}{(\kappa_o^2 - \kappa_c^2)}. \tag{5.36}$$

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

$$|+\rangle = +\cos\theta \, |1, m_S\rangle + \sin\theta \, |0,0\rangle \tag{5.37a}$$

$$|-\rangle = -\sin\theta \, |1, m_S\rangle + \cos\theta \, |0,0\rangle \,. \tag{5.37b}$$

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 $r \leq r_0$,

$$|\psi\rangle = A_+ \frac{\sin q_+ r}{q_+ r} \, |+\rangle + A_- \frac{\sin q_- r}{q_- r} \, |-\rangle \,. \tag{5.38}$$

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 $r \geq r_0$ the wavefunction is a pure triplet state we rewrite Eq. (5.38) 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,

$$\begin{aligned} |\psi(r)\rangle = & \left\{ A_+ \cos\theta \frac{\sin q_+ r}{q_+ r} - A_- \sin\theta \frac{\sin q_- r}{q_- r} \right\} |1, m_S\rangle + \\ & + \left\{ A_+ \sin\theta \frac{\sin q_+ r}{q_+ r} + A_- \cos\theta \frac{\sin q_- r}{q_- r} \right\} |0,0\rangle \,. \end{aligned} \tag{5.39}$$

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

$$\frac{A_-}{A_+} = -\frac{q_- \sin q_+ r_0}{q_+ \sin q_- r_0} \tan\theta. \tag{5.40}$$

Further, the amplitude $\psi_t(r)$ of the triplet component should be continuous in $r = r_0$, which implies

$$\psi_t(r_0) = \frac{\sin k(r_0 - a)}{k r_0} = A_+ \left\{ \cos\theta \frac{\sin q_+ r_0}{q_+ r_0} - \frac{A_-}{A_+} \sin\theta \frac{\sin q_- r_0}{q_- r_0} \right\}. \tag{5.41}$$

In combination with Eq. (5.40) this equation can be rewritten in a form defining the A_+ or A_- coefficients independently,

$$\frac{\sin(k r_0 + \eta_0)}{k r_0} = \frac{\sin q_+ r_0}{q_+ r_0} \frac{A_+}{\cos\theta} = -\frac{\sin q_- r_0}{q_- r_0} \frac{A_-}{\sin\theta}. \tag{5.42}$$

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

$$k\cot(kr_0 + \eta_0) = q_+ \cot q_+ r_0 \cos^2\theta + q_- \cot q_- r_0 \sin^2\theta \equiv Q_+ + Q_- = Q, \tag{5.43}$$

which reduces in the limit $k \to 0$ to

$$\frac{1}{r_0 - a} = Q_+ + Q_-. \tag{5.44}$$

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. (3.47) and approximating $\cos^2\theta \simeq 1$ and $q_+ \simeq K_+$ this term is written as

$$Q_+ = \frac{q_+ \cos^2\theta}{\tan q_+ r_0} \simeq \frac{1}{r_0 - a_{bg}}, \tag{5.45}$$

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. (5.44) 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. (5.44) 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

$$Q_- = \frac{q_- \sin^2\theta}{\tan q_- r_0} \simeq -\frac{2\kappa_c^2\theta^2}{\varepsilon_c r_0}. \tag{5.46}$$

Thus, combining Eqs.(5.45) and (5.46), we arrive at the following important expression for the scattering length:

$$\frac{1}{r_0 - a} = \frac{1}{r_0 - a_{bg}} - \frac{\gamma}{\varepsilon_c}, \tag{5.47}$$

where $\gamma = 2\kappa_c^2\theta^2/r_0$ is known as the *Feshbach coupling strength*. Eq. (5.47) 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*.

5.3.3 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

$$k\cot\eta_0 = 0 \Leftrightarrow \eta_0 = (n + \tfrac{1}{2})\pi. \tag{5.48}$$

Indeed, in this case the scattering amplitude diverges in accordance with the unitarity limit,

$$f_0 = \frac{1}{k\cot\eta_0 - ik} = -\frac{1}{ik} \tag{5.49}$$

Our first task is to obtain a criterion for the occurrence of Feshbach resonances. Writing the boundary condition (5.43) in the form

$$\eta_0 \simeq -kr_0 + \tan^{-1}\frac{k}{Q_+ + Q_-} \tag{5.50}$$

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 $|\delta k| k_{\rm res} \ll Q_{\rm res}^2 \equiv \kappa_c^2 + k_{\rm res}^2$

$$q_- \simeq [\kappa_0^2 + k_{\rm res}^2 + 2\delta k\, k_{\rm res}]^{1/2} \simeq Q_{\rm res} + \delta k\, k_{\rm res}/Q_{\rm res}. \tag{5.51}$$

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

$$\frac{k}{Q_+ + Q_-} \simeq -\frac{1}{Q_+ + \delta k\, r_0 \theta^2} \simeq \frac{-\left(k + k_{\rm res}\right)}{Q_+ + (k^2 - k_{\rm res}^2) r_0}. \tag{5.52}$$

Using this expression the resonant phase shift can be written as a function of the collision energy $E = \hbar^2 k^2 / 2\mu$

$$\tan \eta_{\rm res} = \frac{-\Gamma/2}{\delta E_{\rm res} + E - E_{\rm res}}, \tag{5.53}$$

where $\Gamma(k) = \hbar^2 \left(k + k_{\rm res}\right) / (\mu r_0 \sin \theta^2)$ is called the *width* and $E_{\rm res} - \delta E_{\rm res} = \hbar^2 k_{\rm res}^2 / 2\mu - \delta E_{\rm res}$ the *position*

$$\frac{\hbar^2 \left(k + k_{\rm res}\right)}{2\mu r_0} \frac{r_0}{(r_0 - a)}$$

we can apply the angle-addition formula for the tangent. Restricting ourselves to slow collisions ($k r_0 \ll 1$) the boundary condition becomes

$$k \cot \eta_0 = \frac{1}{r_0} \frac{Q r_0 + k^2 r_0^2 + \cdots}{1 + k^2 r_0^2 - (Q r_0 + k^2 r_0^2)(1 + \frac{1}{3} k^2 r_0^2 + \cdots)}. \tag{5.54}$$

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 $k r_0 \ll 1$. Comparing Eqs. (5.48) and (5.50) the criterion for the occurrence of a Feshbach resonance is found to be

$$Q r_0 + k^2 r_0^2 \simeq 1 + Q_- r_0 = 0. \tag{5.55}$$

Deviding Eq. (5.54) in numerator and denominator by $\left(Q + k^2 r_0 + \cdots\right)$ the boundary condition takes the form

$$k \cot \eta_0 = \frac{1}{r_0} \frac{1}{a_{res}(k) - r_0 (1 + \frac{1}{3} k^2 r_0^2 + \cdots)}, \tag{5.56}$$

where $a_{res}(k)$ is the k-dependent resonant contribution to the scattering length

$$a_{res}(k) = \frac{r_0}{1 + Q_- r_0}. \tag{5.57}$$

In this notation the scattering amplitude and the cross section are given by

$$f_0 = \frac{a_{res}(k) - r_0 (1 + \frac{1}{3} k^2 r_0^2 + \cdots)}{1 - ik[a_{res}(k) - r_0]} \tag{5.58a}$$

$$\sigma(k) = 4\pi \frac{[a_{res}(k) - r_0]^2}{1 + k^2 [a_{res}(k) - r_0]^2}. \tag{5.58b}$$

Here we used $a_{res}(k) k^2 r_0^3 \ll [a_{res}(k) - r_0]^2$. 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

$$\sigma(k) = 4\pi \frac{a^2}{1+k^2a^2}, \tag{5.59}$$

and a is given by

$$a = r_0 \left(1 - \frac{1}{1+Q_- r_0}\right). \tag{5.60}$$

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 ($\kappa_c r_0 \gg 1$) 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, $q_n r_0 = n\pi$ and accounting for the change in well depth (5.34), $-\left(\kappa_o^2 - \kappa_c^2\right)\tan^2\theta$, 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 $q_n r_0 + \frac{1}{2}\pi$ in the form

$$q_- r_0 \simeq \left(q_n r_0 + \tfrac{1}{2}\pi\right) - \tfrac{1}{2}\pi - \tfrac{1}{2}\varepsilon_n r_0/q_n - \tfrac{1}{2}\tan^2\theta\,\left(\kappa_o^2 - \kappa_c^2\right) r_0^2/q_n.$$

For very weak coupling,

$$\tfrac{1}{2}\left(\kappa_o^2 - \kappa_c^2\right) r_0^2 \frac{\tan^2\theta}{q_n r_0} \ll \tfrac{1}{2}\pi,$$

we can neglect the change in well depth and obtain

$$\begin{aligned} 1 + Q_- r_0 &= 1 + q_- r_0 \cot q_- r_0 \sin^2\theta \\ &= 1 - \tfrac{1}{2}\pi q_n r_0 \sin^2\theta + \tfrac{1}{2}\varepsilon_n r_0^2 \sin^2\theta\left(1 + \tfrac{1}{2}\varepsilon_n r_0/q_n\right), \end{aligned}$$

where the expansion of the cotangent is only valid as long as $\frac{1}{2}\varepsilon_n r_0/q_n \ll \frac{1}{2}\pi$. Furthermore, for very weak coupling, $\frac{1}{2}\pi q_n r_0 \sin^2\theta \ll 1$, we may further approximate,

$$\frac{1}{1+Q_- r_0} = \frac{\Gamma/2}{\Gamma/2 + \varepsilon_n}.$$

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 $B_0 = B_n - \Delta_B$

$$\Delta_B = \frac{\hbar^2}{2\mu}\frac{2}{r_0^2\sin^2\theta}$$

$$a = r_0\left(1 + \frac{\mu_{rel}\Delta_B}{\hbar^2k^2/2\mu - \mu_{rel}\left(B - B_0\right)}\right). \tag{5.61}$$

The phase shift is given by

$$\eta_0 = -kr_0 - \tan^{-1}\frac{kr_0\mu_{rel}\Delta_B}{\hbar^2k^2/2\mu - \mu_{rel}\left(B - B_0\right)}. \tag{5.62}$$

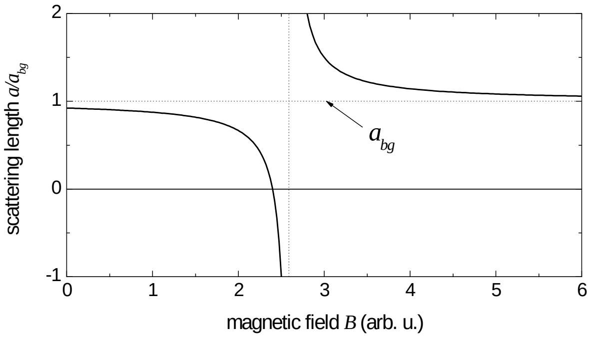

Figure 5.4: Example of the magnetic field dependence of a scattering length in the presence of a Feshbach resonance. Note that far from the resonance the scattering length attains its *background* value a_{bg}.

5.3.4 Feshbach resonances induced by magnetic fields

In general, 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 analyze this for the spin 1/2 atoms of section 5.2. 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. (5.47) can be written as

$$\frac{1}{r_0 - a} = \frac{1}{r_0 - a_{bg}} - \frac{B_\gamma}{(r_0 - a_{bg})(B - B_{res})}, \tag{5.63}$$

where we introduced $B_\gamma = \left(\hbar^2/m\right)\gamma\left(a_{bg} - r_0\right)/\mu_M$, a characteristic field reflecting the strength of the resonance and chosen to be *positive for* $a_{bg} > r_0$. Eq. (5.63) can be rewritten as

$$a = a_{bg}\left[1 + \frac{(r_0 - a_{bg})}{a_{bg}}\left(\frac{B_\gamma}{B - B_{res} + B_\gamma}\right)\right] = a_{bg}\left(1 - \frac{\Delta_B}{B - B_0}\right), \tag{5.64}$$

where $\Delta_B = B_\gamma\left(r_0 - a_{bg}\right)/a_{bg} = \left(\hbar^2/m\right)\gamma\left(a_{bg} - r_0\right)^2/a_{bg}\mu_M$ is the Feshbach resonance width, again chosen to be *positive for* $a_{bg} > r_0$, and $B_0 = B_{res} - B_\gamma$ the apparent Feshbach resonance field. Not surprisingly, in case of weak Feshbach coupling ($B_\gamma \ll B_{res}$) one has $B_0 \simeq B_{res}$ and Eq. (5.64) reduces to

$$a \simeq a_{bg}\left(1 - \frac{\Delta_B}{B - B_{res}}\right). \tag{5.65}$$

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. 5.4). 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*.

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 $d\mathbf{r}'d\mathbf{p}' = \left|\partial(\mathbf{r}', \mathbf{p}')/\partial(\mathbf{r}, \mathbf{p})\right| d\mathbf{r}d\mathbf{p}$ 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),

$$f_0(\mathbf{r},\mathbf{p},t) = n_0 \Lambda^3 \exp[-H_0(\mathbf{r},\mathbf{p})/k_B T]. \tag{6.7}$$

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 $V_e = \int \exp[-\mathcal{U}(\mathbf{r})/k_B T] d\mathbf{r}$ the effective volume and $\Lambda = (2\pi\hbar^2/mk_B T)^{1/2}$ 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 subsitution 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

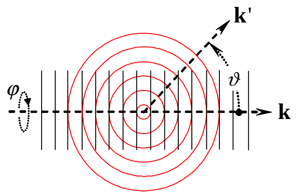

Figure 6.1: Elastic scattering of a matter wave from a centrally symmetric scattering potential in the center-of-mass-fixed coordinate system. Indicated are the scattering angle (polar angle) ϑ and the azimuthal angle φ, which defines the scattering plane.

A.1 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 distinguigh between identical bosons and identical fermions by symmetrization (+) and anti-symetization (−) 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* ($\mathbf{r} \to -\mathbf{r}$),

$$\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle = \langle -\mathbf{p}_i, -\mathbf{p}_j | T | -\mathbf{p}'_i, -\mathbf{p}'_j \rangle \quad \text{(time reversal)} \tag{6.20}$$

$$\langle \mathbf{p}'_i, \mathbf{p}'_j | T | \mathbf{p}_i, \mathbf{p}_j \rangle = \langle -\mathbf{p}'_i, -\mathbf{p}'_j | T | -\mathbf{p}_i, -\mathbf{p}_j \rangle \quad \text{(space inversion).} \tag{6.21}$$

Hence, the T matrix is also invariant under the combination of these two operations, which is the *state inversion* of initial and final states,[2]

$$\langle \mathbf{p}_i', \mathbf{p}_j' | T | \mathbf{p}_i, \mathbf{p}_j \rangle = \langle \mathbf{p}_i, \mathbf{p}_j | T | \mathbf{p}_i', \mathbf{p}_j' \rangle \qquad \text{(state inversion)}. \tag{6.22}$$

To determine the relation between the T matrix and the scattering amplitude $f(v_{ij}, \Omega')$ we make the continuum transition (1.13) 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[3]

$$R_{ij} = \frac{L^6}{4\pi^2\hbar^4} \int d\mathbf{p}' \delta(p^2/2\mu - p'^2/2\mu) \times \begin{cases} |\langle \mathbf{p}' | T | \mathbf{p} \rangle|^2 & (i \neq j) \\ |\langle \mathbf{p}' | T | \mathbf{p} \rangle \pm \langle \mathbf{p}' | T | -\mathbf{p} \rangle|^2 & (i = j)\,. \end{cases} \tag{6.28}$$

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'

$$R_{ij} = v_{ij} \int d\Omega' \sigma_{ij}(v_{ij}, \Omega'), \tag{6.29}$$

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[2] The invariance under state inversion remains valid also in the presence of spin.

[3] Recalling Eq. (1.13) we substitute $\int d\mathbf{P}' \langle \mathbf{P} | \mathbf{P}' \rangle \langle \mathbf{P}' | \mathbf{P} \rangle = (2\pi\hbar/L)^3 \int d\mathbf{P}' \langle \mathbf{P} | \mathbf{P}' \rangle \delta(\mathbf{P} - \mathbf{P}')$.

where we restaured 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 $\mathbf{r}$.[4] 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 (1.13) 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

$$\Gamma_{\mathrm{c}}^{(+)}(\mathbf{r},\mathbf{p}_i,t) = \sum_{j=1}^{\nu}\frac{1}{(2\pi\hbar)^3}\int d\mathbf{p}_j\int d\Omega'\, f_i(\mathbf{r},\mathbf{p}'_i,t)f_j(\mathbf{r},\mathbf{p}'_j,t)v_{ij}\sigma_{ij}(v_{ij},\Omega'). \tag{6.35}$$

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'.

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[4] Note that for the loss/gain contribution the primed quantities refer to the initial/final states.

6.2.4 Boltzmann equation

Combining the gain and loss terms we obtain the Boltzmann equation for component i of a ν component mixture

$$(\mathbf{v}\cdot\partial_{\mathbf{r}}+\mathbf{F}_i\cdot\partial_{\mathbf{p}_i}+\partial_t)\,f_i=\sum_{j=1}^{\nu}\frac{1}{(2\pi\hbar)^3}\int d\mathbf{p}_j d\Omega' v_{ij}\sigma_{ij}(v_{ij},\Omega')(f_i'f_j'-f_if_j). \tag{6.36}$$

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

$$\mathbf{p}_i'=(m_i/M_{ij})\,(\mathbf{p}_i+\mathbf{p}_j)+\mu_{ij}\left|\mathbf{p}_i/m_i-\mathbf{p}_j/m_j\right|\hat{\mathbf{p}}_{ij}' \tag{6.37a}$$
$$\mathbf{p}_j'=(m_j/M_{ij})\,(\mathbf{p}_i+\mathbf{p}_j)-\mu_{ij}\left|\mathbf{p}_i/m_i-\mathbf{p}_j/m_j\right|\hat{\mathbf{p}}_{ij}'. \tag{6.37b}$$

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

$$\dot{N}_i=-\sum_{j=1}^{\nu}\frac{1}{(2\pi\hbar)^6}\int d\mathbf{r}d\mathbf{p}_id\mathbf{p}_jf_i(\mathbf{r},\mathbf{p}_i,t)f_j(\mathbf{r},\mathbf{p}_j,t)v_{ij}\sigma_{ij}(v_{ij}). \tag{6.41}$$

Next we substitute the equilibrium distributions

$$f_i(\mathbf{r},\mathbf{p}_i)=n_i\Lambda_i^3e^{-H_i(\mathbf{r},\mathbf{p}_i)/k_BT}, \tag{6.42}$$

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 $\Lambda_i=(2\pi\hbar^2/m_ik_BT)^{1/2}$ the thermal wavelength, both at temperature T. Turning to center of mass and relative coordinates, $\int d\mathbf{p}_id\mathbf{p}_j=\int d\mathbf{P}d\mathbf{p}$, 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.[5] 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.[6] 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,

$$f_i(\mathbf{r}, \mathbf{p}_i, t) = n_i \Lambda_i^3 e^{-H_i(\mathbf{r}, \mathbf{p}_i)/k_BT_i}. \tag{6.47}$$

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.

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[5] Spin relaxation is an example of relaxation by inelastic collisions.

[6] 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).

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. (1.76). Because the collisions conserve the energy of the pair we obtain to first order in the deviation

$$f_1' f_2' - f_1 f_2 = f_1^{(0)} f_2^{(0)} \frac{p_2'^2 - p_2^2}{2m_2} \frac{k_B}{(k_BT)^2} \delta T\,(t)\,, \quad (6.49)$$

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.2). 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 $0 \leq \theta, \theta' \leq \pi$ 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. (1.78)

$$E_2 = \langle H_2(\mathbf{r}, \mathbf{p}_2)\rangle = (\gamma + 3/2)\, N_2 k_B T_2(t). \quad (6.53)$$

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)

$$\dot{E}_2 = \frac{\sigma_{12}}{(2\pi\hbar)^6 4\pi} \int d\mathbf{r}\, d\mathbf{p}_1 d\mathbf{p}_2 d\Omega' H_2(\mathbf{r}, \mathbf{p}_2) v_{12}(f_1' f_2' - f_1 f_2). \quad (6.55)$$

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

$$\dot{E}_2 = \frac{\pi\,\sigma_{12}\,k_B}{(2\pi\hbar)^6} \int d\mathbf{r} d\mathbf{P} p^2 dp\, f_1^{(0)} f_2^{(0)} \int_{-1}^{+1} du du' H_2(\mathbf{r}, \mathbf{p}_2) \frac{Pp^2}{\mu M}\,(u - u')\, \frac{k_B \delta T\,(t)}{(k_BT)^2}. \quad (6.57)$$

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

$$\frac{1}{\tau} = -\frac{4\pi^2\,\sigma_{12}V_{2e}n_1\Lambda_1^3 n_2\Lambda_2^3}{(2\pi\hbar)^6\,(\gamma+3/2)\,N_2\,(k_BT)^2}\int_0^\infty dPdp\, e^{-(P/\alpha)^2-(p/\beta)^2}\int_{-1}^{+1} du\frac{P^4p^5}{\mu M^2}u^2. \tag{6.60}$$

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

$$\tau_{th}^{-1} = \xi\frac{n_1\bar{v}_{rel}\sigma_{12}}{2\,(\gamma+3/2)}\frac{V_{2e}}{V_e}, \tag{6.61}$$

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

$$\tau_{th}^{-1} = \frac{\xi}{2\,(\gamma+3/2)}\tau_c^{-1}, \tag{6.62}$$

where $\xi = 4\mu/M$ a the mass-mismatch factor (cf. Appendix A.2). 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

To describe quantum gases, the classical description of a gas by a set of N points in the 6-dimensional phase space has to be replaced by the wavefunction of a quantum mechanical N-body state in Hilbert space. In parallel, to calculate the energy the classical hamiltonian has to be replaced by the Hamilton operator. In many respects the quantization is of little consequence because gas clouds are usually macroscopically large and the spacing of the energy levels is accordingly small (typically of the order of a few nK). Therefore, at all but the lowest temperatures, the discrete energy spectrum may be replaced by a quasi-classical continuum.

For one specific quantum mechanical effect, known as *indistinguishability of identical particles*, the situation is dramatically different. Two atoms are called identical if they are of the same atomic species. If all atoms of a gas are identical the Hamilton operator is invariant under permutation of any two of these atoms. As we will discuss in the present chapter this exposes an important underlying symmetry, which forces the energy eigenstates to be either *symmetric* or *antisymmetric* under exchange of two identical atoms. To distinguish between the two situations the atoms are referred to as *bosons* (symmetric) or *fermions* (antisymmetric). It will be shown that the occupation of a given single-atom state affects the probability of occupation of this state by other atoms and through this also the occupation of all other states. Under quasi-classical conditions this is of no consequence because the probability of multiple occupation is negligible. However, as soon as we reach the quantum resolution limit we have to deal with this issue, which means that new statistics - *quantum statistics* - have to be developed. In the case of fermions double occupation should be excluded (Pauli principle) whereas for bosons the normalization of the wavefunction should be adjusted to the degeneracy of occupation. Fortunately a powerful and intuitively convenient formalism has been developed to take care of these complications. This formalism is known as the *occupation number representation,* often referred to as *second quantization.*

7.2 Quantization of the gaseous state

7.2.1 Single-atom states

To introduce the physical situation we consider an external potential $\mathcal{U}(\mathbf{r})$ representing a cubic box of length L and volume $V = L^3$. 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[1]

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_k\psi_{\mathbf{k}}(\mathbf{r}), \tag{7.1}$$

where the eigenfunctions and corresponding eigenvalues are given by

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}} \text{ and } \varepsilon_k = \frac{\hbar^2k^2}{2m}. \tag{7.2}$$

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, $k = |\mathbf{k}| = 2\pi/\lambda$ the *wave number* and λ the *de Broglie wavelength.* 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 $\alpha \in \{x, y, z\}$.

7.2.2 Pair wavefunctions

The hamiltonian for the motion of two atoms with interatomic interaction $\mathcal{V}(r_{12})$ and confined by the cubic box potential $\mathcal{U}(\mathbf{r})$ defined above is given by

$$\mathcal{H} = \sum_{i=1,2}\left(-\frac{\hbar^2}{2m_i}\nabla_i^2 + \mathcal{U}(\mathbf{r}_i)\right) + \mathcal{V}(r_{12}). \tag{7.3}$$

When the cubic box $\mathcal{U}(\mathbf{r})$ is macroscopically large the pair is in the extreme collisionless limit and the dynamics may be described accurately by neglecting the interaction $\mathcal{V}(r_{12})$, *i.e.* the Schrödinger equation takes the form

$$\left(-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2\right)\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = E_{k_1,k_2}\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2). \tag{7.4}$$

In this limit we have complete separation of variables so that the pair solution can be written in the form of a product wavefunction

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V}\mathrm{e}^{i\mathbf{k}_1\cdot\mathbf{r}_1}\mathrm{e}^{i\mathbf{k}_2\cdot\mathbf{r}_2}, \tag{7.5}$$

with $\mathbf{k}_i$ the wavevector of atom i, quantized as $k_{i\alpha} = (2\pi/L)\,n_{i\alpha}$ with $n_{i\alpha} \in \{0, \pm1, \pm2, \cdots\}$. This wavefunction is normalized to unity (one pair). The energy eigenvalues are

$$E_{k_1,k_2} = \frac{\hbar^2k_1^2}{2m_1} + \frac{\hbar^2k_2^2}{2m_2}. \tag{7.6}$$

Importantly, the product wavefunctions (7.5) represent proper quantum mechanical energy eigenstates only for pairs of *unlike* atoms. By unlike we mean that the atoms may be distinguished from each other because they are of different species. For *identical* atoms the situation is fundamentally different. First of all we notice that the product wavefunctions (7.5) are degenerate with pair wavefunctions in which the atoms are exchanged, *i.e.* $E_{k_1,k_2} = E_{k_2,k_1}$. Therefore, any linear combination of the type

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V}\frac{1}{\sqrt{|c_1|^2+|c_2|^2}}(c_1\mathrm{e}^{i\mathbf{k}_1\cdot\mathbf{r}_1}\mathrm{e}^{i\mathbf{k}_2\cdot\mathbf{r}_2} + c_2\mathrm{e}^{i\mathbf{k}_1\cdot\mathbf{r}_2}\mathrm{e}^{i\mathbf{k}_2\cdot\mathbf{r}_1}) \tag{7.7}$$

represents a properly normalized energy eigenstate of the pair. However, as we shall see in the next section, only symmetric or antisymmetric linear combinations correspond to proper physical solutions. This is a profound feature of *quantum mechanical indistinguishability.*

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[1] Here we neglect the internal state of the atom.

7.2.3 Identical atoms - bosons and fermions

For two identical atoms, *i.e.* particles of the same atomic species, the pair hamiltonian is invariant under exchange of the atoms of the pair, *i.e.* the *permutation operator* $\mathcal{P}$ commutes with the hamiltonian. For identical atoms *in the same internal state* the operator $\mathcal{P}$ is defined by[2]

$$\mathcal{P}\psi(\mathbf{r}_1,\mathbf{r}_2)=\psi(\mathbf{r}_2,\mathbf{r}_1), \tag{7.8}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of the atoms. Because $\mathcal{P}$ is a *norm-conserving* operator we have $\mathcal{P}^\dagger\mathcal{P}=\mathbf{1}$, where $\mathbf{1}$ is the unit operator. Furthermore, exchanging the atoms twice must leave the wavefunction unchanged. Therefore, we have $\mathcal{P}^2=\mathbf{1}$ and writing $\mathcal{P}^\dagger=\mathcal{P}^\dagger\mathcal{P}^2=\mathcal{P}$ we see that $\mathcal{P}$ is *hermitian*, *i.e.* it has real eigenvalues, which have to be ±1 for the norm to be conserved.

Any pair wavefunction can be written as the sum of a *symmetric* $(+)$ and an *antisymmetric* $(-)$ part (cf. problem 7.1). 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*. Remarkably, in nature atoms of a given species are found to show always the same symmetry under permutation, corresponding to *only one* of the eigenvalues of $\mathcal{P}$. This important observation means that for *identical* atoms the pair wavefunction *must* be an eigenfunction of the permutation operator. In other words: linear combinations of symmetric and antisymmetric pair wavefunctions (like the simple product wavefunction) *violate* experimental observation. When the wavefunction is symmetric under exchange of two atoms the atoms are called *bosons*, when antisymmetric the atoms are called *fermions*. We do not enter in the relation between spin and statistics except from mentioning that the bosonic atoms turn out to have *integral* total (electronic plus nuclear) *spin angular momentum* and the fermions have *half-integral* total spin.

In particular, as $\mathcal{P}$ and $\mathcal{H}$ share a complete set of eigenstates, the energy eigenfunctions (7.7) must be either symmetric or antisymmetric under exchange of the atoms,

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{V}\sqrt{\tfrac{1}{2!}}\left(\mathrm{e}^{i\mathbf{k}_1\cdot\mathbf{r}_1}\mathrm{e}^{i\mathbf{k}_2\cdot\mathbf{r}_2}\pm\mathrm{e}^{i\mathbf{k}_2\cdot\mathbf{r}_1}\mathrm{e}^{i\mathbf{k}_1\cdot\mathbf{r}_2}\right). \tag{7.9}$$

For $\mathbf{k}_1\neq\mathbf{k}_2$ this form is appropriate because it is symmetric or antisymmetric depending on the $\pm$ sign and also has the proper normalization of unity, $\langle\mathbf{k}_1,\mathbf{k}_2|\mathbf{k}_1,\mathbf{k}_2\rangle=1$ (cf. problem 7.2). For $\mathbf{k}_1=\mathbf{k}_2=\mathbf{k}$ the situation is different. For two fermions Eq. (7.9) yields identically zero,

$$\psi_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)=0 \quad (\text{fermions}). \tag{7.10}$$

Thus, also its norm $|\psi_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)|^2$ is zero. Apparently two (identical) fermions cannot occupy the same state; such a coincidence is *entirely* destroyed by *interference*. This is the well-known *Pauli exclusion principle.*

For bosons with $\mathbf{k}_1=\mathbf{k}_2=\mathbf{k}$ Eq. (7.9) yields norm 2 rather than the physically required value unity. In this case the properly symmetrized and normalized wavefunction is the product wavefunction

$$\psi_{\mathbf{k},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{V}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}_1}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}_2} \quad (\text{bosons}), \tag{7.11}$$

with $\langle\mathbf{k},\mathbf{k}|\mathbf{k},\mathbf{k}\rangle=1$. Explicit symmetrization is superfluous because the product wavefunction is symmetrized to begin with. The general form (7.9) may still be used provided the normalization is corrected for the *degeneracy of occupation* (in this case we should divide by an extra factor $\sqrt{2!}$).

Thus we found that the quantum mechanical *indistinguishability* of *identical* particles affects the distribution of atoms over the single-particle states. Also the distribution of the atoms in configuration space is affected. Remarkably, these *kinematic correlations* happen in the complete absence of forces between the atoms: it is a purely *quantum statistical effect.*

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[2] In general the permutation of complete atoms requires the exchange of all position and spin coordinates. As the atoms are presumed here to be in identical internal states (including spin) only the exchange of position needs to be considered.

Problem 7.1 *Show that any wavefunction can be written as the sum of a part symmetric under permutation and a part antisymmetric under permutation.*

Solution: For any state we have $|\psi\rangle = \frac{1}{2}(\mathbf{1}+\mathcal{P})|\psi\rangle + \frac{1}{2}(\mathbf{1}-\mathcal{P})|\psi\rangle$, where $\mathcal{P}$ is the permutation operator, $\mathcal{P}^2 = \mathbf{1}$. The first term is symmetric, $\mathcal{P}(\mathbf{1}+\mathcal{P})|\psi\rangle = \left(\mathcal{P}+\mathcal{P}^2\right)|\psi\rangle = (\mathbf{1}+\mathcal{P})|\psi\rangle$, and the second term is antisymmetric, $\mathcal{P}(\mathbf{1}-\mathcal{P})|\psi\rangle = \left(\mathcal{P}-\mathcal{P}^2\right)|\psi\rangle = -(\mathbf{1}-\mathcal{P})|\psi\rangle$. ▶

Problem 7.2 *Show that Eq. (7.9) has unit normalization for* $\mathbf{k}_1 \neq \mathbf{k}_2$,

$$\mathcal{N} = \langle \mathbf{k}_1, \mathbf{k}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle = \frac{1}{V^2}\frac{1}{2}\iint_V \left| e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{-i\mathbf{k}_2\cdot\mathbf{r}_2} \pm e^{i\mathbf{k}_2\cdot\mathbf{r}_1} e^{-i\mathbf{k}_1\cdot\mathbf{r}_2} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \underset{V\to\infty}{=} 1.$$

Solution: By definition the norm is given by

$$\begin{aligned}
\mathcal{N} &= \frac{1}{V^2}\frac{1}{2}\iint_V \left| e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2} \pm e^{i\mathbf{k}_2\cdot\mathbf{r}_1} e^{i\mathbf{k}_1\cdot\mathbf{r}_2} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{1}{V^2}\frac{1}{2}\iint_V \left[2 \pm e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_1} e^{-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_2} \pm e^{-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_1} e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_2} \right] d\mathbf{r}_1 d\mathbf{r}_2 \\
&= 1 \pm \frac{1}{2}\int_V e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_1} d\mathbf{r}_1 \int_V e^{-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_2} d\mathbf{r}_2 \pm \frac{1}{2}\int_V e^{-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_1} d\mathbf{r}_1 \int_V e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_2} d\mathbf{r}_2 \\
&\underset{V\to\infty}{=} 1 \pm (2\pi)^2\,\delta(\mathbf{k}_1-\mathbf{k}_2)\,\delta(\mathbf{k}_1-\mathbf{k}_2) = 1 \quad \text{because } \mathbf{k}_1 \neq \mathbf{k}_2.
\end{aligned}$$ ▶

7.2.4 Symmetrized many-body states

Dealing with quantum gases means dealing with symmetrized many-body states. 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 $\{|\mathbf{k}\rangle_i\}$,

$${}_i\langle \mathbf{k}'|\mathbf{k}\rangle_i = \delta_{\mathbf{k},\mathbf{k}'} \quad \text{and} \quad \textstyle\sum_{\mathbf{k}} |\mathbf{k}\rangle_{i\,i}\langle \mathbf{k}| = \mathbf{1}. \tag{7.12}$$

Here $\mathbf{1}$ is the unit operator defined by $\mathbf{1}\,|\psi\rangle = 1\,|\psi\rangle$ for arbitrary $|\psi\rangle$. In principle $|\mathbf{k}\rangle_i$ 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). In practice we deal with the internal states implicitly by calling the particles identical (indistinguishable) or unlike (distinguishable). Thus, in the present context, $|\mathbf{k}\rangle_i$ only stands for the kinetic state of particle i. The wavefunctions of the Schrödinger picture are obtained as the probability amplitude to find the particle at position $\mathbf{r}_i$,

$$\psi_{\mathbf{k}}(\mathbf{r}_i) = \langle \mathbf{r}_i | \mathbf{k}\rangle_i\,. \tag{7.13}$$

For atoms in the box potential $\mathcal{U}(\mathbf{r})$ introduced earlier these wavefunctions are best chosen to be the plane waves given by Eq. (7.2); for harmonic trapping potentials they will be harmonic oscillator eigenstates, *etc.*. Also in the presence of interactions such wavefunctions remain a good basis set but the simple interpretation as eigenstates of the atoms is lost.

For the N-body system we can define a Hilbert space as the tensor product space

$$\mathbf{H}^N = \mathbf{H}_1 \otimes \mathbf{H}_2 \otimes \cdots \otimes \mathbf{H}_N$$

of the N single-particle Hilbert spaces $\mathbf{H}_i$ and spanned by the orthonormal basis $\{|\mathbf{k}_1, \cdots, \mathbf{k}_N)\}$, where

$$|\mathbf{k}_1, \cdots, \mathbf{k}_N) \equiv |\mathbf{k}_1\rangle_1 \cdots |\mathbf{k}_N\rangle_N \tag{7.14}$$

is a product state with normalization $(\mathbf{k}_1', \cdots, \mathbf{k}_N' | \mathbf{k}_1, \cdots, \mathbf{k}_N) = \delta_{\mathbf{k}_1,\mathbf{k}_1'} \cdots \delta_{\mathbf{k}_N,\mathbf{k}_N'}$ and closure

$$\sum_{\mathbf{k}_1,\cdots,\mathbf{k}_N} |\mathbf{k}_1, \cdots, \mathbf{k}_N)\,(\mathbf{k}_1, \cdots, \mathbf{k}_N| = \prod_{i=1}^{N} \Big(\sum_{\mathbf{k}_s} |\mathbf{k}_s\rangle_{i\,i}\langle \mathbf{k}_s|\Big) = \mathbf{1}.$$

The notation of curved brackets $|\mathbf{k}_1,\cdots,\mathbf{k}_N)$ is reserved for unsymmetrized many-body states, *i.e.* product states written with the convention of referring always in the same order from left to right to the states of particle 1 through N.

For identical *bosons* the N-body state has to be symmetrized.[3] This is done by summing over all permutations while correcting for the degeneracy of occupation (just like in the two-body case) in order to maintain unit normalization,[4]

$$|\mathbf{k}_1,\mathbf{k}_1,\cdots,\mathbf{k}_l\rangle \equiv \sqrt{\frac{1}{N!n_1!\cdots n_l!}}\sum_{\mathcal{P}} \underbrace{|\mathbf{k}_1\rangle_1\,|\mathbf{k}_1\rangle_2\cdots}_{n_1}\underbrace{|\mathbf{k}_2\rangle_{n_1+1}\cdots}_{n_2}\cdots\underbrace{\cdots|\mathbf{k}_l\rangle_N}_{n_l}, \tag{7.15}$$

where we could have written more compactly $|\mathbf{k}_1,\mathbf{k}_1,\cdots,\mathbf{k}_2,\cdots,\mathbf{k}_l)$ for the unsymmetrized product states. To adhere to the ordering convention we permute the states rather than the atom index. Note that in the fully symmetric form there is no significance in the order in which the states are written. This property only holds for bosons.

As an example 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.* $|\mathbf{k}_s,\cdots,\mathbf{k}_s\rangle = |\mathbf{k}_s,\cdots,\mathbf{k}_s)$.

For identical *fermions* the N-body state has to be antisymmetric

$$|\mathbf{k}_1,\cdots,\mathbf{k}_N\rangle = \sqrt{\frac{1}{N!}}\sum_{\mathcal{P}}(-1)^{\mathcal{P}}\,|\mathbf{k}_1\rangle_1\cdots|\mathbf{k}_N\rangle_N\ . \tag{7.16}$$

This expression represents a $N\times N$ determinant, which is known as the *Slater* determinant. It is indeed antisymmetric because a determinant changes sign under exchange of any two columns or rows. Furthermore, a determinant is identically zero if two columns or two rows are the same. Therefore, in accordance with the Pauli principle no two fermions are found in the same state.

The notation of symmetrized states can be further compacted by listing only the occupations of the states,

$$|n_1,n_2,\cdots,n_l\rangle \equiv |\mathbf{k}_1,\mathbf{k}_1,\cdots,\mathbf{k}_2,\mathbf{k}_2,\cdots,\cdots,\mathbf{k}_l\rangle\,. \tag{7.17}$$

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 same notation is used 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. (7.15) and (7.16) the number states (7.17) have normalization

$$\langle n_1',n_2',\cdots|n_1,n_1,\cdots\rangle = \delta_{n_1,n_1'}\delta_{n_2,n_2'}\cdots \tag{7.18}$$

and closure

$$\textstyle\sum_{n_1,n_2\cdots}'|n_1,n_2,\cdots\rangle\,\langle n_1,n_2,\cdots| = \mathbf{1}, \tag{7.19}$$

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 $\mathbf{H}^N$.

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[3] The adjective *identical* appears because in our notation we omit the spin coordinates. The word has become practice in the literature to indicate that the particles are in the same spin state, *i.e.* for atoms hyperfine state.

[4] We use the convention in which all classically defined permutations are included in the summation. In an alternative convention the permutations of atoms in identical states are omitted. This results in a different normalization factor in the definition of the same symmetrized state.

7.3 Occupation number representation

7.3.1 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

$$\hat{n}_s \left| n_s, n_t, \cdots, n_l \right\rangle = n_s \left| n_s, n_t, \cdots, n_l \right\rangle . \tag{7.20}$$

With this definition the expectation value of $\hat{n}_s$ is *exclusively* determined by the occupation of state $|s\rangle$; it is independent of 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 this 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 (7.17) 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 $|\gamma\rangle = |q, q, t, \cdots, l\rangle$.

The basic operators in Grand Hilbert space are the *construction operators* defined as

$$\hat{a}_s^\dagger \left| n_s, n_t, \cdots, n_l \right\rangle \equiv \sqrt{n_s + 1} \left| n_s + 1, n_t, \cdots, n_l \right\rangle \tag{7.21a}$$

$$\hat{a}_s \left| n_s, n_t, \cdots, n_l \right\rangle \equiv \sqrt{n_s} \left| n_s - 1, n_t, \cdots, n_l \right\rangle , \tag{7.21b}$$

where the $\hat{a}_s^\dagger$ and $\hat{a}_s$ are known as *creation* and *annihilation* operators, respectively. The creation operators transform a symmetrized N-body eigenstate in $\mathbf{H}^N$ into a symmetrized $N+1$ body eigenstate in $\mathbf{H}^{N+1}$. Analogously, the annihilation operators transform a symmetrized N-body eigenstate in $\mathbf{H}^N$ into a symmetrized $N-1$ body eigenstate 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,

$$\langle n_s + 1 | \hat{a}_s^\dagger \left| n_s \right\rangle = \langle n_s | \hat{a}_s \left| n_s + 1 \right\rangle^* = \sqrt{n_s + 1}.$$

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,

$$\hat{a}_s^\dagger \left| n_q, \cdots, 1_s, \cdots, n_l \right\rangle = 0. \tag{7.22}$$

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 $\mathcal{P}$ between *occupied* states to bring the occupation number to the most left position in the fermion state vector,

$$\hat{a}_s^\dagger \left| 1_q, \cdots, 0_s, \cdots \right\rangle = (-1)^{\mathcal{P}} \left| 1_q, \cdots, 1_s, \cdots \right\rangle \tag{7.23a}$$

$$\hat{a}_s \left| 1_q, \cdots, 1_s, \cdots \right\rangle = (-1)^{\mathcal{P}} \left| 1_q, \cdots, 0_s, \cdots \right\rangle . \tag{7.23b}$$

For example $\hat{a}_s^\dagger \left| 0_q, 0_s, \cdots \right\rangle = + \left| 0_q, 1_s, \cdots \right\rangle$, $\hat{a}_s^\dagger \left| 1_q, 0_s, \cdots \right\rangle = - \left| 1_q, 1_s, \cdots \right\rangle$, $\hat{a}_s \left| 0_q, 1_s, \cdots \right\rangle = \left| 1_q, 0_s, \cdots \right\rangle$ 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 $\hat{a}_s^{\dagger}$,

$$\left(\hat{a}_s^{\dagger}\right)^{n_s}|0_s,n_t,\cdots\rangle=\sqrt{n_s!}\,|n_s,n_t,\cdots\rangle\,. \tag{7.24}$$

The notation can even be further compacted by using many-body state vectors $|\gamma\rangle$ and many-body state occupations $|\tilde{n}_\gamma\rangle\equiv|n_q,n_t,\cdots,n_l\rangle$. For instance, the state $|\gamma\rangle=|q,q,t,\cdots,l\rangle$ corresponds to $|\tilde{n}_\gamma\rangle=|2_q,1_t,\cdots,1_l\rangle$. By straightforward generalization of Eq. (7.24) *any* number state $|\tilde{n}_\gamma\rangle$ can be created by repetitive use of a set of creation operators

$$|\tilde{n}_\gamma\rangle=\prod_{s\in\gamma}\frac{\left(\hat{a}_s^{\dagger}\right)^{n_s}}{\sqrt{n_s!}}\,|0\rangle\,. \tag{7.25}$$

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 $|s\rangle$

$$|s\rangle\equiv|1_s\rangle\equiv|\tilde{1}_s\rangle=\hat{a}_s^{\dagger}\,|0\rangle\,. \tag{7.26}$$

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 may be obtained with any 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 (7.19) the restricted sum may be replaced by an *unrestricted* sum, thus allowing for all possible values of N,

$$\textstyle\sum_\gamma|\tilde{n}_\gamma\rangle\langle\tilde{n}_\gamma|=\sum_{n_1,n_2\cdots}|n_1,n_2,\cdots\rangle\langle n_1,n_2,\cdots|=\mathbf{1}. \tag{7.27}$$

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 7.4). Further we can derive the following commutation relations for bosons $(-)$ and anticommutation relations for fermions $(+)$:[5]

$$\left[\hat{a}_q,\hat{a}_s^{\dagger}\right]_{\pm}=\delta_{qs}\ ;\quad\left[\hat{a}_q,\hat{a}_s\right]_{\pm}=\left[\hat{a}_q^{\dagger},\hat{a}_s^{\dagger}\right]_{\pm}=0, \tag{7.28}$$

For *both bosons and fermions* we have

$$\left[\hat{n}_q,\hat{a}_s^{\dagger}\right]=+\hat{a}_s^{\dagger}\delta_{qs}\ ;\quad\left[\hat{n}_q,\hat{a}_s\right]=-\hat{a}_s\delta_{qs}\,. \tag{7.29}$$

Problem 7.3 *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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[5] 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

$$\begin{aligned}\left[\hat{a}_s, \hat{a}_s^\dagger\right] |n_s, \cdots\rangle &= \hat{a}_s\sqrt{n_s+1}\,|n_s+1, \cdots\rangle - \hat{a}_s^\dagger\sqrt{n_s}\,|n_s-1, \cdots\rangle \\ &= (n_s+1)\,|n_s, \cdots\rangle - n_s\,|n_s, \cdots\rangle \\ &= |n_s, \cdots\rangle\,. \ \blacktriangleright\end{aligned}$$

Problem 7.4 *Show that the occupation number operator can be expressed as*

$$\hat{n}_s = \hat{a}_s^\dagger \hat{a}_s. \tag{7.30}$$

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 7.5 *Show that for both bosons and fermions the following commutation relation holds*

$$\left[\hat{n}_q, \hat{a}_s^\dagger\right] = +\hat{a}_s^\dagger\delta_{qs}.$$

7.3.2 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

$$G = \sum_i g^{(i)} + \frac{1}{2!}\sum_{i,j}{}' g^{(i,j)} + \frac{1}{3!}\sum_{i,j,k}{}' g^{(i,j,k)} + \cdots, \tag{7.31}$$

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 (1.5) 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 *replacement operator*

$$A_{s's} \equiv \textstyle\sum_i |s'\rangle_{ii}\langle s|\,. \tag{7.32}$$

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

$$A_{s's} \equiv \textstyle\sum_i |s'\rangle_{ii}\langle s| \quad \Rightarrow \quad \hat{A}_{s's} = \hat{a}_{s'}^\dagger\hat{a}_s. \tag{7.33}$$

Although this extension may be intuitively clear it is better characterized by 'misleadingly simple'. In this respect the proof in problem 7.6 may speak for itself. The full complexity of the symmetrization procedure is contained in an algebra in which we only create and annihilate particles. The role of the permutation operator is absorbed in the properties of the construction operators, in particular their commutation relations. The extension of the two-body replacement operator is given by

$$A_{s't'ts} \equiv \sum_{i,j}{}' |s'\rangle_j\,|t'\rangle_{ii}\langle t|_j\langle s| \quad \Rightarrow \quad \hat{A}_{s't'ts} = \hat{a}_{s'}^\dagger\hat{a}_{t'}^\dagger\hat{a}_t\hat{a}_s, \tag{7.34}$$

where the primed summation symbol implies $i \neq j$. The extensions $\hat{A}_{s't'ts} = \hat{a}_{s'}^{\dagger}\hat{a}_{t'}^{\dagger}\hat{a}_t\hat{a}_s$ of the two-body replacement operator, $\hat{A}_{t's'u'uts} = \hat{a}_{s'}^{\dagger}\hat{a}_{t'}^{\dagger}\hat{a}_{u'}^{\dagger}\hat{a}_u\hat{a}_t\hat{a}_s$ of the three-body replacement 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 (7.12) this expression can be rewritten as

$$G^{(1)} = \sum_{i=1}^{N}\left(\sum_{s'}|s'\rangle_{ii}\langle s'|\right) g^{(i)} \left(\sum_{s}|s\rangle_{ii}\langle s|\right) = \sum_{s's}\langle s'|\, g^{(1)}\,|s\rangle \sum_{i=1}^{N}|s'\rangle_{ii}\langle s|\,. \tag{7.35}$$

The index i on the matrix element ${}_i\langle s'|\, g^{(i)}\,|s\rangle_i$ was dropped because the corresponding integral yields the same value $\langle s'|\, g^{(1)}\,|s\rangle$ for all atoms. Recognizing the replacement operator $A_{s's} \equiv \sum_i |s'\rangle_{ii}\langle s|$ in Eq. (7.35) we have established that the extension of the operator $G^{(1)}$ is given by

$$\hat{G}^{(1)} = \sum_{s's}\hat{a}_{s'}^{\dagger}\,\langle s'|\, g^{(1)}\,|s\rangle\,\hat{a}_s. \tag{7.36}$$

Using the same approach for the pair terms and the three-body terms we obtain for the extension of the full operator G into the Grand Hilbert space,

$$\hat{G} = \sum_{s's}\hat{a}_{s'}^{\dagger}\,\langle s'|\, g^{(1)}\,|s\rangle\,\hat{a}_s \tag{7.37a}$$

$$+\frac{1}{2!}\sum_{t't}\sum_{s's}\hat{a}_{s'}^{\dagger}\hat{a}_{t'}^{\dagger}(s',t'|g^{(1,2)}|s,t)\hat{a}_t\hat{a}_s \tag{7.37b}$$

$$+\frac{1}{3!}\sum_{u'u}\sum_{t't}\sum_{s's}\hat{a}_{s'}^{\dagger}\hat{a}_{t'}^{\dagger}\hat{a}_{u'}^{\dagger}(s',t',u'|g^{(1,2,3)}|s,t,u)\hat{a}_u\hat{a}_t\hat{a}_s+\cdots\,. \tag{7.37c}$$

This expression, $\hat{G} = G^{(1)} + G^{(2)} + G^{(3)} + \cdots$, is the central operator to calculate expectation values in many-body systems, *including the effects of interactions between the particles.*

It is important to note the order in which the construction operators appear. Because the matrix element is non-symmetrized the indices s and s' are attached to particle 1, 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 $\hat{a}_{s'}^{\dagger}, \hat{a}_{t'}^{\dagger}, \hat{a}_{u'}^{\dagger}$ commute. For fermions, however this is not the case and mistakes in the order of the operators can give rise to sign errors.

Problem 7.6 *Show that the extension of the replacement 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 7.2.4. 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 $s \in \{1, 2, \cdots l\}$. In this notation the replacement operator is written as $A_{21} = \sum_i |\mathbf{k}_2\rangle_{i\,i}\langle\mathbf{k}_1|$. It acts on the number state $|n_1, n_2, \cdots, n_l\rangle$ defined for bosons through (7.17) by the N-body state given in Eq. (7.15), replacing all particles in state $|\mathbf{k}_1\rangle$ by particles in state $|\mathbf{k}_2\rangle$,

$$A_{21}\,|n_1, n_2, \cdots, n_l\rangle = n_1\sqrt{\frac{1}{N!n_1!\cdots n_l!}}\sum_{\mathcal{P}}\underbrace{|\mathbf{k}_1\rangle_1\,|\mathbf{k}_1\rangle_2\cdots}_{n_1-1}\underbrace{|\mathbf{k}_2\rangle_i\,|\mathbf{k}_2\rangle_{n_1+1}\cdots}_{n_2+1}\cdots|\mathbf{k}_l\rangle_N \tag{7.38a}$$

$$= \sqrt{n_2+1}\sqrt{n_1}\,|n_1-1, n_2+1, \cdots, n_l\rangle\,. \tag{7.38b}$$

Note that term i of the replacement operator only yields a non-zero result if particle i is in state $|\mathbf{k}_1\rangle$. This follows directly from the orthonormality relations (7.12), $|\mathbf{k}_2\rangle_{i\,i}\langle\mathbf{k}_1|\mathbf{k}_s\rangle_i = |\mathbf{k}_2\rangle_i\,\delta_{s,1}$. 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. (7.38a) results for every value of $\mathcal{P}$ from a different subset of n_1 terms from the replacement operator. Note that if the state $|\mathbf{k}_1\rangle$ is not occupied at all the operator A_{21} is orthogonal to the number state and the procedure yields zero. Hence, in view of the definitions (7.21) we infer from Eq. (7.38b) 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 replacement 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.

For fermions we use a number state defined by the antisymmetric state (7.16):

$$A_{s's}\,|1_1,\cdots,1_s,\cdots,1_N\rangle = \sqrt{\frac{1}{N!}}\sum_{\mathcal{P}}(-1)^{\mathcal{P}}\,|\mathbf{k}_1\rangle_1\cdots|\mathbf{k}'_s\rangle_i\cdots|\mathbf{k}_N\rangle_N = |1_1,\cdots,1_{s'},\cdots,1_N\rangle\,.$$

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 $\hat{A}_{s's} = \hat{a}_s^\dagger \hat{a}_s$,

$$\begin{aligned}\hat{A}_{s's}\,|1_1,\cdots,1_s,\cdots,1_N\rangle &= (-1)^{\mathcal{P}}\hat{a}_{s'}^\dagger \hat{a}_s\,|1_s,1_1,\cdots,1_N\rangle \\ &= (-1)^{\mathcal{P}}\,|1_{s'},\cdots,1_N\rangle = |1_1,\cdots,1_{s'},\cdots,1_N\rangle\,,\end{aligned}$$

where $\mathcal{P}$ is the permutation that brings the column containing all particles in state $|\mathbf{k}_s\rangle$ to the first position in the bracket. ▶

7.3.3 Example: The total number operator

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 $\mathbf{1}$ summed over all particles of a system,

$$N = \sum_{i=1}^{N}\mathbf{1}.$$

In the notation of the previous section the one-body operator in this example is $g^{(1)} = \mathbf{1}$ and the more-body operators are all zero, *i.e.* $g^{(\nu)} = 0$ for $\nu \geq 2$. By substitution into Eq. (7.37) we obtain

$$\hat{N} = \sum_{s's}\hat{a}_{s'}^\dagger\,\langle s'|\,\mathbf{1}\,|s\rangle\,\hat{a}_s = \sum_{s's}\hat{a}_{s'}^\dagger \hat{a}_s \delta_{s's}$$

and substituting $\hat{n}_s = \hat{a}_s^\dagger \hat{a}_s$ the extension of the total number operator into Grand Hilbert space is found to be

$$\hat{N} = \sum_s \hat{n}_s.$$

7.3.4 The hamiltonian in the occupation number representation

As an important application of the many-body formalism we consider the hamiltonian

$$\mathcal{H} = \sum_i\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 + \mathcal{U}(\mathbf{r}_i)\right) + \frac{1}{2}\sum_{i,j}{}'\mathcal{V}(r_{ij}), \tag{7.39}$$

representing a gas of N atoms interacting pair-wise through the central potential $\mathcal{V}(r)$ and trapped in an external potential $\mathcal{U}(\mathbf{r})$. In the language of the previous section the one-body contribution to the Hamilton operator is

$$g^{(1)} = \mathcal{H}^{(1)}(\mathbf{p},\mathbf{r}) = \mathcal{H}_0(\mathbf{p},\mathbf{r}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \mathcal{U}(\mathbf{r}). \tag{7.40}$$

The two-body contribution is

$$g^{(1,2)} = \mathcal{H}^{(1,2)}(\mathbf{r}_1,\mathbf{r}_2) = \mathcal{V}(|\mathbf{r}_1 - \mathbf{r}_2|), \tag{7.41}$$

and because we only consider binary interaction all more-body contributions are zero, *i.e.* $g^{(\nu)} = 0$ for $\nu \geq 3$. Thus, according to Eq. (7.37), the extension of the hamiltonian to the occupation number representation is given by the expression

$$\hat{H} = \sum_{s,s'} \hat{a}^\dagger_{s'} \langle s'| \mathcal{H}^{(1)} |s\rangle \, \hat{a}_s + \frac{1}{2}\sum_{t,t'}\sum_{s,s'} \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}(s',t'|\mathcal{H}^{(1,2)}|s,t)\hat{a}_t\hat{a}_s. \tag{7.42}$$

This expression can be simplified by turning to a specific representation in which the occupation numbers refer to the eigenstates $|s\rangle$ of $\mathcal{H}_0$ defined by

$$\mathcal{H}_0 \,|s\rangle = \varepsilon_s \,|s\rangle \,.$$

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 the extension becomes

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} = \sum_s \varepsilon_s \hat{n}_s + \frac{1}{2}\sum_{t,t'}\sum_{s,s'} \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}(s',t'|\mathcal{V}(r_{12})|s,t)\hat{a}_t\hat{a}_s. \tag{7.43}$$

For an ideal gas the expression further simplifies to

$$\hat{H} = \hat{H}^{(1)} = \sum_s \varepsilon_s \hat{n}_s, \tag{7.44}$$

as could be written down without much knowledge of the underlying formalism.

It very instructive to proceed to the interaction term in Eq. (7.42). Because the interaction potential $\mathcal{V}(|\mathbf{r}_1 - \mathbf{r}_2|)$ depends on position we evaluate $\hat{H}^{(2)}$ in the position representation,

$$\hat{H}^{(2)} = \frac{1}{2}\sum_{t,t' s,s'} \int d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}_1 d\mathbf{r}_2 \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}(s',t'|\mathbf{r}'_1,\mathbf{r}'_2)(\mathbf{r}'_1,\mathbf{r}'_2|\mathcal{V}(|\underline{\mathbf{r}}_1 - \underline{\mathbf{r}}_2|)|\mathbf{r}_1,\mathbf{r}_2)(\mathbf{r}_1,\mathbf{r}_2|s,t)\hat{a}_t\hat{a}_s. \tag{7.45}$$

Here we emphasized in the notation that $\underline{\mathbf{r}}$ is a *position operator* defined by $\underline{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}\,|\mathbf{r}\rangle$, where $|\mathbf{r}\rangle$ is the *position state* representing a single-particle at position $\mathbf{r}$. Since the operator $\mathcal{V}(|\underline{\mathbf{r}}_1 - \underline{\mathbf{r}}_2|)$ is diagonal in the position representation we have

$$\hat{H}^{(2)} = \frac{1}{2}\sum_{t,t' s,s'} \int d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}_1 d\mathbf{r}_2 \hat{a}^\dagger_{s'}\hat{a}^\dagger_{t'}\langle t'|\mathbf{r}'_2\rangle\langle s'|\mathbf{r}'_1\rangle\mathcal{V}(|\mathbf{r}_1 - \mathbf{r}_2|)\langle \mathbf{r}'_1|\mathbf{r}_1\rangle\langle \mathbf{r}'_2|\mathbf{r}_2\rangle\langle \mathbf{r}_2|t\rangle\langle \mathbf{r}_1|s\rangle\hat{a}_t\hat{a}_s, \tag{7.46}$$

where $\mathcal{V}(|\mathbf{r}_1 - \mathbf{r}_2|)$ is not an operator but a function of the positions $\mathbf{r}_1$ and $\mathbf{r}_2$. 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. (7.46) reduces to

$$\hat{H}^{(2)} = \frac{1}{2}\sum_{t,t' s,s'} \int d\mathbf{r}_1 d\mathbf{r}_2 \hat{a}^\dagger_{s'}\varphi^*_{s'}(\mathbf{r}_1)\hat{a}^\dagger_{t'}\varphi^*_{t'}(\mathbf{r}_2)\mathcal{V}(|\mathbf{r}_1 - \mathbf{r}_2|)\hat{a}_t\varphi_t(\mathbf{r}_2)\hat{a}_s\varphi_s(\mathbf{r}_1). \tag{7.47}$$

Note that the indices s and s' (t and t') are attached to particle 1 (2).

7.3.5 Momentum representation in free space

A case of special importance is the homogeneous system, where the wavefunctions are given by plane waves,

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{7.48}$$

$$\hat{H}^{(2)} = \frac{1}{2}\sum_{\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2'} \hat{a}^\dagger_{\mathbf{k}_1'}\hat{a}^\dagger_{\mathbf{k}_2'}\hat{a}_{\mathbf{k}_2}\hat{a}_{\mathbf{k}_1}\frac{1}{V^2}\int d\mathbf{r}_1 d\mathbf{r}_2 e^{i\left(\mathbf{k}_1-\mathbf{k}_1'\right)\cdot\mathbf{r}_1} e^{i\left(\mathbf{k}_2-\mathbf{k}_2'\right)\cdot\mathbf{r}_2}\mathcal{V}(|\mathbf{r}_1-\mathbf{r}_2|). \tag{7.49}$$

Turning to center of mass and relative coordinates, $\mathbf{r}_1 = \mathbf{R} + \mathbf{r}/2$ and $\mathbf{r}_2 = \mathbf{R} - \mathbf{r}/2$, this expression becomes

$$\hat{H}^{(2)} = \frac{1}{2}\sum_{\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2'} \hat{a}^\dagger_{\mathbf{k}_1'}\hat{a}^\dagger_{\mathbf{k}_2'}\hat{a}_{\mathbf{k}_2}\hat{a}_{\mathbf{k}_1}\frac{1}{V^2}\int d\mathbf{R} e^{i\left(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_1'-\mathbf{k}_2'\right)\cdot\mathbf{R}}\int d\mathbf{r} e^{i\left(\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_1'+\mathbf{k}_2'\right)\cdot\mathbf{r}/2}\mathcal{V}(r), \tag{7.50}$$

which is zero unless the operator conserves momentum

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2'. \tag{7.51}$$

Hence,

$$\hat{H}^{(2)} = \frac{1}{2}\sum_{\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2} \hat{a}^\dagger_{\mathbf{k}_1'}\hat{a}^\dagger_{\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_1'}\hat{a}_{\mathbf{k}_2}\hat{a}_{\mathbf{k}_1}\frac{1}{V}\int d\mathbf{r} e^{i\left(\mathbf{k}_1-\mathbf{k}_1'\right)\cdot\mathbf{r}}\mathcal{V}(r), \tag{7.52}$$

In the limit $k_1 r_0, k_1' r_0 \ll 1$ the exponent is unity except for distances $r \gg r_0$ where the potential vanishes. Therefore, in this limit Eq.() may be replaced by reduces to

$$\hat{H}^{(2)} = \frac{1}{2}\sum_{\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2} \hat{a}^\dagger_{\mathbf{k}_1'}\hat{a}^\dagger_{\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_1'}\hat{a}_{\mathbf{k}_2}\hat{a}_{\mathbf{k}_1}\frac{1}{V}\int d\mathbf{r}\mathcal{V}(r), \tag{7.53}$$

7.4 Field operators

Introducing the operator densities

$$\hat{\psi}(\mathbf{r}) \equiv \sum_s \varphi_s(\mathbf{r})\hat{a}_s \tag{7.54a}$$

$$\hat{\psi}^\dagger(\mathbf{r}) \equiv \sum_s \varphi_s^*(\mathbf{r})\hat{a}_s^\dagger \tag{7.54b}$$

Eq. (7.47) can be further simplified to the form

$$\hat{H}^{(2)} = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \mathcal{V}(|\mathbf{r}_1-\mathbf{r}_2|)\hat{\psi}^\dagger(\mathbf{r}_1)\hat{\psi}^\dagger(\mathbf{r}_2)\hat{\psi}(\mathbf{r}_2)\hat{\psi}(\mathbf{r}_1), \tag{7.55}$$

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. (7.55). The operator densities $\hat{\psi}_s(\mathbf{r})$ and $\hat{\psi}_s^\dagger(\mathbf{r})$ are called *field operators* because they depend on position.

Analogously it is straightforward to show

$$\hat{H}^{(1)} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\mathcal{H}_0(\mathbf{r})\hat{\psi}(\mathbf{r}). \tag{7.56}$$

Let us explore the properties of the field operators defined by Eqs. (7.54). This is done by operating $\hat{\psi}^\dagger(\mathbf{r})$ onto vacuum

$$\hat{\psi}^\dagger(\mathbf{r})|0\rangle = \sum_s \varphi_s^*(\mathbf{r})\hat{a}_s^\dagger|0\rangle = \sum_s |s\rangle\langle s|\mathbf{r}\rangle = |\mathbf{r}\rangle, \tag{7.57}$$

where we used the closure relation $\sum_s |s\rangle\langle s| = \mathbf{1}$. Thus we found that $\hat{\psi}^\dagger(\mathbf{r})$ is itself also a creation operator, creating from the vacuum a particle in state $|\mathbf{r}\rangle$, *i.e.* at position $\mathbf{r}$. Similarly we can show that $\hat{\psi}(\mathbf{r})$ is the corresponding annihilation operator (cf. Problem 7.9)

$$\hat{\psi}(\mathbf{r})|\mathbf{r}\rangle = |0\rangle. \tag{7.58}$$

Having the field operators we can introduce the *number-density operator*

$$\hat{n}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}). \tag{7.59}$$

Substituting the definitions (7.54) we obtain

$$\hat{n}(\mathbf{r}) = \sum_s \varphi_s^*(\mathbf{r})\hat{a}_s^\dagger \sum_t \varphi_t(\mathbf{r})\hat{a}_t = \sum_s |\varphi_s(\mathbf{r})|^2 \hat{a}_s^\dagger \hat{a}_s + \sum_{t\neq s} \varphi_s^*(\mathbf{r})\varphi_t(\mathbf{r})\hat{a}_s^\dagger \hat{a}_t. \tag{7.60}$$

We recognize two contributions, a part diagonal in the number representation of $\{|s\rangle\}$

$$\sum_s |\varphi_s(\mathbf{r})|^2 \hat{n}_s |\tilde{n}_\gamma\rangle = \sum_s |\varphi_s(\mathbf{r})|^2 n_s |\tilde{n}_\gamma\rangle = n(\mathbf{r}) |\tilde{n}_\gamma\rangle, \tag{7.61}$$

having the expectation value of the *number density* as its eigenvalue, and a part off-diagonal in this representation, representing the *density fluctuations* around the average,

$$\sum_{t\neq s} \varphi_s^*(\mathbf{r})\varphi_t(\mathbf{r})\hat{a}_s^\dagger \hat{a}_t |\tilde{n}_\gamma\rangle = [\hat{n}(\mathbf{r}) - n(\mathbf{r})] |\tilde{n}_\gamma\rangle. \tag{7.62}$$

Integrating the number-density operator over position we obtain the *total-number operator*,

$$\int \hat{n}(\mathbf{r})d\mathbf{r} = \int d\mathbf{r} \sum_{s,t} \langle s|\mathbf{r}\rangle\langle\mathbf{r}|t\rangle \hat{a}_s^\dagger \hat{a}_t = \sum_s \hat{a}_s^\dagger \hat{a}_s = \sum_s \hat{n}_s = \hat{N}. \tag{7.63}$$

Here we used the closure relation $\int d\mathbf{r}\, |\mathbf{r}\rangle\langle\mathbf{r}| = \mathbf{1}$ and the orthonormality of states $\langle s|t\rangle = \delta_{s,t}$.

It is straightforward to show (cf. Problem 7.8) 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 $\hat{a}_s^\dagger$ and $\hat{a}_s$ (cf. Section 7.3.1)

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm = \delta(\mathbf{r}-\mathbf{r}') \ ; \qquad [\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')]_\pm = [\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm = 0. \tag{7.64}$$

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*

$$[\hat{n}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')] = +\hat{\psi}^\dagger(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') \ ; \quad [\hat{n}(\mathbf{r}), \hat{\psi}(\mathbf{r}')] = -\hat{\psi}(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'). \tag{7.65}$$

Problem 7.7 *Show that the following commutation relation holds for both fermions and bosons,*

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(1)}] = \mathcal{H}_0(\mathbf{p}, \mathbf{r})\hat{\psi}(\mathbf{r}). \tag{7.66}$$

Solution: The operator

$$\hat{H}^{(1)} = \int d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}')\mathcal{H}_0(\mathbf{p}, \mathbf{r}')\hat{\psi}(\mathbf{r}')$$

is a construction operator for the one-body hamiltonian $\mathcal{H}_0(\mathbf{p}, \mathbf{r})$. Using subsequently 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

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(1)}] = \int d\mathbf{r}' \left[\hat{\psi}(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\mathcal{H}_0(\mathbf{p}, \mathbf{r}')\hat{\psi}(\mathbf{r}') - \hat{\psi}^\dagger(\mathbf{r}')\mathcal{H}_0(\mathbf{p}, \mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})\right] \tag{7.67}$$

$$= \int d\mathbf{r}' \left[\hat{\psi}(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\mathcal{H}_0(\mathbf{p}, \mathbf{r}')\hat{\psi}(\mathbf{r}') \pm \hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r})\mathcal{H}_0(\mathbf{p}, \mathbf{r}')\hat{\psi}(\mathbf{r}')\right] \tag{7.68}$$

$$= \int d\mathbf{r}' [\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')]_\pm \mathcal{H}_0(\mathbf{p}, \mathbf{r}')\hat{\psi}(\mathbf{r}'). \tag{7.69}$$

Substituting $[\hat{\psi}(\mathbf{r}'), \hat{\psi}^\dagger(\mathbf{r}')]_\pm = \delta(\mathbf{r}-\mathbf{r}')$ and integrating over $\mathbf{r}'$ we obtain the requested expression. ▶

Problem 7.8 *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

$$\begin{aligned}[\hat{\psi}(\mathbf{r}),\hat{\psi}^{\dagger}(\mathbf{r}')]_{\pm} &= \sum_q \varphi_q(\mathbf{r})\hat{a}_q \sum_s \varphi_s^*(\mathbf{r}')\hat{a}_s^{\dagger} \pm \sum_s \varphi_s^*(\mathbf{r}')\hat{a}_s^{\dagger} \sum_q \varphi_q(\mathbf{r})\hat{a}_q \\ &= \sum_{q,s} \varphi_s^*(\mathbf{r}')\varphi_q(\mathbf{r})\hat{a}_q\hat{a}_s^{\dagger} \pm \sum_{q,s} \varphi_s^*(\mathbf{r}')\varphi_q(\mathbf{r})\hat{a}_s^{\dagger}\hat{a}_q \\ &= \sum_{q,s} \varphi_s^*(\mathbf{r}')\varphi_q(\mathbf{r})[\hat{a}_q,\hat{a}_s^{\dagger}]_{\pm} \\ &= \sum_s \langle \mathbf{r}|s\rangle\langle s|\mathbf{r}'\rangle.\end{aligned}$$

In the last step we used the commutation relation $[\hat{a}_q,\hat{a}_s^{\dagger}]_{\pm}=\delta_{q,s}$. Substituting the closure relation $\sum_s |s\rangle\langle s| = \mathbf{1}$ we arrive at $[\hat{\psi}(\mathbf{r}),\hat{\psi}^{\dagger}(\mathbf{r}')]_{\pm}=\langle\mathbf{r}|\mathbf{r}'\rangle=\delta(\mathbf{r}-\mathbf{r}')$. ▶

Problem 7.9 *Show that* $\hat{\psi}(\mathbf{r})|\mathbf{r}\rangle=|0\rangle$.

Solution: Inserting the closure relation $\sum_{s'}|s'\rangle\langle s'|=\mathbf{1}$ 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 closure relation $\sum_s|\varphi_s(\mathbf{r})|^2=\mathbf{1}$.

7.4.1 The Schrödinger and Heisenberg pictures

There are two equivalent ways to handle time-dependence in quantum mechanics. These are referred to as the *Schrödinger picture* and the *Heisenberg picture*. In this section we summarize these pictures for the context of the quantum gases in which *the hamiltonian has no explicit time dependence.*

In Schrödinger picture the states $|\psi_S(t)\rangle$ carry the time-dependence, which is described by the Schrödinger equation of motion,

$$i\hbar\frac{\partial}{\partial t}|\psi_S(t)\rangle=\mathcal{H}|\psi_S(t)\rangle. \tag{7.70}$$

Rather than writing $\mathcal{H}_S$ we have chosen to omit the subscript in the case of the hamiltonian and simply write $\mathcal{H}$. For all other operators in the Schrödinger picture we will use the explicit notation with subscript, *e.g.* A_S. The solution of Eq. (7.70) is given by form

$$|\psi_S(t)\rangle=U(t,t_0)|\psi_S(t_0)\rangle, \tag{7.71}$$

where $U(t,t_0)=e^{-(i/\hbar)\mathcal{H}(t-t_0)}$ is the evolution operator covering the time dependence from $t_0\to t$ and $|\psi_S(t_0)\rangle$ is the state of the system on time t_0. Because the hamiltonian is hermitian, $\mathcal{H}^{\dagger}=\mathcal{H}$, the evolution operator is unitary,

$$U^{\dagger}(t,t_0)=e^{(i/\hbar)\mathcal{H}^{\dagger}(t-t_0)}=e^{(i/\hbar)\mathcal{H}(t-t_0)}=U^{-1}(t,t_0), \tag{7.72}$$

i.e. $U^{\dagger}U=UU^{\dagger}=\mathbf{1}$. Importantly, the evolution operator commutes with the hamiltonian,

$$[U(t,t_0),\mathcal{H}]=0, \tag{7.73}$$

as follows with Eq. (B.20). The equations of motion of the evolution operator and its hermitian conjugate are given by

$$i\hbar\frac{\partial}{\partial t}U(t,t_0) = \mathcal{H}U(t,t_0) \qquad \Leftrightarrow \qquad -i\hbar\frac{\partial}{\partial t}U^{\dagger}(t,t_0) = U^{\dagger}(t,t_0)\mathcal{H}. \tag{7.74}$$

In the Schrödinger picture the operators A_S are time independent (*e.g.* $\mathcal{H}$), except in cases where an explicit time dependence is present. As is well-known, the expectation value for a, say time-independent, observable A as a function of time t is given by

$$\langle A\,(t)\rangle = \frac{\langle\psi_S\,(t)\,|A_S\,|\psi_S\,(t)\rangle}{\langle\psi_S\,(t)\,|\psi_S\,(t)\rangle}. \tag{7.75}$$

The *Heisenberg picture* is obtained by a unitary transformation of the Schrödinger vectors and operators in Hilbert space. The unitary transformation

$$|\psi_H\rangle \equiv U^{\dagger}(t,t_0)\,|\psi_S\,(t)\rangle = |\psi_S\,(t_0)\rangle\,, \tag{7.76}$$

is chosen such that it removes the time dependence from the Schrödinger state $|\psi_S\,(t)\rangle$ by evolving it back to $t = t_0$. The same unitary transformation by $U(t,t_0)$ puts an implicit time dependence on the operators,

$$A_H(t) = U^{\dagger}(t,t_0)A_S(t)U(t,t_0). \tag{7.77}$$

Thus, the Heisenberg and Schrödinger pictures coincide at $t = t_0$,

$$A_H(t_0) = A_S(t_0) \quad \text{and} \quad |\psi_H\rangle = |\psi_S\,(t_0)\rangle\,. \tag{7.78}$$

Importantly, since $U(t,t_0)$ commutes with the hamiltonian $\mathcal{H}$, the transformation to the Heisenberg picture leaves the hamiltonian unchanged,

$$\mathcal{H}_H(t) = \mathcal{H}.$$

It is straightforward to show starting from Eqs. (7.75) that in the Heisenberg picture the expectation value for the observable A on time t is given by

$$\langle A\,(t)\rangle = \frac{\langle\psi_H|A_H(t)\,|\psi_H\rangle}{\langle\psi_H\,|\psi_H\rangle}. \tag{7.79}$$

All time dependence of the expectation value $\langle A\,(t)\rangle$ is contained in the *Heisenberg equation of motion* for the operators (cf. Problem 7.10)

$$i\hbar\frac{\partial}{\partial t}A_H(t) = [A_H(t),\mathcal{H}] + i\hbar\,(\partial A_S(t)/\partial t)_H\,. \tag{7.80}$$

This equation of motion is completely equivalent to the Schrödinger equation in the Schrödinger picture. Note that in the absence of an explicit time dependence of the operator in the Schrödinger picture, *i.e.* for $\partial A_S(t)/\partial t = 0$, the Heisenberg equation of motion reduces to

$$i\hbar\frac{\partial}{\partial t}A_H(t) = [A_H(t),\mathcal{H}]. \tag{7.81}$$

Problem 7.10 *Derive the Heisenberg equation of motion (7.80) for an operator $A(t)$ with an explicit time dependence.*

Solution: The answer is obtained by repetitive use of the definition (7.77) of Heisenberg operators, the equations of motion (7.74) and the commutation relation (7.73),

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}A_H(t) &= i\hbar\partial[U^\dagger(t)A_S(t)U(t)]/\partial t\\
&= i\hbar\left[\partial U^\dagger(t)/\partial t\right]A_S(t)U(t) + i\hbar U^\dagger(t)\left[\partial A_S(t)/\partial t\right]U(t) + i\hbar U^\dagger(t)A_S(t)\left[\partial U(t)/\partial t\right]\\
&= -\mathcal{H}U^\dagger(t)A_S(t)U(t) + i\hbar\left(\partial A_S(t)/\partial t\right)_H + U^\dagger(t)A_S(t)U(t)\mathcal{H}\\
&= -\mathcal{H}A_H(t) + i\hbar\left(\partial A_S(t)/\partial t\right)_H + A_H(t)\mathcal{H}\\
&= [A_H(t),\mathcal{H}] + i\hbar\left(\partial A_S(t)/\partial t\right)_H. \;\blacktriangleright
\end{aligned}$$

7.4.2 Time-dependent field operators - second quantized form

Let us consider the hamiltonian of an ideal gas (non-interacting many-body system),

$$\mathcal{H} = \sum_i -\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 + \mathcal{U}(\mathbf{r}_i) = \sum_i \mathcal{H}_0(\mathbf{p}_i,\mathbf{r}_i). \tag{7.82}$$

In terms of field operators this hamiltonian can be written in the form $\hat{H} = \hat{H}^{(1)}$,

$$\hat{H}^{(1)} = \int d\mathbf{r}\hat{\psi}^\dagger(\mathbf{r})\mathcal{H}_0(\mathbf{p},\mathbf{r})\hat{\psi}(\mathbf{r}), \tag{7.83}$$

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. (7.54). Let $\hat{\psi}_H(t) \equiv \hat{\psi}(\mathbf{r},t)$ 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. (7.81) and we have

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r},t) = [\hat{\psi}(\mathbf{r},t),\hat{H}^{(1)}]. \tag{7.84}$$

Applying Eq. (7.66) we obtain

$$i\hbar\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r},t) = \mathcal{H}_0(\mathbf{p},\mathbf{r})\hat{\psi}(\mathbf{r},t). \tag{7.85}$$

With this equation we have regained for the Heisenberg equation of motion the form of the Schrödinger equation! This interesting feature has given rise to the term *second quantization.*

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 with the number of microstates $\Omega(E^*,N^*)$ with 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 near E and atom number near N is called the *grand canonical ensemble*.

The probability P_γ that the small system is 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 that $\Omega_\gamma(E_\gamma, N_\gamma) = 1$ 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 have $k_B\beta = (\partial S^*/\partial E^*)_{N^*}$. 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* with normalization $\sum_\gamma P_\gamma = 1$. The normalization constant

$$\mathcal{Z}_{gr} = \sum_\gamma e^{-\beta E_\gamma - \alpha N_\gamma}$$

is the *grand partition function.* It differs from the canonical partition function (1.21) in that the summation over all many-body states $|\tilde{n}_\gamma\rangle$ not only includes states of different energy but also states of different number of atoms. Therefore, the sum over the ensemble of states $\{|\tilde{n}_\gamma\rangle\}$ can be separated into a double sum in which we first sum over all possible N-atom states $\{|N, \tilde{n}_\gamma\rangle\}$ of the subsystem and subsequently over all possible values of N of the subsystem,

$$\mathcal{Z}_{gr} = \sum\nolimits_N e^{-\alpha N} \sum\nolimits_\gamma^{(N)} e^{-\beta E_\gamma} = \sum\nolimits_N e^{-\alpha N} Z(N). \tag{8.4}$$

Here $Z(N) \equiv \sum_\gamma^{(N)} e^{-\beta E_\gamma}$ is recognized as the canonical partition function of a N-body subsystem.

$$\ln \mathcal{Z}_{gr} = \ln \sum\nolimits_N e^{-\alpha N} + \ln Z_N$$

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

$$dS = \frac{1}{T} dU - \frac{1}{T} dW - \frac{\mu}{T} dN, \tag{8.5}$$

where $đW$ is the *mechanical work* done on the small system, U its *internal energy* and μ the *chemical potential.* For homogeneous systems $dW = -pdV$ 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 system. Further we identify $k_B\alpha = (\partial S^*/\partial N^*)_{E^*} = (\partial S/\partial N)_U$ with $\alpha = -\mu/k_BT$, where μ is the chemical potential of the system.

8.2.1 The statistical operator

Averaged over the grand canonical ensemble the average value of an arbitrary observable A of a system is given by

$$\bar{A} = \sum_{\gamma} A_{\gamma} P_{\gamma},$$

where $A_{\gamma} \equiv \langle \tilde{n}_{\gamma} | \hat{A} | \tilde{n}_{\gamma} \rangle$ is the expectation value of $\hat{A}$ with the system in state $|\tilde{n}_{\gamma}\rangle$ and P_{γ} the probability to find the system in this state, given by Eq. (8.3). Within the occupation number representation this result may be obtained by introducing the *statistical operator*

$$\hat{\rho} \equiv \mathcal{Z}_{gr}^{-1} e^{-(\hat{H}-\mu\hat{N})/k_B T}, \tag{8.6}$$

where $\hat{H}$ and $\hat{N}$ are the hamiltonian and total number operator, respectively, and $\mathcal{Z}_{gr}$ is the grand canonical partition function. Using the statistical operator the average of A is given by

$$\bar{A} = \langle \hat{\rho} \hat{A} \rangle. \tag{8.7}$$

To demonstrate that Eq. (8.7) 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 $\hat{\rho}$ is diagonal and Eq. (8.7) can be rewritten as

$$\bar{A} = \sum_{\gamma} \langle \tilde{n}_{\gamma} | \hat{\rho} | \tilde{n}_{\gamma} \rangle \, \langle \tilde{n}_{\gamma} | \hat{A} | \tilde{n}_{\gamma} \rangle.$$

Using $A_{\gamma} \equiv \langle \tilde{n}_{\gamma} | \hat{A} | \tilde{n}_{\gamma} \rangle$ and noting with Eq. (8.3) that $\langle \tilde{n}_{\gamma} | \hat{\rho} | \tilde{n}_{\gamma} \rangle = \mathcal{Z}_{gr}^{-1} e^{-(E_{\gamma}-\mu N_{\gamma})/k_B T} = P_{\gamma}$ we find that the average is indeed of the form $\bar{A} = \sum_{\gamma} A_{\gamma} P_{\gamma}$.

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,

$$\overline{n}_s = \mathcal{Z}_{gr}^{-1} \sum_{\gamma} \langle \tilde{n}_{\gamma} | \, e^{-(\hat{H}-\mu\hat{N})/k_B T} \hat{n}_s \, | \tilde{n}_{\gamma} \rangle \,, \tag{8.8}$$

where $\mathcal{Z}_{gr}$ is the grand canonical partition function, defined by the normalization condition $\sum_s \overline{n}_s = N$. To calculate this average we choose the representation of $\hat{H}$. Because the gas is ideal the hamiltonian is given by $\hat{H} = \sum_{t} \varepsilon_t \hat{n}_t$ and Eq. (8.8) can be written in the form

$$\begin{aligned} \overline{n}_s &= \mathcal{Z}_{gr}^{-1} \sum_{n_1, n_2, \cdots} \langle n_1, \cdots, n_s, \cdots | \, e^{-[\hat{n}_1(\varepsilon_1-\mu)+\cdots+\hat{n}_s(\varepsilon_s-\mu)+\cdots]/k_B T} \hat{n}_s \, | n_1 n_1, \cdots, n_s, \cdots \rangle \\ &= \mathcal{Z}_{gr}^{-1} \sum_{n_s} n_s e^{-n_s(\varepsilon_s-\mu)/k_B T} \sum_{n_1, n_2, \cdots}{}^{(n_s)} e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_B T}, \end{aligned} \tag{8.9}$$

where the sums over the occupations $n_1, n_2, \cdots$ run from zero up, unrestricted for the case of bosons and restricted to the maximum value 1 for the case of fermions. 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 function can be written as

$$\mathcal{Z}_{gr} = \sum_{n_s} e^{-n_s(\varepsilon_s-\mu)/k_B T} \sum_{n_1, n_2, \cdots}{}^{(n_s)} e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_B T}. \tag{8.10}$$

Substituting Eq. (8.10) into Eq. (8.9) we obtain for the average thermal occupation

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-n_s(\varepsilon_s-\mu)/k_BT}}{\sum_{n_s} e^{-n_s(\varepsilon_s-\mu)/k_BT}}. \tag{8.11}$$

From this expression we infer that the probability to find n atoms in the *same* state of energy ε is given by

$$P(n) = \mathcal{Z}^{-1} e^{-n(\varepsilon-\mu)/k_BT}, \tag{8.12}$$

with normalization $\sum_n P(n) = 1$ and normalization factor

$$\mathcal{Z} = \sum_n e^{-n(\varepsilon-\mu)/k_BT}. \tag{8.13}$$

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*

$$P(n_2)/P(n_1) = e^{-\Delta n(\varepsilon-\mu)/k_BT}, \tag{8.14}$$

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 $r = e^{-(\varepsilon-\mu)/k_BT}$,

$$\mathcal{Z}_{\mathrm{BE}} = \sum\nolimits_{n=0}^{\infty} r^n = \frac{1}{1-r} \quad (r < 1)\,. \tag{8.15}$$

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

$$\mathcal{Z}_{\mathrm{FD}} = \sum\nolimits_{n=0}^{1} r^n = 1 + r. \tag{8.16}$$

Comparing Eq. (8.15) with (8.16) 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 large *negative* values 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 state $|s\rangle$ and using Eq. (8.12) the average occupation is given by

$$\bar{n}_s = \sum_{n=0}^{\infty} nP_s(n) = \mathcal{Z}_{\mathrm{BE}}^{-1} \sum_{n=0}^{\infty} ne^{-n(\varepsilon_s-\mu)/k_BT} = \mathcal{Z}_{\mathrm{BE}}^{-1} \sum_{n=0}^{\infty} nr_s^n, \tag{8.17}$$

where $r_s = e^{-(\varepsilon_s-\mu)/k_BT}$. Using the relation

$$\sum\nolimits_{n=0}^{\infty} nr^n = r\sum\nolimits_{n=0}^{\infty} nr^{n-1} = r\frac{\partial \mathcal{Z}_{\mathrm{BE}}}{\partial r} = \frac{r}{(1-r)^2}, \tag{8.18}$$

which hold for $r < 1$, and substituting Eqs. (8.15) and (8.18) into Eq. (8.17) we obtain for the average thermal occupation of state $|s\rangle$

$$\bar{n}_s = \frac{r_s}{(1-r_s)} = \frac{1}{e^{(\varepsilon_s-\mu)/k_BT} - 1} \equiv f_{\mathrm{BE}}(\varepsilon_s). \tag{8.19}$$

As $\bar{n}_s$ depends for given values of T and μ only on the *energy* of state $|s\rangle$, we introduced in Eq. (8.19) the *Bose-Einstein (BE) distribution function* $f_{\mathrm{BE}}(\varepsilon)$, which gives the BE-occupation of *any* single-particle state of energy ε for given values of T and μ. The average total number of atoms is given by

$$\textstyle\sum_s \bar{n}_s = \bar{N},$$

where $\bar{N}$ is the average number of trapped atoms of the grand canonical ensemble.

To apply the grand canonical ensemble to a gas of N identical atoms at temperature T we use the condition

$$\textstyle\sum_s \bar{n}_s = N \tag{8.20}$$

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. (8.19). This 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 have to 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 must 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 $-\mu \lll \varepsilon_1 \ll k_B T$ can be satisfied. In this case we have

$$N_0 = \frac{1}{e^{-\mu/k_B T} - 1} \simeq \frac{k_B T}{-\mu} \tag{8.21}$$

which can indeed become arbitrarily large, whereas the occupation of all excited states $|s \neq 0\rangle$ remains finite, $n_s = k_B T/\varepsilon_s$. The ground state occupation remains regular as long as

$$N_0 \lll N \Leftrightarrow -\mu/k_B T \ggg 1/N. \tag{8.22}$$

Note that Eqs. (8.21) and (8.22) can indeed be simultaneously satisfied if $1/N \lll -\mu/k_B T \ll 1$, which is possible because N is a macroscopic number ($N \ggg 1$). In classical statistics (Boltzmann statistics) macroscopic occupation of the ground state could also occur but *only* in the zero temperature limit ($k_B T \ll \varepsilon_1$).

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 known as the *thermal cloud*. As will appear from the next sections, the occurrence of BEC depends 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, as introduced in Section 1.3.1) exceeds unity.

8.3.3 Fermi-Dirac statistics

For identical fermions the occupation n of a given state is restricted to the values 0 or 1, so the average occupation of state $|s\rangle$ is given by

$$\bar{n}_s = \sum_{n=0}^{1} n P_s(n) = \mathcal{Z}_{\mathrm{FD}}^{-1} e^{-(\varepsilon_s - \mu)/k_B T} = \frac{r_s}{(1 + r_s)}, \tag{8.23}$$

where $r_s \equiv e^{-(\varepsilon_s-\mu)/k_BT}$. Hence,

$$\bar{n}_s = \frac{1}{e^{(\varepsilon_s-\mu)/k_BT}+1} \equiv f_{\mathrm{FD}}(\varepsilon_s). \tag{8.24}$$

Note that $\bar{n}_s < 1$ for any finite temperature. As $\bar{n}_s$ depends for given values of T and μ only on the *energy* of the state $|s\rangle$ we have introduced the *Fermi-Dirac (FD) distribution function* $f_{\mathrm{FD}}(\varepsilon)$, which gives the FD-occupation of *any* single-particle state of energy ε for given values of T and μ. Note that 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 - quasi-classical approximation

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

$$N = \sum_s \bar{n}_s = \sum_s \frac{1}{e^{(\varepsilon_s-\mu)/k_BT} \pm 1}, \tag{8.25}$$

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. (8.25) may be replaced by the integration $(2\pi\hbar)^{-3} \int d\mathbf{p}d\mathbf{r}$ over phase space,

$$N = \frac{1}{(2\pi\hbar)^3} \int \frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT} \pm 1} d\mathbf{r}d\mathbf{p}, \tag{8.26}$$

with the energy of the states given by the classical hamiltonian, $\varepsilon_s = H_0(\mathbf{r},\mathbf{p})$. 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 because for $k_BT \gg \hbar\omega$ only a small error is made by neglecting the discrete structure of the spectrum, $\varepsilon_0 \simeq H_0(0,0) = 0$. At this point we realize that the description has remained mostly classical. Only the quantum mechanical condition on the level occupation, *i.e.* the quantum statistics, affects the results.

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, $N = \int n(\mathbf{r})d\mathbf{r}$. Hence, for given temperature and chemical potential $n(\mathbf{r})$ is obtained by integrating the integrand of Eq. (8.26) only over momentum space,

$$n(\mathbf{r}) = \frac{1}{(2\pi\hbar)^3} \int \frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT} \pm 1} d\mathbf{p}. \tag{8.27}$$

Recalling the expression for the one-body hamiltonian,

$$H_0(\mathbf{r},\mathbf{p}) = p^2/2m + \mathcal{U}(\mathbf{r}), \tag{8.28}$$

we obtain for the density in the minimum of the trap ($\mathbf{r} = 0$)

$$n_0 = \frac{1}{(2\pi\hbar)^3} \int \frac{4\pi p^2}{e^{(p^2/2m-\mu)/k_BT} \pm 1} dp. \tag{8.29}$$

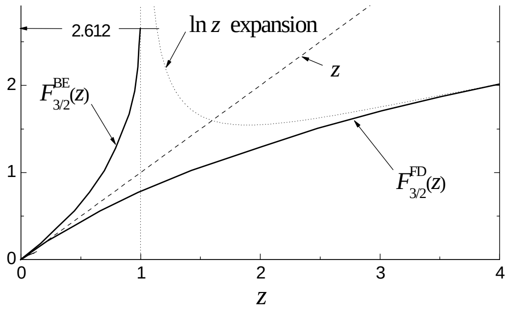

Figure 8.1: Bose-Einstein (BE) and Fermi-Dirac (FD) integrals as a function of the fugacity z. For comparison also the linear dependence of Maxwell-Boltzmann statistics is shown. The dotted line corresponds to the expansion (8.71) for fermions.

Note that this result is obtained *irrespective* of the shape of the trap and coincides with the result for a homogeneous gas.[1]

Local density approximation

Eqs. (8.27) and (8.28) suggest to make a *local density approximation*

$$n(\mathbf{r})=\frac{1}{(2\pi\hbar)^3}\int_0^\infty\frac{4\pi p^2}{e^{(p^2/2m+\mathcal{U}(\mathbf{r})-\mu)/k_BT}\pm 1}dp. \tag{8.30}$$

Introducing the dimensionless quantity

$$z(\mathbf{r})=ze^{-\mathcal{U}(\mathbf{r})/k_BT}, \tag{8.31}$$

where

$$z=e^{\mu/k_BT} \tag{8.32}$$

is called the *fugacity*, the local density can be written in the following very compact form

$$n(\mathbf{r})=\frac{1}{\Lambda^3}F_{3/2}^{\mathrm{FD/BE}}\left(z(\mathbf{r})\right), \tag{8.33}$$

where

$$F_{3/2}^{\mathrm{FD/BE}}(z)=\frac{4}{\sqrt{\pi}}\int_0^\infty\frac{x^2}{z^{-1}e^{x^2}\pm 1}dx=\frac{2}{\sqrt{\pi}}\int_0^\infty\frac{t^{1/2}}{z^{-1}e^{t}\pm 1}dt \tag{8.34}$$

is a dimensionless integral and the ± sign distinguishes between BE ($-$) and FD ($+$) statistics. The $F_{3/2}(z)$ integrals are monotonically increasing functions of z as shown in Fig. 8.1. From Eq. (8.33) we infer that the $F_{3/2}(z)$ 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,

$$D=n_0\Lambda^3=F_{3/2}^{\mathrm{FD/BE}}(z).$$

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[1] V. Bagnato, D.E. Pritchard and D. Kleppner, *Physical Review* A **35**, 4354 (1987). Note that this well-known result does not hold for reduced dimensinality.

8.3.5 Grand partition function

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 function Z_N. The grand partition function $\mathcal{Z}_{gr}$ plays a similar role for the quantum gases. In preparation for the discussion of this topic in Section 8.3.6 we first derive expressions for $\mathcal{Z}_{gr}$ for the cases of BE- and FD-statistics. Starting from the definition

$$\mathcal{Z}_{gr} = \sum_{n_1,n_2,\cdots} e^{-[n_1(\varepsilon_1-\mu)+n_2(\varepsilon_2-\mu)+\cdots]/k_BT}, \tag{8.35}$$

we note that we can sequentially factor-out the contributions of all single-particle states, just as was done for state s in Eq. (8.36),

$$\mathcal{Z}_{gr} = \prod_s \sum_{n_s} e^{-n_s(\varepsilon_s-\mu)/k_BT}. \tag{8.36}$$

Introducing the quantity $r_s = e^{-(\varepsilon_s-\mu)/k_BT}$, Eq. (8.36) can be further simplified to the form

$$\mathcal{Z}_{gr} = \prod_s \sum_{n_s} r_s^{n_s}. \tag{8.37}$$

- 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,

$$\mathcal{Z}_{gr} = \prod_s \frac{1}{1-r_s} \qquad \text{(bosons)}. \tag{8.38}$$

- For identical fermions the state occupations n_s are restricted to the values $0, 1$ and we have only two terms in the sum,

$$\mathcal{Z}_{gr} = \prod_s (1+r_s) \qquad \text{(fermions)}. \tag{8.39}$$

- Combining Eqs. (8.38) and (8.39) we obtain a single formula,

$$\ln \mathcal{Z}_{gr} = \pm \sum_s \ln(1 \pm r_s), \tag{8.40}$$

  where the ± sign distinguishes between Bose-Einstein (−) and Fermi-Dirac (+) statistics.

Let us derive an expression for $\ln \mathcal{Z}_{gr}$ in the quasi-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,

$$\ln \mathcal{Z}_{gr} = \frac{1}{(2\pi\hbar)^3} \int \ln\left(1 \pm z e^{-H_0(\mathbf{p},\mathbf{r})/k_BT}\right) d\mathbf{p}d\mathbf{r}, \tag{8.41}$$

where $H_0(\mathbf{r},\mathbf{p})$ is again the one-body hamiltonian (1.33). For inhomogeneous gases we write $\ln \mathcal{Z}_{gr}$ in the form

$$\ln \mathcal{Z}_{gr} = \Lambda^{-3} \int F_{5/2}(z e^{-\mathcal{U}(\mathbf{r})/k_BT}) d\mathbf{r}, \tag{8.42}$$

where the local contribution to $\ln \mathcal{Z}_{gr}$ is given by

$$\ln \mathcal{Z}_{gr}(\mathbf{r}) = \Lambda^{-3} F_{5/2}(z e^{-\mathcal{U}(\mathbf{r})/k_BT}). \tag{8.43}$$

Recalling Eq. (8.33) for the local density this expression may be reformulated in the form

$$\ln \mathcal{Z}_{gr}(\mathbf{r}) = \frac{F_{5/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT})}{F_{3/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT})} n(\mathbf{r}). \tag{8.44}$$

For homogeneous gases $\mathcal{U}(\mathbf{r}) = 0$ and we can simply integrate (8.42) over configuration space,

$$\ln \mathcal{Z}_{gr} = \left(V/\Lambda^3\right) F_{5/2}(z). \tag{8.45}$$

Introducing $\alpha = \sqrt{2mk_BT}$ and changing to the integration variable $t = (p/\alpha)^2$ the function $F_{5/2}(z)$ can be written as

$$\begin{aligned} F_{5/2}(z) &= \frac{\Lambda^3}{(2\pi\hbar)^3} \int_0^\infty \ln\left(1 \pm ze^{-(p/\alpha)^2}\right) 4\pi p^2 dp \\ &= \frac{1}{\Gamma(3/2)} \int_0^\infty \ln\left(1 \pm ze^{-t}\right) t^{1/2} dt, \end{aligned} \tag{8.46}$$

which can be rewritten by partial integration in the form of the interal representation of the polylogarithm (see Appendix B.2),

$$F_{5/2}(z) = \frac{1}{\Gamma(5/2)} \int_0^\infty \frac{t^{3/2}}{z^{-1}e^t \pm 1} dt. \tag{8.47}$$

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. (8.11) in the form

$$\overline{n}_s = \frac{r_s \sum_{n_s} n_s r_s^{n_s - 1}}{\sum_{n_s} r_s^{n_s}} \frac{\prod_{t \neq s} \sum_{n_t} r_t^{n_t}}{\prod_{t \neq s} \sum_{n_t} r_t^{n_t}}, \tag{8.48}$$

we recognize in the denominator the expression (8.37) for $\mathcal{Z}_{gr}$ and in the numerator a derivative of $\mathcal{Z}_{gr}$,

$$\overline{n}_s = \frac{r_s}{\mathcal{Z}_{gr}} \frac{\partial \mathcal{Z}_{gr}}{\partial r_s} = r_s \partial \ln \mathcal{Z}_{gr} / \partial r_s. \tag{8.49}$$

Substituting Eq. (8.40) yields in one line the BE (−) and FD (+) distribution functions,

$$\overline{n}_s = \frac{r_s}{1 \pm r_s} = \frac{1}{e^{(\varepsilon_s - \mu)/k_BT} \pm 1}. \tag{8.50}$$

8.3.6 Link to the thermodynamics

Let us explore how the thermodynamic properties can be obtained from the grand partition function. The starting point is to indentify the grand canonical average of the total energy E of a system with the thermodynamic internal energy U of that system,

$$U = \bar{E} = \sum_s \varepsilon_s \bar{n}_s = \sum_s \frac{\varepsilon_s}{e^{(\varepsilon_s - \mu)/k_BT} \pm 1}. \tag{8.51}$$

In the quasi-classical approximation this becomes

$$U = \int u(\mathbf{r}) d\mathbf{r} = \frac{1}{(2\pi\hbar)^3} \int \frac{H_0(\mathbf{r}, \mathbf{p})}{e^{(H_0(\mathbf{r}, \mathbf{p}) - \mu)/k_BT} \pm 1} d\mathbf{p} d\mathbf{r}, \tag{8.52}$$

where the local energy density $u(\mathbf{r})$ is given by

$$u(\mathbf{r}) = k_BT\frac{1}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int\frac{t^{3/2}}{e^{-\mathcal{U}(\mathbf{r})/k_BT}z^{-1}e^t \pm 1}dt + \frac{\mathcal{U}(\mathbf{r})}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int\frac{t^{1/2}}{e^{-\mathcal{U}(\mathbf{r})/k_BT}z^{-1}e^t \pm 1}dt. \tag{8.53}$$

Here we recognize two polylogarithms,

$$u(\mathbf{r}) = \frac{3}{2}k_BT\frac{1}{\Lambda^3}F_{5/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT}) + \mathcal{U}(\mathbf{r})\frac{1}{\Lambda^3}F_{3/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT}). \tag{8.54}$$

Substituting Eqs. (8.43) and (8.33) the expression for $u(\mathbf{r})$ reduces to the compact form

$$u(\mathbf{r}) = \frac{3}{2}k_BT\ln\mathcal{Z}_{gr}(\mathbf{r}) + \mathcal{U}(\mathbf{r})n(\mathbf{r}). \tag{8.55}$$

Returning to Eq. (8.54) and using the properties of the polylogarithm we find that Eq. (8.54) is equivalent with

$$\begin{aligned} u(\mathbf{r}) = &-k_BT\frac{1}{\Lambda^3}F_{5/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT}) \\ &+ T\left(\frac{\partial}{\partial T}k_BT\frac{1}{\Lambda^3}F_{5/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT})\right)_{\mathcal{U},\mu} + \mu\frac{1}{\Lambda^3}F_{3/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT}). \end{aligned} \tag{8.56}$$

In the first two terms we recognize the expression (8.43) for $\ln\mathcal{Z}_{gr}(\mathbf{r})$. 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 $\ln\mathcal{Z}_{gr}(\mathbf{r})$ (see Problem 8.1),

$$n(\mathbf{r}) = \left(\frac{\partial}{\partial\mu}k_BT\ln\mathcal{Z}_{gr}(\mathbf{r})\right)_{\mathcal{U},T}, \tag{8.57}$$

Thus Eq. (8.56) can be written in a form containing only $k_BT\ln\mathcal{Z}_{gr}(\mathbf{r})$ and its derivatives. Suppressing the explicit position dependence on $\mathcal{Z}_{gr}(\mathbf{r})$ we have

$$u(\mathbf{r}) = -k_BT\ln\mathcal{Z}_{gr} + T[\partial(k_BT\ln\mathcal{Z}_{gr})/\partial T]_{\mathcal{U},\mu} + \mu\partial[k_BT\ln\mathcal{Z}_{gr})/\partial\mu]_{\mathcal{U},T}. \tag{8.58}$$

This expression suggests to define the quantity

$$\Omega(\mathbf{r}) = -k_BT\ln\mathcal{Z}_{gr}(\mathbf{r}) \Leftrightarrow \mathcal{Z}_{gr}(\mathbf{r}) = e^{-\Omega(\mathbf{r})/k_BT}. \tag{8.59}$$

By substitution of Eq. (8.44) $\Omega(\mathbf{r})$ can be expressed in the form

$$\Omega(\mathbf{r}) = -\frac{F_{5/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT})}{F_{3/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT})}n(\mathbf{r})k_BT. \tag{8.60}$$

We are now in a position to make the connection to thermodynamics. First we will do this for the *homogeneous* gas. From Eq. (8.58) we see that the internal energy can be expressed in terms of $\Omega = \int\Omega(\mathbf{r})\mathbf{dr} = \Omega_0V$ and its derivatives,

$$U = \Omega - T\left(\frac{\partial\Omega}{\partial T}\right)_{\mathcal{U},\mu} - \mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{\mathcal{U},T} = \Omega - T\left(\frac{\partial\Omega}{\partial T}\right)_{\mathcal{U},z}. \tag{8.61}$$

Comparing this relation with the thermodynamic relation $\Omega = U - TS - \mu N$, we recognize in Ω the *grand potential* Ω. Once Ω is known the thermodynamic properties of the small system can be 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 $d\Omega = đW - SdT - Nd\mu$. Hence, we identify

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{\mathcal{U},\mu}, \quad N = \left(\frac{\partial\Omega}{\partial\mu}\right)_{\mathcal{U},T}. \tag{8.62}$$

In a homogeneous gas one has $đW = -pdV$ and

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = -\Omega_0 \quad \Leftrightarrow \quad \Omega = -pV. \tag{8.63}$$

For *inhomogeneous* systems we obtain similarly for the entropy density and the number density,

$$S(\mathbf{r}) = -\left(\partial\Omega(\mathbf{r})/\partial T\right)_{\mathcal{U},\mu} \text{ and } \quad n(\mathbf{r}) = -\left(\partial\Omega(\mathbf{r})/\partial\mu\right)_{\mathcal{U},T}. \tag{8.64}$$

The corresponding relation for the local pressure $p(\mathbf{r})$ remains to be determined.

Problem 8.1 *Show that the relation between the local density and $\mathcal{Z}_{gr}$ is given by*

$$n(\mathbf{r}) = \left(\frac{\partial}{\partial\mu} k_B T \ln \mathcal{Z}_{gr}(\mathbf{r})\right)_{\mathcal{U},T}.$$

Solution: Starting from the r.h.s. of Eq. (8.57) we have for constant $\mathcal{U}(\mathbf{r})$ and T

$$\frac{\partial}{\partial\mu} k_B T \ln \mathcal{Z}_{gr}(\mathbf{r}) = k_B T \frac{1}{\Lambda^3} \frac{\partial}{\partial\mu} F_{5/2}(ze^{-\mathcal{U}(\mathbf{r})/k_BT}).$$

Introducing the notation $z(\mathbf{r}) = ze^{-\mathcal{U}(\mathbf{r})/k_BT}$ and noting the property $\partial z(\mathbf{r})/\partial\mu = z(\mathbf{r})/k_BT$ the above expression takes the form

$$k_B T \frac{1}{\Lambda^3} \frac{\partial}{\partial z(\mathbf{r})} F_{5/2}(z(\mathbf{r})) \frac{\partial z(\mathbf{r})}{\partial\mu} = \frac{1}{\Lambda^3} \frac{F_{3/2}(z(\mathbf{r}))}{z(\mathbf{r})} = n(\mathbf{r}),$$

where Eq. (8.33) was used in the final step. ▶

8.3.7 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 classified in terms of the value of the fugacity.

The case $0 < z \leq 1$

For $\mu(\mathbf{r})/k_BT \leq 0$ the fugacity is small and we can rewrite both the BE and FD integrals in the form

$$F_\alpha^{\mathrm{FD/BE}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty \frac{t^{\alpha-1}}{z^{-1}e^t \pm 1} dt. \tag{8.65}$$

Since $z \leq 1$ and $e^{-t} \leq 1$ the denominator of the integrand can be expanded in powers of ze^{-x^2},

$$\frac{ze^{-t}}{1 \pm ze^{-t}} = \sum_{\ell=0} (\pm z)^\ell e^{-\ell t} \tag{8.66}$$

and substituting this expansion into Eq. (8.65) we obtain after swapping summation and integration

$$F_\alpha^{\mathrm{FD/BE}}(z) = \sum_{\ell=1} (\pm)^{\ell+1} z^\ell \frac{1}{\Gamma(\alpha)} \int_0^\infty e^{-\ell t} t^{\alpha-1} dt. \tag{8.67}$$

Note that this swap is allowed because the series converges uniformly (for $0 < z \leq 1$). Evaluating the integral gives

$$\frac{1}{\Gamma(\alpha)}\int_0^\infty e^{-\ell t}t^{\alpha-1}dt = \frac{1}{\ell^\alpha}$$

and we obtain

$$F_\alpha^{\mathrm{BE}}(z) = \sum_{\ell=1} \frac{z^\ell}{\ell^\alpha} \equiv g_\alpha(z) = \mathrm{Li}_\alpha(z) \tag{8.68a}$$

$$F_\alpha^{\mathrm{FD}}(z) = \sum_{\ell=1} (-)^{\ell+1}\frac{z^\ell}{\ell^\alpha} \equiv f_\alpha(z) = -\mathrm{Li}_\alpha(-z), \tag{8.68b}$$

where $\mathrm{Li}_\alpha(z)$ is the polylogarithm (see Appendix B.2). These expressions are known as the *fugacity expansions* of the BE-function $g_\alpha(z)$ and FD-function $f_\alpha(z)$.

The case $z \uparrow 1$

Highly degenerate bosonic gases are characterized by this limit ($0 \leq -\mu \ll k_B T$). In this case the integral $F_\alpha^{\mathrm{BE}}(z)$ can be expanded in powers of $u = -\ln z = -\mu/k_B T$ (see Appendix B.3). In particular we have

$$F_{3/2}^{\mathrm{BE}}(z) = \zeta(3/2) + \Gamma(-1/2)\sqrt{-\ln z} + \cdots \quad \text{for } (-\mu \ll k_B T)\,. \tag{8.69}$$

$$F_{5/2}^{\mathrm{BE}}(z) = \zeta(5/2) - \zeta(3/2)\,(-\ln z) + \Gamma\,(-3/2)\,(-\ln z)^{3/2} + \cdots\,, \quad \text{for } (-\mu \ll k_B T)\,. \tag{8.70}$$

Note that these expressions satisfy the recursion relations (B.9). Note further that these relations break down for $z > 1$ (see Fig. 8.1).

The case $z \gg 1$

Highly degenerate fermionic gases are characterized by this limit ($\mu \gg k_B T$). In this case the integral $F_{3/2}^{\mathrm{FD}}(z)$ can be expanded in powers of $\nu = \ln z = \mu/k_B T$ (see Appendix B.4),

$$F_{3/2}^{\mathrm{FD}}(z) = \frac{4}{3\sqrt{\pi}}\,(\ln z)^{3/2}\left[1 + \frac{\pi^2}{8}\,(\ln z)^{-2} + \cdots\right] \quad \text{for } (\mu \gg k_B T)\,. \tag{8.71}$$

$$F_{5/2}^{\mathrm{FD}}(z) = \frac{8}{15\sqrt{\pi}}\,(\ln z)^{5/2}\left[1 + \frac{5\pi^2}{8}\,(\ln z)^{-2} + \cdots\right] \quad \text{for } (\mu \gg k_B T)\,. \tag{8.72}$$

Note that these expressions satisfy the recursion relations (B.9). Note further that $F_{3/2}^{\mathrm{FD}}(z)$ and $F_{5/2}^{\mathrm{FD}}(z)$ diverge logarithmically with z. The approximation by the first two terms of Eq. (8.71) is shown for $F_{3/2}^{\mathrm{FD}}(z)$ as the dotted line in Fig. 8.1. Note that this approximation is already excellent for $\mu/k_B T \gtrsim \ln 4 \approx 1.3$.

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 ($k_B T \gg \hbar\omega$). 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,

$$\mathcal{H}_0(\mathbf{p}, \mathbf{r}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 + \mathcal{U}(\mathbf{r}_i). \tag{9.2}$$

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

$$f_{\mathrm{BE}}(\varepsilon_s; \mu, T) = \frac{1}{e^{(\varepsilon_s - \mu)/k_B T} - 1}. \tag{9.3}$$

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). Excluding the ground state, the BE-distribution is a quasi-continuous function of ε_s, even for $-\mu \ll k_B T$, as is illustrated in Fig. 9.1. In the absence of a condensate, *i.e.* for $-\mu/k_B T \ggg 1/N$, this allows us to make the quasi-classical approximation (8.26), 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 when, with the onset of BEC, the ground-state occupation N_0 grows disproportionately and $f_{\mathrm{BE}}(\varepsilon_s)$ becomes discontinuous at $\varepsilon_s = 0$. 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 (8.25). In this way the quasi-classical approximation remains valid for the summation over excited states and we can write

$$N = N_0 + {\sum_s}' \bar{n}_s = \frac{1}{e^{-\mu/k_B T} - 1} + \frac{1}{(2\pi\hbar)^3} \int \frac{1}{e^{(H_0(\mathbf{r},\mathbf{p}) - \mu)/k_B T} - 1} d\mathbf{r} d\mathbf{p}. \tag{9.4}$$

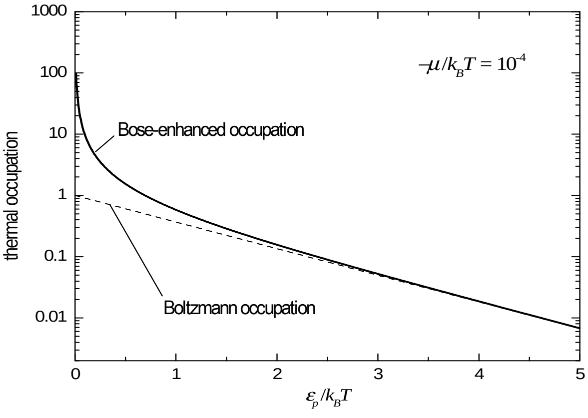

Figure 9.1: Average thermal occupation $\bar{n}_s \equiv f_{\mathrm{BE}}(\varepsilon_s/T)$ of states of energy ε_s for $-\mu/k_BT = 10^{-4}$ (solid line). The occupation of the lowest levels ($\varepsilon_s < k_BT$) is strongly enhanced as compared to the classical (Boltzmann) occupation (dashed line). 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*,

$$\sum_s{}'\bar{n}_s \equiv N' = N - N_0. \tag{9.5}$$

As is readily verified, like the N_0-term also the BE-integral in Eq. (9.4) 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. (9.4) can be satisfied for any value of N and T by choosing the appropriate value for μ.

Because the chemical potential is always negative, the *fugacity*

$$z \equiv e^{\mu/k_BT} \tag{9.6}$$

is bounded to the interval $0 < z < 1$. Since also $0 < \exp[-H_0(\mathbf{r},\mathbf{p})/k_BT] \leq 1$ we can use the fugacity expansion (see Section 8.3.7) for the BE-integral in Eq. (9.4),

$$N = N_0 + N' = \frac{z}{1-z} + \sum_{\ell=1}^{\infty} z^{\ell} \frac{1}{(2\pi\hbar)^3} \int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT} d\mathbf{r}d\mathbf{p}. \tag{9.7}$$

Hence, recalling Eq. (1.35) we can express the total number of trapped atoms N in terms of the ground-state occupation N_0 plus a sum over the single-particle canonical partition functions $Z_1(T)$ of a *classical* ideal gas at temperatures $T, T/2, \cdots, T/\ell, \cdots$,

$$N = N_0 + N' = \frac{z}{1-z} + \sum_{\ell=1}^{\infty} z^{\ell} Z_1(T/\ell). \tag{9.8}$$

Making the local density approximation (8.33), the density distribution $n'(\mathbf{r})$ of a thermal cloud of bosons in a trap $\mathcal{U}(\mathbf{r})$ is given by

$$n'(\mathbf{r}) = \frac{1}{\Lambda^3} F_{3/2}^{\mathrm{BE}}\left(ze^{-\mathcal{U}(\mathbf{r})/k_BT}\right), \tag{9.9}$$

where

$$N' = \int n'(\mathbf{r})d\mathbf{r} \tag{9.10}$$

is the total number of atoms in the thermal cloud. Since $0 < ze^{-\mathcal{U}(\mathbf{r})/k_BT} < 1$ the fugacity expansion (8.68a) is valid and Eq. (9.9) can be written in the form

$$n'(\mathbf{r}) = \frac{1}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2}}e^{-\ell\mathcal{U}(\mathbf{r})/k_BT}. \tag{9.11}$$

In particular we have at the trap minimum ($\mathbf{r} = 0$)

$$n_0'\Lambda^3 = \sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2}} \equiv g_{3/2}(z). \tag{9.12}$$

Note that Eq. (9.12) 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.

9.2 Classical regime $\left(n_0\Lambda^3 \ll 1\right)$

At constant n_0' the l.h.s. of Eq. (9.12) 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

$$z \underset{T\to\infty}{\simeq} n_0\Lambda^3 \Leftrightarrow \mu = k_BT\ln[n_0\Lambda^3]. \tag{9.13}$$

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 (9.13) was obtained for the classical gas starting from the Helmholtz free energy (see Problem 1.13).

9.3 The onset of quantum degeneracy $\left(1 \lesssim n_0\Lambda^3 < 2.612\right)$

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

$$n(\mathbf{r}) = \frac{1}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{1}{\ell^{3/2}}\exp[-\ell\mathcal{U}(\mathbf{r})/k_BT_c].$$

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. We thus established that the parameter $D = n_0\Lambda^3$ is indeed a good indicator for the presence of quantum degeneracy, *i.e.* for the deviation from classical statistics. For the trap center we have at T_c

$$D = n_0\Lambda^3 = \sum_{\ell=1}^{\infty}\frac{1}{\ell^{3/2}} \equiv \zeta\,(3/2) \approx 2.612. \tag{9.14}$$

Hence, T_c only depends on the density in the trap center and *not on the trap shape,*

$$k_BT_c \simeq 3.31\left(\hbar^2/m\right)n_0^{2/3}. \tag{9.15}$$

9.4 Fully degenerate Bose gases and Bose-Einstein condensation

In this section we have a closer look at what happens close to T_c, where the general expression (9.8) holds,

$$N = N_0 + N' = \frac{z}{1-z} + \sum_{\ell=1}^{\infty} z^{\ell} Z_1(T/\ell) \tag{9.16}$$

and the partition function is given by Eq. (1.47),

$$Z_1(T/\ell) = \frac{V_e(T/\ell)}{[\Lambda(T/\ell)]^3} = \frac{V_e(T/\ell)}{\Lambda^3}\frac{1}{\ell^{3/2}}. \tag{9.17}$$

In accordance with Eq. (1.45)

$$V_e(T/\ell) = \int e^{-\ell \mathcal{U}(\mathbf{r})/k_B T} d\mathbf{r} \tag{9.18}$$

is the effective volume V_e of a *classical* cloud at temperature T/ℓ. Although this volume cannot be observed in the quantum gas it is convenient from the mathematical point of view.

We first analyze Eq. (9.16) for the homogeneous gas confined to a volume V. Since for a homogeneous gas $V_e(T/\ell) = V$ the partition function (9.17) takes the form

$$Z_1(T/\ell) = \frac{V}{\Lambda^3}\frac{1}{\ell^{3/2}} \tag{9.19}$$

and substituting this expression into Eq. (9.8) we obtain

$$N = \frac{z}{1-z} + \frac{V}{\Lambda^3} g_{3/2}(z). \tag{9.20}$$

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 (8.69) in powers of $(-\ln z) = -\mu/k_B T$,

$$N = \frac{k_B T}{-\mu} + \frac{V}{\Lambda^3}\left[\zeta(3/2) + \zeta(1/2)\sqrt{\frac{-\mu}{k_B T}} + \cdots\right] \quad \text{for } (\mu \uparrow 0). \tag{9.21}$$

Just above T_c, *i.e.* for $1/N \lll -\mu/k_B T \ll 1$, the chemical potential can be expressed as

$$\mu = -k_B T \left(\frac{\zeta(3/2) - n_0 \Lambda^3}{\zeta(1/2)}\right)^2, \tag{9.22}$$

which is plotted in Fig. 9.2. As expected, the chemical potential increases with decreasing temperature. For $-\mu \lesssim k_B T$ the curve deviates from the classical expression (9.13) shown as the dashed line in Fig. 9.2. For $-\mu \ll k_B T$, the fugacity expansion approaches its convergence limit and the thermal term of Eq. (9.21) can no longer account for all atoms. For a large but finite number of atoms ($N \ggg 1$) this happens for $T = T_c$ where μ has a small but finite negative value and the following expression is satisfied,

$$N = \frac{V}{\Lambda_c^3}\left[\zeta(3/2) + \zeta(1/2)\sqrt{\frac{-\mu}{k_B T_c}} + \cdots\right] \simeq \frac{V}{\Lambda_c^3}\zeta(3/2). \tag{9.23}$$

Lowering the temperature below T_c the ground state occupation starts to grow from $N_0 = -k_B T/\mu \ll N$ to macroscopic values, which marks the onset of Bose-Einstein condensation. Below T_c the *non-condensed fraction* is given by

$$N'/N = \zeta(3/2)/n\Lambda^3 = (T/T_c)^{3/2}, \tag{9.24}$$

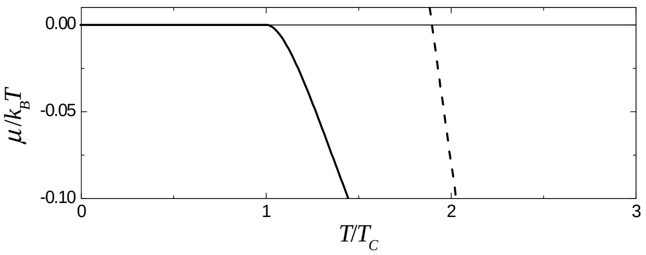

Figure 9.2: Chemical potential as a function of temperature for a homogeneous Bose gas close to T_c (solid line). For comparison the classical expression (9.13) is also plotted (dashed line).

which implies that the number of atoms in the condensate is given by $N_0 = N - N' = -k_BT/\mu$ and *condensate fraction* is growing in accordance with

$$N_0/N = 1 - (T/T_c)^{3/2}. \tag{9.25}$$

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* ($N, V \to \infty$, $N/V = n_0$).

The above analysis can be generalized to inhomogeneous gases. Combining Eqs. (9.10) and (9.11) the number of atoms in the *thermal cloud* can be expressed as

$$N' = \int n'(\mathbf{r})d\mathbf{r} = \frac{1}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2}}V_e(T/\ell). \tag{9.27}$$

Restricting ourselves to power-law traps we can relate the effective volumes at two temperatures with the aid of Eq. (1.71),

$$V_e(T/\ell) = (1/\ell)^\gamma\, V_e(T). \tag{9.28}$$

where γ is the trap parameter. Substituting this relation into Eq. (9.27) we obtain

$$N = \frac{V_e(T)}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2+\gamma}} = \frac{V_e(T)}{\Lambda^3}g_{3/2+\gamma}(z). \tag{9.29}$$

For $T \le T_c$ we have $z = 1$ and

$$N' = \frac{V_e(T)}{\Lambda^3}g_{3/2+\gamma}(1) \le N. \tag{9.30}$$

For power-law traps with trap parameter γ we obtain after substitution of Eq. (1.71) $N'/N = (T/T_c)^{3/2+\gamma}$, which implies for the condensate fraction,

$$N_0/N = 1 - (T/T_c)^{3/2+\gamma}. \tag{9.31}$$

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 $T \le T_c$ we have starting from Eq. (9.8)

$$N' = \sum_{\ell=1}^{\infty}Z_1(T/\ell) = \sum_{\ell=1}^{\infty}\int_0^\infty e^{-\ell\varepsilon/k_BT}\rho(\varepsilon)d\varepsilon, \tag{9.32}$$

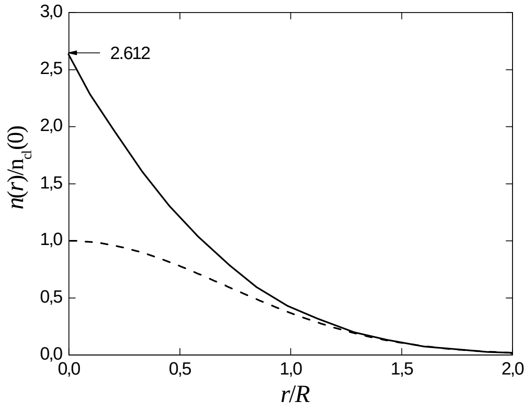

Figure 9.3: The density profile of a fully saturated ($z = 1$) thermal cloud of bosons in an isotropic harmonic trap (solid line). For comparison the gaussian profile of a classical gas is also drawn (dashed line); $R = \sqrt{2kT/m\omega^2}$ is the thermal radius of the classical cloud.

where we used Eq. (1.75). For any trap, isotropic or anisotropic, with a density of states of the type $\rho(\varepsilon) = A\varepsilon^{1/2+\gamma}$ we have

$$N' = A\sum_{\ell=1}^{\infty}\int_0^{\infty} e^{-\ell\varepsilon/k_BT}\varepsilon^{1/2+\gamma}d\varepsilon = A\,(k_BT)^{3/2+\gamma}\sum_{\ell=1}^{\infty}\int_0^{\infty} e^{-\ell x}x^{1/2+\gamma}dx. \tag{9.33}$$

Hence, using the integral relation (B.5) Eq. (9.33) reduces to

$$N' = A\,(k_BT)^{3/2+\gamma}\,\Gamma(3/2+\gamma)g_{3/2+\gamma}(z) \tag{9.34}$$

and Eq. (9.31) for the condensate fraction is seen to hold for all traps with a density of states of the type $\rho(\varepsilon) = A\varepsilon^{1/2+\gamma}$.

9.4.1 Example: BEC in isotropic harmonic traps

As an example we consider the harmonically trapped ideal Bose gas (trap parameter $\gamma = 3/2$) at temperatures $k_BT \gg \hbar\omega$, where $\omega/2\pi$ is the oscillation frequency of a single trapped atom. For this system we have a quasi-continuous level occupation and the quasi-classical single-particle partition function is given by $Z_1 = (k_BT/\hbar\omega)^3$, see Eq. (1.77). The density profile of the thermal cloud is found by substituting $\mathcal{U}(\mathbf{r}) = \frac{1}{2}m\omega^2r^2$ into Eq. (9.9),

$$n'(\mathbf{r}) = \frac{1}{\Lambda^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{3/2}}\exp[-\ell\frac{m\omega^2r^2}{2k_BT}]. \tag{9.35}$$

The profile of a fully saturated ($z = 1$) Bose-Einstein distribution is shown in Fig. 9.3. Note that the cloud is gaussian for $m\omega^2r^2 \gg k_BT$, which means that the tail of the distribution remains quasi 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. (9.8), which takes for harmonic traps the form

$$N = \frac{z}{1-z} + (k_BT/\hbar\omega)^3\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^3}. \tag{9.36}$$

The convergence limit of the series is given by

$$\lim_{z\to 0}\sum_{\ell=1}^{\infty}\frac{z^{\ell}}{\ell^{3}}=g_{3}(1)=\zeta\left(3\right)\approx 1.202. \tag{9.37}$$

Thus at T_c we find with the aid of Eq. (9.36) $N=\left(k_BT_c/\hbar\omega\right)^3\zeta\left(3\right)$, which can be written in the form of an expression for T_c,

$$k_BT_c=\left[N/\zeta\left(3\right)\right]^{1/3}\hbar\omega\simeq N^{1/3}\hbar\omega. \tag{9.38}$$

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 $k_BT\gg\hbar\omega$ 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 ($\upsilon_0 n_0\ll k_BT_c$).

For $T\leq T_c$ Eq. (9.36) takes the form

$$N=N_0+\left(k_BT/\hbar\omega\right)^3\zeta\left(3\right)=N_0+\left(T/T_c\right)^3N, \tag{9.39}$$

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. (9.39) we obtain for the for the condensate fraction of a harmonically trapped gas

$$N_0/N=1-\left(T/T_c\right)^3. \tag{9.40}$$

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 $\varepsilon_1=\hbar\omega\ll k_BT_c\simeq N^{1/3}\hbar\omega$, is given by

$$\bar{n}_1=\frac{1}{e^{\varepsilon_1/k_BT_c}-1}\simeq\frac{k_BT_c}{\hbar\omega}\simeq N^{1/3}.$$

For $N=10^6$ this implies that $\bar{n}_1=100$. ▶

9.5 Release of trapped clouds - momentum distribution of bosons

For a gas of bosons above T_c the momentum distribution is given by

$$n(\mathbf{p})=\sum_{\ell=1}^{\infty}z^{\ell}\frac{1}{(2\pi\hbar)^3}\int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT}d\mathbf{r}=\frac{1}{(2\pi\hbar)^3}\sum_{\ell=1}^{\infty}z^{\ell}e^{-\ell(p/\alpha)^2}V_e\left(T/\ell\right), \tag{9.41}$$

where $\alpha=\sqrt{2mk_BT}$ and $V_e(T/\ell)$ is the effective volume of a *classical* cloud at temperature T/ℓ as defined in Eq. (9.18). 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. (9.28) into Eq. (9.41) we obtain for the momentum distribution

$$n(\mathbf{p})=\frac{V_e\,(T)}{(2\pi\hbar)^3}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^\gamma}e^{-\ell(p/\alpha)^2}=\frac{N}{4\pi\alpha^3}\frac{1}{\frac{1}{4}\sqrt{\pi}}\frac{g_\gamma(ze^{-(p/\alpha)^2})}{g_{\gamma+3/2}(z)},\tag{9.42}$$

where we used

$$N=\int n(\mathbf{p})d\mathbf{p}=\frac{V_e\,(T)}{(2\pi\hbar)^3}4\pi\alpha^3\frac{1}{4}\sqrt{\pi}\,g_{\gamma+3/2}(z).\tag{9.43}$$

Since $\Lambda^3=\pi^{-3/2}\,(2\pi\hbar/\alpha)^3$ the above expression coincides with Eq. (9.29). Interestingly, for *harmonic* traps ($\gamma=3/2$) the momentum distribution (9.42) has exactly the same functional form as the density distribution (9.35).

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

$$\begin{aligned}\langle p^2\rangle&=\int p^2\mathrm{f}_{\mathrm{BE}}(\mathbf{p})d\mathbf{p}=\alpha^2\frac{\frac{3}{8}\sqrt{\pi}g_{\gamma+5/2}(z)}{\frac{1}{4}\sqrt{\pi}g_{\gamma+3/2}(z)}=3mk_BT\frac{g_{\gamma+5/2}(z)}{g_{\gamma+3/2}(z)}\\ \langle p\rangle&=\int p\,\mathrm{f}_{\mathrm{BE}}(\mathbf{p})d\mathbf{p}=\alpha\frac{\frac{1}{2}g_{\gamma+4}(z)}{\frac{1}{4}\sqrt{\pi}g_{\gamma+3/2}(z)}=\sqrt{8mk_BT/\pi}\frac{g_{\gamma+4}(z)}{g_{\gamma+3/2}(z)}\end{aligned}$$

Comparing the first and second moments we obtain

$$\langle p^2\rangle/\langle p\rangle^2=\frac{3\pi}{8}g_{\gamma+5/2}(z)g_{\gamma+3/2}(z)/\left[g_{\gamma+2}(z)\right]^2,$$

which implies that for harmonic traps the ratio $\langle p^2\rangle/\langle p\rangle^2$ 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.

9.6 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,

$$N=\sum_s\bar{n}_s=\sum_{\ell=1}^{\infty}z^\ell\frac{1}{(2\pi\hbar)^2}\int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT}d\mathbf{r}d\mathbf{p}.\tag{9.44}$$

In 2D the phase space is 4-dimensional and after integration we obtain

$$N=\frac{1}{\Lambda^2}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell}\int e^{-\ell\mathcal{U}(\mathbf{r})/k_BT}d\mathbf{r}.\tag{9.45}$$

For the homogeneous gas of N bosons confined to an area A this expression reduces for $\mu\ll k_BT$ to

$$D=n\Lambda^2=\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell}=-\ln{(1-z)}\simeq-\ln(-\mu/k_BT),\tag{9.46}$$

where $n = N/A$ is the two-dimensional density. Because the fugacity expansion does not converge to a finite limit Eq. (9.46) 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. (9.45) can be written as

$$N = \frac{1}{\Lambda^2}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell}A_e(T/\ell) = \frac{A_e}{\Lambda^2}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{1+2\gamma/3}} = \frac{A_e}{\Lambda^2}g_{1+2\gamma/3}(z), \tag{9.47}$$

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,

$$\lim_{z\to 1} g_{1+2\gamma/3}(z) = \zeta(1 + 2\gamma/3). \tag{9.48}$$

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. (9.45) the 2D density in the trap center is independently of γ given by

$$n_0 = \frac{1}{\Lambda^2}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell} \simeq -\frac{1}{\Lambda^2}\ln(-\mu/k_BT). \tag{9.49}$$

Hence, the density in the trap center locally diverges irrespective of the occurrence of BEC and is as such no indicator for BEC.

Problem 9.2 *Show that the effective area of a classical cloud in a 2D isotropic power-law trap is given by*

$$A_e = \frac{2}{3}\pi r_e^2\gamma\Gamma(2\gamma/3)\left(\frac{k_BT}{\mathcal{U}_0}\right)^{\frac{2}{3}\gamma},$$

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

Solution: The effective area is defined as $A_e = \int e^{-\mathcal{U}(r)/k_BT}d\mathbf{r}$. Substituting $\mathcal{U}(\mathbf{r}) = w_0 r^{3/\gamma}$ for the potential of an isotropic power-law trap we find with $w_0 = \mathcal{U}_0 r_e^{-3/\gamma}$

$$V_e = \int e^{-w_0 r^{3/\gamma}/k_BT}2\pi r dr = \frac{2}{3}\pi r_0^2\gamma\left(\frac{k_BT}{\mathcal{U}_0}\right)^{\frac{2}{3}\gamma}\int e^{-x}x^{\frac{2}{3}\gamma-1}dx,$$

where $x = (\mathcal{U}_0/k_BT)\,(r/r_e)^{3/\gamma}$ 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 $\gamma > 3/2$.*

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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).

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. (9.47):

$$N = \frac{1}{\Lambda}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{1/2}}L_e(T/\ell) = \frac{L_e}{\Lambda}\sum_{\ell=1}^{\infty}\frac{z^\ell}{\ell^{1/2+\gamma/3}} = \frac{L_e}{\Lambda}g_{1/2+\gamma/3}(z),$$

where L_e is the classical effective length

$$L_e = \int e^{-w_0 r^{3/\gamma}/k_BT}dr = \frac{1}{3}r_0\gamma\left(\frac{k_BT}{\mathcal{U}_0}\right)^{\frac{1}{3}\gamma}\int e^{-x}x^{\frac{1}{3}\gamma-1}dx = \frac{1}{3}r_0\gamma\left(\frac{k_BT}{\mathcal{U}_0}\right)^{\frac{1}{3}\gamma}\Gamma(1\gamma/3),$$

with $x = (\mathcal{U}_0/k_BT)\,(r/r_e)^{3/\gamma}$ 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] ▶

9.7 Absence of superfluidity in ideal Bose gas - Landau criterion

Superfluidity is the name for a complex of phenomena in degenerate quantum fluids.[3] 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'? The answer knows many layers but in this chapter we restrict ourselves to *ideal* gases and show that in this case 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 9.4. 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 homogenous 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. We will show that an *ideal* Bose gas is not a superfluid because for any speed of the moving body we can identify excitations that can be created under conservation of energy and momentum.

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

$$E_i = p^2/2m_0. \tag{9.50}$$

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

$$E_f = (\mathbf{p}-\hbar\mathbf{k})^2/2m_0 + \varepsilon_k = p^2/2m_0 + \hbar^2k^2/2m_0 - \hbar\mathbf{k}\cdot\mathbf{p}/m_0 + \varepsilon_k. \tag{9.51}$$

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[3] 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).

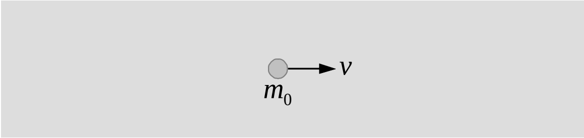

Figure 9.4: A body moving at velocity v through a Bose-Einstein condensate at rest.

Energy conservation excludes excitation if $E_f - E_i > 0$, which is equivalent to $\varepsilon_k > \hbar\mathbf{k}\cdot\mathbf{v} - \hbar^2 k^2/2m_0$. This condition is most difficult to satisfy for $\mathbf{v}$ parallel to $\mathbf{k}$, in which case we obtain after some rearranging

$$v < \varepsilon_k/\hbar k + \hbar k/2m_0 = v_c. \tag{9.52}$$

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 $\varepsilon_k = \hbar^2 k^2/2m$, where m is the mass of the condensate atoms. Substituting this dispersion into Eq. (9.52) we find for the critical velocity in an ideal gas

$$v_c = \hbar k/2\mu, \tag{9.53}$$

where $\mu = mm_0/\left(m + m_0\right)$ 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 excitation spectrum is phonon-like $\varepsilon_k = \hbar ck$, with c the speed of sound. Substituting the linear dispersion into Eq. (9.52) the condition for excitation-free motion becomes

$$v < c + \hbar k/2m_0 = v_c.$$

Apparently, below a critical velocity, the *Landau critical velocity* $v_c = c$, non 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 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.

10

Ideal Fermi gases

10.1 Introduction

In the case of fermionic gases the quasi-classical approximation (8.26) is always valid because as a result of the Pauli principle 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 (8.26),

$$N = \frac{1}{(2\pi\hbar)^3} \int \frac{1}{e^{(H_0(\mathbf{r},\mathbf{p})-\mu)/k_BT}+1} d\mathbf{r}d\mathbf{p}. \tag{10.1}$$

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

$$N = \sum_{\ell=1}^{\infty} (-)^{\ell+1} z^{\ell} \frac{1}{(2\pi\hbar)^3} \int e^{-\ell H_0(\mathbf{r},\mathbf{p})/k_BT} d\mathbf{r}d\mathbf{p}. \tag{10.3}$$

The density distribution is given by Eq. (8.27) 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

$$D \equiv n_0\Lambda^3 = \sum_{\ell=1}^{\infty} (-)^{\ell+1} \frac{z^{\ell}}{\ell^{3/2}} \equiv f_{3/2}(z) = F_{3/2}(u) \quad (\text{for } 0 < z \leq 1), \tag{10.5}$$

where $z \equiv e^{-u}$ with $u \equiv -\mu/k_BT$.

For $\mu > 0$ the series does not converge uniformly. Hence, the interchange of the order of summation and integration as applied in Eq. (10.3) is not allowed and 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 (9.13) 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 $z \gg 1$. In accordance with Eq.(8.71) the local density can be written as

$$n = \frac{1}{\Lambda^3}F_{\mathrm{FD}}(z) \simeq \frac{4}{3\sqrt{\pi}}(\ln z)^{3/2}\left[1 + \frac{\pi^2}{8}(\ln z)^{-2} + \cdots\right]. \tag{10.8}$$

Restoring the position dependence by substituting

$$\ln z = \mu\left(\mathbf{r}\right)/k_BT \tag{10.9}$$

we obtain

$$n\left(\mathbf{r}\right) = \frac{1}{\Lambda^3}\frac{4}{3\sqrt{\pi}}\left(\frac{\mu\left(\mathbf{r}\right)}{k_BT}\right)^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu\left(\mathbf{r}\right)}\right)^2+\cdots\right]. \tag{10.10}$$

Eliminating the chemical potential we obtain

$$\mu\left(\mathbf{r}\right) = \frac{\hbar^2}{2m}\left[6\pi^2 n\left(\mathbf{r}\right)\right]^{2/3}\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\mu\left(\mathbf{r}\right)}\right)^2+\cdots\right]. \tag{10.11}$$

Introducing the *Fermi energy* of the gas

$$\varepsilon_F \equiv \lim_{T\to 0}\mu\left(0\right) = \frac{\hbar^2}{2m}\left[6\pi^2 n_0\right]^{2/3} \tag{10.12}$$

and defining the Fermi temperature as $\varepsilon_F \equiv k_BT_F$ the chemical potential of a homogeneous system can be written as

$$\mu \simeq \varepsilon_F\left[1-\frac{\pi^2}{12}\left(T/T_c\right)^2\right] \qquad (\text{for } T\to 0). \tag{10.13}$$

10.4.1 Thomas-Fermi approximation

The local density approximation in the zero-temperature limit is called the Thomas-Fermi approximation

$$\mu\left(\mathbf{r}\right) = \varepsilon_F - \mathcal{U}(\mathbf{r}) = \frac{\hbar^2}{2m}\left[6\pi^2 n\left(\mathbf{r}\right)\right]^{2/3}. \tag{10.14}$$

The corresponding Thomas-Fermi profile is obtained by eliminating $n\left(\mathbf{r}\right)$ from this equation

$$n\left(\mathbf{r}\right) = \frac{1}{6\pi^2}\left\{\frac{2m}{\hbar^2}\left[\varepsilon_F-\mathcal{U}(\mathbf{r})\right]\right\}^{3/2} = n_0\left[1-\mathcal{U}(\mathbf{r})/\varepsilon_F\right]^{3/2}.$$

11

The weakly-interacting Bose gas for $T \to 0$.

In this chapter we add interactions to our discussion of a gas of N trapped atoms confined by an external potential $\mathcal{U}(\mathbf{r})$ and studied at temperatures T where many single-particle states are populated ($k_B T \gg \hbar\omega$). We consider the weakly interacting limit,

$$n r_0^3 \ll 1, \tag{11.1}$$

defined in Section 1.1 as the regime dominated by binary collisions between the atoms. The hamiltonian for this system can be written in the form

$$\mathcal{H} = \sum_i \mathcal{H}_0(\mathbf{p}_i, \mathbf{r}_i) + \frac{1}{2} \sum_{i,j}{}' \mathcal{V}(\mathbf{r}_i, \mathbf{r}_j) \,. \tag{11.2}$$

where $\mathcal{H}_0(\mathbf{p}_i, \mathbf{r}_i)$ is the single-particle hamiltonian (9.2) and $\mathcal{V}(\mathbf{r}_i, \mathbf{r}_j)$ represents the interaction between particles i and j. Because we are dealing with a quantum many-body system we turn to the hamiltonian in second quantization,

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) \mathcal{H}_0(\mathbf{p}, \mathbf{r}) \hat{\psi}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \mathcal{V}(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}). \tag{11.3}$$

Restricting ourselves to the low temperature limit ($T \to 0$) we know that s-wave collisions dominate the physics. As was discussed in Section 3.3.17 in this case the interaction potential $\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2)$ may be approximated by a contact interaction

$$\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2) = g\, \delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{11.4}$$

where $g = \left(4\pi\hbar^2/m\right) a$, with a being the s-wave scattering length. Within this approximation, the interaction term $\hat{H}^{(2)}$ reduces to

$$\hat{H}^{(2)} = \frac{1}{2} g \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) \hat{n}(\mathbf{r}) \hat{\psi}(\mathbf{r}). \tag{11.5}$$

In the same way as we derived for $\hat{H}^{(1)}$ the commutation relation (7.66),

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(1)}] = \mathcal{H}_0(\mathbf{p}, \mathbf{r}) \hat{\psi}(\mathbf{r}, t), \tag{11.6}$$

we can derive for $\hat{H}^{(2)}$ the commutation relation (see Problem 11.1)

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(2)}] = g\,\hat{n}(\mathbf{r})\hat{\psi}(\mathbf{r}). \tag{11.7}$$

Note the absence of the factor 1/2 on the r.h.s. of this equation.

Problem 11.1 *Derive the commutation relation*

$$[\hat{\psi}(\mathbf{r}), \hat{H}^{(2)}] = g\,\hat{n}(\mathbf{r})\hat{\psi}(\mathbf{r}).$$

Solution: The operator

$$\hat{H}^{(2)} = \frac{1}{2} g \int d\mathbf{r} \hat{\psi}^{\dagger}(\mathbf{r})\hat{n}(\mathbf{r})\hat{\psi}(\mathbf{r})$$

is a construction operator for the two-body interaction $\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2) = g\,\delta(\mathbf{r}_1 - \mathbf{r}_2)$. Using the commutation relations $[\hat{\psi}(\mathbf{r}), \hat{\psi}^{\dagger}(\mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}')$, $[\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')] = 0$ and $[\hat{n}(\mathbf{r}), \hat{\psi}(\mathbf{r}')] = -\hat{\psi}(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}')$ we find after integration over $\mathbf{r}'$

$$\begin{aligned}
[\hat{\psi}(\mathbf{r}), \hat{H}^{(2)}] &= \frac{1}{2} g \int d\mathbf{r}' \left[\hat{\psi}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{n}(\mathbf{r}')\hat{\psi}(\mathbf{r}') - \hat{\psi}^{\dagger}(\mathbf{r}')\hat{n}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})\right] \\
&= \frac{1}{2} g \int d\mathbf{r}' \left[\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r})\hat{n}(\mathbf{r}')\hat{\psi}(\mathbf{r}') - \hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r})\hat{n}(\mathbf{r}')\hat{\psi}(\mathbf{r}') + 2\delta(\mathbf{r} - \mathbf{r}')\hat{n}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\right] \\
&= g\,\hat{n}(\mathbf{r})\hat{\psi}(\mathbf{r}). \ \blacktriangleright
\end{aligned}$$

11.0.2 Gross-Pitaevskii equation

The Heisenberg equation of motion for the field operator $\hat{\psi}(\mathbf{r}, t)$ is given by

$$i\hbar \frac{\partial}{\partial t} \hat{\psi}(\mathbf{r}, t) = [\hat{\psi}(\mathbf{r}, t), \hat{H} - \mu \hat{N}]. \tag{11.8}$$

Here we added to the hamiltonian the term $-\mu\hat{N}$ and ask for the value of μ that makes the field operator stationary. To answer this question we consider a Bose-Einstein condensate of N_0 atoms in the ground state ($s \equiv 0$) represented by the number state $|N_0\rangle$. The total energy of this interacting many-body system is given by $E_0 = \langle N_0|\hat{H}|N_0\rangle$, where E_0 depends on the number of atoms $E_0 = E_0(N_0)$,

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \langle N_0 - 1|\, \hat{\psi}(\mathbf{r}, t)\, |N_0\rangle &= \langle N_0 - 1|\, [\hat{\psi}(\mathbf{r}), \hat{H} - \mu \hat{N}]\, |N_0\rangle \\
&= [E_0(N_0) - E_0(N_0 - 1) - \mu]\, \langle N_0 - 1|\, \hat{\psi}(\mathbf{r}, t)\, |N_0\rangle\,.
\end{aligned} \tag{11.9}$$

Hence, the field operator is stationary, $\hat{\psi}(\mathbf{r}, t) = \hat{\psi}(\mathbf{r}, t_0) = \hat{\psi}(\mathbf{r})$, if we choose μ equal to the *chemical potential* of the system

$$\mu = E_0(N_0) - E_0(N_0 - 1)\,.$$

Substituting Eq. (11.6) and (11.7) into the *Heisenberg equation of motion* for the field operator $\hat{\psi}(\mathbf{r})$ we obtain for stationary conditions

$$i\hbar \frac{\partial}{\partial t} \hat{\psi}(\mathbf{r}, t) = [\mathcal{H}_0(\mathbf{p}, \mathbf{r}) + g\,\hat{n}(\mathbf{r}, t) - \mu]\, \hat{\psi}(\mathbf{r}, t) = 0. \tag{11.10}$$

Recalling the definition of the field operator $\hat{\psi}(\mathbf{r})$,

$$\hat{\psi}(\mathbf{r}) \equiv \sum_s \varphi_s(\mathbf{r})\hat{a}_s = \varphi_0(\mathbf{r})\hat{a}_0 + \sum_{s \neq 0} \varphi_s(\mathbf{r})\hat{a}_s, \tag{11.11}$$

we can introduce the *order parameter* $\psi_{N_0}(\mathbf{r},t)$,

$$\langle N_0-1|\,\hat{\psi}(\mathbf{r},t)\,|N_0\rangle = \langle N_0-1|\,\sqrt{N_0}\varphi_0^{(N_0)}(\mathbf{r},t)\,|N_0-1\rangle = \sqrt{N_0}\varphi_0^{(N_0)}(\mathbf{r},t) \equiv \psi_{N_0}(\mathbf{r},t), \tag{11.12}$$

where $\varphi_0^{(N_0)}(\mathbf{r},t)$ is the unit-normalized N_0-particle ground state wavefunction. The order parameter serves to calculate the properties of a Bose-Einstein condensate. To find the order parameter we have to solve Eq. (11.9),

$$i\hbar\frac{\partial}{\partial t}\psi_{N_0}(\mathbf{r},t) = \left[\mathcal{H}_0(\mathbf{p},\mathbf{r}) + g\,\langle N_0-1|\,\hat{n}(\mathbf{r},t)\,|N_0-1\rangle - \mu\right]\psi_{N_0}(\mathbf{r},t). \tag{11.13}$$

For $N_0 \ggg 1$ the *shape* of the condensate wavefunction $\varphi_0^{(N_0)}(\mathbf{r},t)$ depends only very weakly (and in an infinite homogeneous system not at all) on the exact value of N_0, *i.e.* $\varphi_0^{(N_0-1)}(\mathbf{r},t) \simeq \varphi_0^{(N_0)}(\mathbf{r},t)$. Hence, using the definition of the order parameter we have

$$\psi_{N_0-1}(\mathbf{r},t) \simeq \sqrt{\frac{N_0}{N_0-1}}\psi_{N_0}(\mathbf{r},t) \simeq \psi_{N_0}(\mathbf{r},t) \qquad (\text{for } N_0 \ggg 1) \tag{11.14}$$

and the expectation value of the density operator becomes

$$\langle N_0-1|\,\hat{n}(\mathbf{r},t)\,|N_0-1\rangle \simeq \psi_{N_0-1}(\mathbf{r},t) \simeq |\psi_{N_0}(\mathbf{r},t)|^2 = n_{N_0}(\mathbf{r},t). \tag{11.15}$$

At this point we omit the explicit use of the subscript N_0, replacing it by the normalization condition

$$\int |\psi(\mathbf{r})|^2 d\mathbf{r} = N_0. \tag{11.16}$$

In this notation the action of the field operator acting on the N-times occupied ground state is given by

$$\hat{\psi}(\mathbf{r})\,|N\rangle = \psi(\mathbf{r})\,|N-1\rangle \tag{11.17}$$

with a similar expression for $\hat{\psi}^\dagger(\mathbf{r})$. Thus we arrive at the equation of motion for the order parameter,

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) \simeq \left[\mathcal{H}_0(\mathbf{p},\mathbf{r}) + g\,|\psi(\mathbf{r},t)|^2 - \mu\right]\psi(\mathbf{r},t) \qquad (\text{for } N_0 \ggg 1). \tag{11.18}$$

The stationary solution has the form of a non-linear Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\Delta + \mathcal{U}(\mathbf{r}) + g\,|\psi(\mathbf{r})|^2\right]\psi(\mathbf{r}) = \mu\psi(\mathbf{r}) \qquad (\text{for } N_0 \ggg 1) \tag{11.19}$$

and is called the *Gross-Pitaevskii equation.*[1] With the concept of the order parameter we found a powerful tool to describe the collective properties of a many-body system *while properly accounting for the internal correlations between the atoms.* This is certainly one of the deepest achievements of condensed matter physics.

11.0.3 Thomas-Fermi approximation

The Gross-Pitaevskii equation is easily solved analytically for conditions where the interactions are repulsive ($g > 0$) and dominate over the kinetic energy, *i.e.* for $g\,n(\mathbf{r}) \gg |\left(\hbar^2/2m\right)\Delta\psi(\mathbf{r})|$. Under these conditions the kinetic energy term can be simply neglected, which is known as the

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[1] E.P. Gross, Nuovo Cimento, **20**, 454 (1961). L.P. Pitaevskii, Zh. Eksp. Teor. Phys., **40**, 646 [Sov.Phys. JETP, 451 (1961)].

Thomas-Fermi approximation. For instance, for the homogeneous gas we obtain, using $\mathcal{U}(\mathbf{r}) = 0$ and $n(\mathbf{r}) = |\psi(\mathbf{r})|^2$,

$$\mu = g\, n(\mathbf{r}). \tag{11.20}$$

For the inhomogeneous gas, the Gross-Pitaevskii equation reduces to

$$\mu = g\, n(\mathbf{r}) + \mathcal{U}(\mathbf{r}) = g\, n_0. \tag{11.21}$$

Extracting the density we obtain the famous *Thomas-Fermi density profile* observed in the very first experiments with Bose-Einstein condensed gases,[2]

$$n(\mathbf{r}) = [\mu - \mathcal{U}(\mathbf{r})]/g \quad \text{with } N_0 = \int n(\mathbf{r}) d\mathbf{r}. \tag{11.22}$$

Note that at the edge of the Thomas-Fermi profile the approximation must break down because the density (and thus the interaction energy) vanishes. For condensates with many atoms this 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. (11.21)

$$\tfrac{1}{2} m\omega^2 R_0^2 = \mu \Leftrightarrow R_0 = \sqrt{2\mu/m\omega^2}. \tag{11.23}$$

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 (cf. Section 1.3.2),

$$\tfrac{1}{2} m\omega^2 R_{cr}^2 = k_B T_c \Leftrightarrow R_{cr} = \sqrt{2k_B T_c/m\omega^2}, \tag{11.24}$$

and with on the other hand the *harmonic oscillator length*, which is defined by

$$\tfrac{1}{2} m\omega^2 l_0^2 = \tfrac{1}{2}\hbar\omega \Leftrightarrow l_0 = \sqrt{\hbar\omega/m\omega^2}. \tag{11.25}$$

One may show that aside from exceptional experimental cases the following inequalities are satisfied:

$$\tfrac{1}{2}\hbar\omega \ll \mu \ll k_B T_c \Leftrightarrow l_0 \ll R_0 \ll R_{cr}. \tag{11.26}$$

This means that down to $T = T_c$ the interactions may be neglected ($g\, n_0 \ll k_B T_c$). 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 ($g\, n_0 \gg \hbar\omega$). 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

$$\frac{\hbar^2}{2mR_0^2} = \frac{\hbar^2\omega^2}{4\mu} \ll \tfrac{1}{2}\hbar\omega \ll \mu, \tag{11.27}$$

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 $N_0 = \int n(\mathbf{r}) d\mathbf{r}$ is obtained by integrating over the density distribution (11.22),

$$g\, N_0 = \int \left[\mu - \tfrac{1}{2} m\omega^2 r^2\right] d\mathbf{r} = \mu \frac{4\pi}{3} R_0^2 - \frac{2\pi}{5} m\omega^2 R_0^5. \tag{11.28}$$

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[2] See M.H. Anderson, J.R. Ensher, M.R. Matthews, C.E. Wieman, and E.A. Cornell, Science **269**, 198 (1995); K. B. Davis, M.-O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, Phys. Rev. Lett., **75**, 3969 (1995).

With the aid of Eq. (11.23) we can eliminate μ from Eq. (11.28) and obtain

$$R_0 = \left(\frac{15}{4\pi} \frac{g\,N_0}{m\omega^2} \right)^{1/5} = l_0 \left(15 \frac{a}{l_0} N_0 \right)^{1/5} \tag{11.29}$$

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 and growth of the condensate volume.

Appendix A

Various physical concepts and definitions

A.1 Center of mass and relative coordinates

In this section we introduce *center of mass* and *relative coordinates*. These coordinates are optimally suited to deal with interatomic interactions and collisions between particles. The position of particle 1 relative to particle 2 is given by

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{A.1}$$

Taking the derivative with respect to time we find for the relative velocity of particle 1 with respect to particle 2

$$\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2. \tag{A.2}$$

The total momentum of the pair (the center of mass momentum) is a conserved quantity and given by

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 = m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = m_1\dot{\mathbf{r}}_1 + m_2\dot{\mathbf{r}}_2 \tag{A.3}$$

and the total mass by $M = (m_1 + m_2)$. With the definition $\mathbf{P} = M\dot{\mathbf{R}}$ we find for the position of the center of mass

$$\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2). \tag{A.4}$$

Adding and subtracting Eqs. (A.3) and (A.2) allows us to express $\mathbf{v}_1$ and $\mathbf{v}_2$ in terms of $\mathbf{P}$ and $\mathbf{v}$,

$$\mathbf{P} + m_2\mathbf{v} = (m_1 + m_2)\,\mathbf{v}_1 \tag{A.5a}$$

$$\mathbf{P} - m_1\mathbf{v} = (m_1 + m_2)\,\mathbf{v}_2. \tag{A.5b}$$

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

$$E = \frac{1}{2}m_1\mathbf{v}_1^2 + \frac{1}{2}m_2\mathbf{v}_2^2 = \frac{1}{2}m_1\frac{(\mathbf{P} + m_2\mathbf{v})^2}{(m_1 + m_2)^2} + \frac{1}{2}m_2\frac{(\mathbf{P} - m_1\mathbf{v})^2}{(m_1 + m_2)^2} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu}, \tag{A.6}$$

where

$$\mathbf{p} = \mu\mathbf{v} = \mu\dot{\mathbf{r}} = \frac{\mu}{m_1}\mathbf{p}_1 - \frac{\mu}{m_2}\mathbf{p}_2 \tag{A.7}$$

is the relative momentum and

$$\mu = m_1 m_2/(m_1 + m_2) \tag{A.8}$$

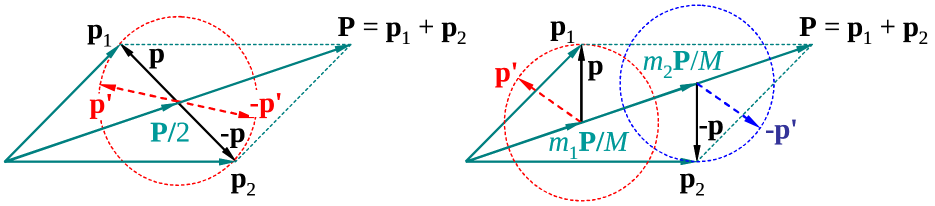

Figure A.1: Center of mass and relative momenta for two colliding atoms: *left*: equal mass; *right*: unequal mass with $m_1/m_2 = 1/3$.

the *reduced mass* of the pair. Adding and subtracting Eqs. (A.1) and (A.4) we can express $\mathbf{r}_1$ and $\mathbf{r}_2$ in terms of $\mathbf{R}$ and $\mathbf{r}$,

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r} \text{ and } \mathbf{r}_2 = \mathbf{R} - \frac{m_1}{M}\mathbf{r}. \tag{A.9}$$

Similarly combining Eqs. (A.3) and (A.7) we can express $\mathbf{p}_1$ and $\mathbf{p}_2$ in terms of $\mathbf{P}$ and $\mathbf{p}$,

$$\mathbf{p}_1 = \frac{m_1}{M}\mathbf{P} + \mathbf{p} \text{ and } \mathbf{p}_2 = \frac{m_2}{M}\mathbf{P} - \mathbf{p}. \tag{A.10}$$

The vector diagram is shown in Fig. A.1.

Problem A.1 *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 unity.*

Solution: Because the x, y and z-directions separate we can write the Jacobian as the product of three 1D Jacobians.

$$\left|\frac{\partial(\mathbf{r}_1,\mathbf{r}_2)}{\partial(\mathbf{R},\mathbf{r})}\right| = \prod_{i=x,y,z}\left|\frac{\partial(r_{1i},r_{2i})}{\partial(R_i,r_i)}\right| = \prod_{i=x,y,z} | \begin{vmatrix} 1 & m_1/M \\ 1 & -m_2/M \end{vmatrix} | = 1. \blacktriangleright$$

Problem A.2 *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 unity.*

Solution: Because the x, y and z-directions separate we can write the Jacobian as the product of three 1D Jacobians.

$$\left|\frac{\partial(\mathbf{p}_1,\mathbf{p}_2)}{\partial(\mathbf{P},\mathbf{p})}\right| = \prod_{i=x,y,z}\left|\frac{\partial(p_{1i},p_{2i})}{\partial(P_i,p_i)}\right| = \prod_{i=x,y,z} | \begin{vmatrix} m_1/M & 1 \\ m_2/M & -1 \end{vmatrix} | = 1. \blacktriangleright$$

A.2 The 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 $\mathbf{p}^2/2\mu$ 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 Eqs. (A.5) the momenta of the particles before and after the collision (see Fig. A.1) are given by

$$\mathbf{p}_1 = m_1\mathbf{P}/M + \mathbf{p} \longrightarrow \mathbf{p}_1' = m_1\mathbf{P}/M + \mathbf{p}' \tag{A.11a}$$

$$\mathbf{p}_2 = m_2\mathbf{P}/M - \mathbf{p} \longrightarrow \mathbf{p}_2' = m_2\mathbf{P}/M - \mathbf{p}'. \tag{A.11b}$$

Hence, the momentum transfer is

$$\Delta\mathbf{p}_1 = \mathbf{p}_1' - \mathbf{p}_1 = \mathbf{p}' - \mathbf{p} = \mathbf{q} \tag{A.12a}$$

$$\Delta\mathbf{p}_2 = \mathbf{p}_2' - \mathbf{p}_2 = \mathbf{p} - \mathbf{p}' = -\mathbf{q}. \tag{A.12b}$$

The energy transfer is

$$\Delta E_1 = \frac{\mathbf{p}_1'^2}{2m_1} - \frac{\mathbf{p}_1^2}{2m_1} = \frac{(m_1\mathbf{P}/M + \mathbf{p}')^2}{2m_1} - \frac{(m_1\mathbf{P}/M + \mathbf{p})^2}{2m_1} = \frac{\mathbf{P}\cdot\mathbf{q}}{M} \tag{A.13}$$

$$\Delta E_2 = \frac{\mathbf{p}_2'^2}{2m_2} - \frac{\mathbf{p}_2^2}{2m_2} = \frac{(m_2\mathbf{P}/M - \mathbf{p}')^2}{2m_2} - \frac{(m_2\mathbf{P}/M - \mathbf{p})^2}{2m_2} = -\frac{\mathbf{P}\cdot\mathbf{q}}{M}. \tag{A.14}$$

In the special case $\mathbf{p}_1 = 0$ we have

$$\mathbf{P} = \mathbf{p}_2 = \frac{-\mathbf{p}}{1 - m_2/M} = -\frac{M}{m_1}\mathbf{p} \tag{A.15}$$

or

$$\mathbf{p} = -\mu\mathbf{v}_2. \tag{A.16}$$

The momentum transfer becomes

$$q = \sqrt{\mathbf{q}^2} = \sqrt{(\mathbf{p}' - \mathbf{p})^2} = \sqrt{2\mathbf{p}^2 - 2\mathbf{p}'\cdot\mathbf{p}} = p\sqrt{2 - 2\cos\vartheta} \tag{A.17}$$

For small angles this implies

$$\vartheta = q/p. \tag{A.18}$$

The energy transfer becomes

$$\Delta E_1 = \frac{\mathbf{P}\cdot\mathbf{q}}{M} = -\frac{\mathbf{p}\cdot(\mathbf{p}' - \mathbf{p})}{m_1} = \frac{\mathbf{p}^2}{m_1}(1 - \cos\vartheta) = \frac{\mu^2}{m_1}\mathbf{v}_2^2(1 - \cos\vartheta), \tag{A.19}$$

where θ is the scattering angle. This can be written in the form

$$\Delta E_1 = \xi\frac{1}{4}m_2\mathbf{v}_2^2(1 - \cos\vartheta), \tag{A.20}$$

where

$$\xi = \frac{4\mu^2}{m_1 m_2} = \frac{4m_1 m_2}{(m_1 + m_2)^2}$$

is the thermalization efficiency parameter. For $m_1 = m_2$ this parameter reaches its maximum value ($\xi = 1$) and we obtain

$$\Delta E_1 = \frac{1}{2}E_2(1 - \cos\theta).$$

For $m_1 \ll m_2$ the efficiency parameter is given by $\xi \simeq 4m_1/m_2$.

A.3 Conservation of normalization and current density

The rate of change of normalization of a wave function can be written as a continuity equation

$$\frac{\partial}{\partial t}|\Psi(r,t)|^2 + \boldsymbol{\nabla}\cdot\mathbf{j} = 0, \tag{A.21}$$

which defines $\mathbf{j}$ as the probability probability current density of the wave function. With the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t) = H\Psi(r,t) \tag{A.22}$$

$$-i\hbar\frac{\partial}{\partial t}\Psi^*(r,t) = H\,\Psi^*(r,t) \tag{A.23}$$

we find

$$\begin{aligned}\frac{\partial}{\partial t}\left|\Psi(r,t)\right|^2 &= \Psi^*(r,t)\frac{\partial}{\partial t}\Psi(r,t) + \Psi(r,t)\frac{\partial}{\partial t}\Psi^*(r,t)\\ &= \frac{1}{i\hbar}\left[\psi^*(H\psi) - (H\psi^*)\psi\right].\end{aligned}$$

Hence,

$$\boldsymbol{\nabla}\cdot\mathbf{j} = \frac{i}{\hbar}\left[\psi^*(H\psi) - (H\psi^*)\psi\right]. \tag{A.24}$$

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

$$H = -\frac{\hbar^2}{2\mu}\Delta + V(r)$$

the probability current density is given by the expression

$$\mathbf{j} = \frac{i\hbar}{2\mu}\left(\psi\boldsymbol{\nabla}\psi^* - \psi^*\boldsymbol{\nabla}\psi\right) \tag{A.25}$$

as follows with the vector rule

$$\begin{aligned}\int \mathbf{j}\cdot d\mathbf{S} = \int\left(\boldsymbol{\nabla}\cdot\mathbf{j}\right)\,d\mathbf{r} &= -\frac{i\hbar}{2\mu}\int\left[\psi^*(\Delta\psi) - (\Delta\psi^*)\psi\right]d\mathbf{r}\\ &= -\frac{i\hbar}{2\mu}\int\boldsymbol{\nabla}\cdot\left[\psi^*(\boldsymbol{\nabla}\psi) - (\boldsymbol{\nabla}\psi^*)\psi\right]d\mathbf{r}\\ &= -\frac{i\hbar}{2\mu}\int\left[\psi^*(\boldsymbol{\nabla}\psi) - (\boldsymbol{\nabla}\psi^*)\psi\right]d\mathbf{S}.\end{aligned}$$

Note that the probability current density is a real quantity and can be written in the form[1]

$$\mathbf{j} = \frac{i\hbar}{2\mu}\left(\psi\boldsymbol{\nabla}\psi^* - \psi^*\boldsymbol{\nabla}\psi\right) = \mathrm{Re}\left[\frac{-i\hbar}{\mu}\psi^*\boldsymbol{\nabla}\psi\right] = \mathrm{Re}\left[\psi^*\mathbf{v}\psi\right],$$

where $\mathbf{v} = \mathbf{p}/\mu = (-i\hbar/\mu)\,\boldsymbol{\nabla}$ is the velocity operator.

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[1] Here we use $\mathrm{Re}[e^{i\varphi}] = \cos\varphi = \frac{1}{2i}[e^{i\varphi} + e^{-i\varphi}]$.

Appendix B

Special functions, integrals and associated formulas

B.1 Gamma function

The gamma function is defined for the complex z plane excluding the non-positive integers

$$\int_0^\infty e^{-x} x^{z-1} dx = \Gamma(z). \tag{B.1}$$

For integer values $z - 1 = n = 0, 1, 2, \cdots$ the gamma function coincides with the factorial function,

$$\int_0^\infty e^{-x} x^n dx = \Gamma(n+1) = n! \tag{B.2}$$

Some special values are:

$$\begin{array}{lll}
\Gamma(-1/2) = -2\sqrt{\pi} = -3.545, & \Gamma(1/2) = \sqrt{\pi} = 1.772, & \Gamma(1) = 1 \\
\Gamma(-3/2) = \frac{4}{3}\sqrt{\pi} = 2.363, & \Gamma(3/2) = \frac{1}{2}\sqrt{\pi} = 0.886, & \Gamma(2) = 1 \\
 & \Gamma(5/2) = \frac{3}{4}\sqrt{\pi} = 1.329, & \Gamma(3) = 2 \\
 & \Gamma(7/2) = \frac{15}{8}\sqrt{\pi} = 3.323, & \Gamma(4) = 6.
\end{array}$$

Some related integrals are

$$\int_0^\infty e^{-x^2} x^{2n+1} dx = \frac{1}{2} n! \tag{B.3}$$

$$\int_0^\infty e^{-x^2} x^{2n} dx = \frac{(2n-1)!!}{2^{n+1}} \sqrt{\pi}. \tag{B.4}$$

A useful integral relation is

$$\int_0^\infty e^{-\ell x^n} x^m dx = \frac{1}{\ell^{(m+1)/n}} \int_0^\infty e^{-x^n} x^m dx. \tag{B.5}$$

B.2 Polylogarithm

The polylogarithm $\mathrm{Li}_\alpha(z)$ is a special function defined over the unit disk in the complex plane by the series expansion

$$\mathrm{Li}_\alpha(z) = \mathrm{PolyLog}[\alpha, z] \equiv \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^\alpha} \qquad (|z| < 1), \tag{B.6}$$

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

$$F_{\alpha}^{\mathrm{BE}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^{\infty} \frac{x^{\alpha-1}}{z^{-1}e^{x} - 1} dx \qquad (z < 1) \tag{B.7}$$

and the Fermi-Dirac integrals

$$F_{\alpha}^{\mathrm{FD}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^{\infty} \frac{x^{\alpha-1}}{z^{-1}e^{x} + 1} dx \qquad (z \geq -1). \tag{B.8}$$

Recurrence relations:

$$\mathrm{Li}_{\alpha}(z) = z\frac{d}{dz}\mathrm{Li}_{\alpha+1}(z) \qquad \Leftrightarrow \qquad \mathrm{Li}_{\alpha}(e^{u}) = \frac{d}{du}\mathrm{Li}_{\alpha+1}(e^{u}). \tag{B.9}$$

B.3 Bose-Einstein function

The Bose-Einstein (BE) integrals are defined for real z and $\alpha > 1$ as

$$F_{\alpha}^{\mathrm{BE}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^{\infty} \frac{x^{\alpha-1}}{z^{-1}e^{x} - 1} dx \qquad (z < 1). \tag{B.10}$$

The integrals can be expanded in powers of z on the interval $0 < z < 1$,

$$F_{\alpha}^{\mathrm{BE}}(z) = \frac{1}{\Gamma(\alpha)} \sum_{\ell=1}^{\infty} \int_0^{\infty} x^{\alpha-1} z^{\ell} e^{-\ell x} dx = \sum_{\ell=1}^{\infty} \frac{z^{\ell}}{\ell^{\alpha}} = g_{\alpha}(z) = \mathrm{Li}_{\alpha}(z), \tag{B.11}$$

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]

$$F_{\alpha}^{\mathrm{BE}}(e^{-u}) = \Gamma(1-\alpha)\, u^{\alpha-1} + \sum_{n=0}^{\infty} \frac{(-1)^{n}}{n!} \zeta(\alpha - n) u^{n}, \tag{B.12}$$

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

$$F_{m}^{\mathrm{BE}}(e^{-u}) = \frac{(-u)^{m-1}}{(m-1)!} \left(1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{m-1} - \ln u\right) u^{m-1} + \sum_{\substack{n=0 \\ \neq m-1}}^{\infty} \frac{\zeta(m-n)}{n!} u^{n}, \tag{B.13}$$

with convergence for $0 < u \leq 2\pi$.

B.4 Fermi-Dirac function

The Fermi-Dirac (FD) integrals are defined for real z and $\alpha > 1$ as

$$F_{\alpha}^{\mathrm{FD}}(z) = \frac{1}{\Gamma(\alpha)} \int_0^{\infty} \frac{x^{\alpha-1}}{z^{-1}e^{x} + 1} dx \qquad (z \geq -1). \tag{B.14}$$

The integrals can be expanded in powers of z on the interval $0 < z \leq 1$,

$$F_{\alpha}^{\mathrm{FD}}(z) = \frac{-1}{\Gamma(\alpha)} \sum_{\ell=1}^{\infty} \int_0^{\infty} x^{\alpha-1} (-z)^{\ell} e^{-\ell x} dx = -\sum_{\ell=1}^{\infty} \frac{(-z)^{\ell}}{\ell^{\alpha}} = f_{\alpha}(z) = -\mathrm{Li}_{\alpha}(-z), \tag{B.15}$$

where $\mathrm{Li}_{\alpha}(z)$ is the polylogarithm.

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[1] For a derivation see J.E. Robinson, Phys. Rev. 83, 678 (1951).

B.5 Riemann zeta function

The Riemann zeta function is defined as a Dirichlet series

$$\lim_{z\to 1} g_\alpha\left(z\right) = \zeta\left(\alpha\right) = \sum_{\ell=1}^{\infty} \frac{1}{\ell^\alpha}. \tag{B.16}$$

Some special values are:

$$\begin{array}{llll} \zeta\left(1/2\right) = -1.460, & \zeta\left(3/2\right) = 2.612, & \zeta\left(5/2\right) = 1.341, & \zeta\left(7/2\right) = 1.127, \\ \zeta\left(1\right) \to \infty, & \zeta\left(2\right) = \pi^2/6 = 1.645, & \zeta\left(3\right) = 1.202, & \zeta\left(4\right) = \pi^4/90 = 1.082. \end{array}$$

B.6 Special integrals

For $\delta > 0$ and $\varepsilon > 0$

$$\int_0^\varepsilon \sqrt{x}\left(\varepsilon - x\right)^{\delta-1} dx = \frac{\sqrt{\pi}\Gamma(\delta)}{2\Gamma\left(3/2+\delta\right)} \varepsilon^{1/2+\delta} \tag{B.17}$$

B.7 Commutator algebra

If A, B, C and D are four arbitrary linear operators the following relations hold:

$$\begin{aligned} \left[A, B\right] &= -\left[B, A\right] && \text{(B.18a)} \\ \left[A, B + C\right] &= \left[A, B\right] + \left[A, C\right] && \text{(B.18b)} \\ \left[A, BC\right] &= \left[A, B\right] C + B\left[A, C\right] && \text{(B.18c)} \\ \left[AB, CD\right] &= A\left[B, C\right] D + C\left[A, D\right] B && \text{(B.18d)} \\ 0 &= \left[A, \left[B, C\right]\right] + \left[B, \left[C, A\right]\right] + \left[C, \left[A, B\right]\right]. && \text{(B.18e)} \end{aligned}$$

Commutators containing B^n:

$$\begin{aligned} \left[A, B^n\right] &= \sum_{s=0}^{n-1} B^s \left[A, B\right] B^{n-s-1} && \text{(B.19a)} \\ \left[A, B^n\right] &= nB^{n-1}\left[A, B\right] \quad \text{if } B \text{ commutes with } \left[A, B\right]. && \text{(B.19b)} \end{aligned}$$

Exponential operator:

$$e^A \equiv \sum_{n=0}^{\infty} \frac{A^n}{n!}. \tag{B.20}$$

Expressions containing exponential operators:

$$\begin{aligned} e^A e^B &= e^{A+B+\frac{1}{2}\left[A,B\right]} \quad \text{if } A \text{ and } B \text{ commute with } \left[A, B\right] && \text{(B.21a)} \\ e^A B e^{-A} &= B + \left[A, B\right] + \frac{1}{2!}\left[A, \left[A, B\right]\right] + \frac{1}{3!}\left[A, \left[A, \left[A, B\right]\right]\right] + \cdots && \text{(B.21b)} \\ e^A B e^{-A} &= B + \left[A, B\right] \quad \text{if } A \text{ commutes with } \left[A, B\right] && \text{(B.21c)} \\ e^A B e^{-A} &= e^\gamma B \quad \text{if } \left[A, B\right] = \gamma B, \text{ with } \gamma \text{ a constant.} && \text{(B.21d)} \end{aligned}$$

B.8 Legendre polynomials

The Legendre differential equation is given by,

$$\left[(1-u^2)\frac{d^2}{du^2}-2u\frac{d}{du}-\frac{m^2}{1-u^2}+l(l+1)\right]P_l^m(u)=0. \tag{B.22}$$

The $m=0$ solutions are the Legendre polynomials

$$P_l(u)=\frac{1}{2^l l!}\frac{d^l}{du^l}(u^2-1)^l. \tag{B.23}$$

$P_l(u)$ is a polynomial of degree l, parity

$$P_l(-u)=(-1)^l P_l(u) \tag{B.24}$$

and having l zeros in the interval $-1\le u\le 1$. The lowest order Legendre polynomials are

$$P_0(u)=1,\quad P_1(u)=u,\quad P_2(u)=\frac{1}{2}(3u^2-1) \tag{B.25}$$

$$P_3(u)=\frac{1}{2}(5u^3-3u),\quad P_4(u)=\frac{1}{8}(35u^4-30u^2+3). \tag{B.26}$$

The associated Legendre functions $P_l^m(u)$, with $|m|\le l$ are obtained by differentiation of the Legendre polynomials $P_l(u)$,

$$P_l^m(u)=(1-u^2)^{m/2}\frac{d^m}{du^m}P_l(u). \tag{B.27}$$

$P_l^m(u)$ is the product of $(1-u^2)^{m/2}$ and a polynomial of degree $(l-m)$, parity $(-1)^{l-m}$ and having $(l-m)$ zeros in the interval $-1\le u\le 1$. In particular,

$$P_l^0(u)=P_l(u),\quad P_l^l(u)=(2l-1)!!(1-u^2)^{l/2}.$$

The ortho-normalization of the associated Legendre functions is expressed by

$$\int_{-1}^{1}P_l^m(u)P_{l'}^m(u)du=\frac{2}{2l+1}\frac{(l+m)!}{(l-m)!}\delta_{ll'}. \tag{B.28}$$

B.8.1 Spherical harmonics $Y_{lm}(\theta,\phi)$

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 for $m\ge 0$

$$Y_{lm}(\theta,\varphi)=(-1)^m\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\varphi}. \tag{B.29}$$

The inclusion of the prefactor $(-1)^m$ is called the Condon and Shortly phase convention, commonly adopted in the quantum mechanics literature.[2] The complex conjugation and parity (space inversion) operations are given by

$$Y_l^{m*}(\hat{\mathbf{r}})=(-1)^m Y_l^{-m}(\hat{\mathbf{r}}) \tag{B.30}$$

$$Y_l^{m*}(-\hat{\mathbf{r}})=(-1)^l Y_l^{-m}(\hat{\mathbf{r}}). \tag{B.31}$$

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[2] Note that this convention differs from the convention adopted by *Mathematica.*

where $\hat{\mathbf{r}} = (\theta, \varphi)$ and $-\hat{\mathbf{r}} = (\pi - \theta, \pi + \varphi)$. The lowest order spherical harmonics are

$$Y_0^0(\theta,\varphi) = \sqrt{\frac{1}{4\pi}} \tag{B.32a}$$

$$Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{B.32b}$$

$$Y_1^{\pm1}(\theta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\; e^{\pm i\varphi} \tag{B.32c}$$

$$Y_2^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{5}{4\pi}}\left(3\cos^2\theta - 1\right) \tag{B.32d}$$

$$Y_2^{\pm1}(\theta,\varphi) = \mp\sqrt{\frac{3}{2}}\sqrt{\frac{5}{4\pi}}\sin\theta\cos\theta\; e^{\pm i\varphi} \tag{B.32e}$$

$$Y_2^{\pm2}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2}}\sqrt{\frac{5}{4\pi}}\sin^2\theta\; e^{\pm 2i\varphi}. \tag{B.32f}$$

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,

$$\frac{2l+1}{4\pi}P_l(\cos\theta_{12}) = \sum_{m=-l}^{l} Y_l^{m*}(\hat{\mathbf{r}}_1)Y_l^m(\hat{\mathbf{r}}_2). \tag{B.33}$$

$$Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}}) = \sum_{L=|l-l'|}^{l+l'}\sum_{M=-L}^{L}(-1)^M\sqrt{\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}}\begin{pmatrix} l & l' & L \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l' & L \\ m & m' & M\end{pmatrix}Y_L^{-M}(\hat{\mathbf{r}}). \tag{B.34}$$

An important relation is the *integral over three spherical harmonics*

$$\int Y_{l_1}^{m_1}(\hat{\mathbf{r}})Y_{l_2}^{m_2}(\hat{\mathbf{r}})Y_{l_3}^{m_3}(\hat{\mathbf{r}})d\hat{\mathbf{r}} = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3\end{pmatrix}, \tag{B.35}$$

where the Wigner $3j$ symbols are defined by

$$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M\end{pmatrix} \equiv \frac{(-)^{j_1-j_2+M}}{\sqrt{2J+1}}\left\langle j_1 j_2 m_1 m_2 | JM\right\rangle, \tag{B.36}$$

with $\langle j_1 j_2 m_1 m_2 | JM\rangle$ Clebsch-Gordan coefficients. In Dirac notation we have

$$\langle l'm'|\,Y_k^q(\hat{\mathbf{r}})\,|lm\rangle = (-1)^{m'}\sqrt{\frac{(2l'+1)(2k+1)(2l+1)}{4\pi}}\begin{pmatrix} l' & k & l \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & k & l \\ -m' & q & m\end{pmatrix}. \tag{B.37}$$

Some special cases are:

- $k = 1$: In this case $l' = l \pm 1$ and we have $(l + l' + 1)/2 = \max(l, l')$, which can be even or odd,

$$\sqrt{\frac{4\pi}{3}}\int Y_{l'}^{m'}(\hat{\mathbf{r}})Y_1^q(\hat{\mathbf{r}})Y_l^m(\hat{\mathbf{r}})d\hat{\mathbf{r}} = (-1)^{\max(l,l')}\sqrt{\max(l,l')}\begin{pmatrix} l' & 1 & l \\ m' & q & m\end{pmatrix} \tag{B.38a}$$

$$\langle l'm'|\,Y_1^q(\hat{\mathbf{r}})\,|lm\rangle = (-1)^{m'+\max(l,l')}\sqrt{\max(l,l')}\sqrt{\frac{3}{4\pi}}\begin{pmatrix} l' & 1 & l \\ -m' & q & m\end{pmatrix} \qquad l \neq l \tag{B.38b}$$

$$\langle lm|\,Y_1^q(\hat{\mathbf{r}})\,|lm\rangle = 0 \qquad\qquad l = l \tag{B.38c}$$

- $k = 2$: In this case $l' = l, l \pm 2$ and we have $(l + l' + 2)/2 = \max(l, l')$, which is even if l is even and odd if l is odd,

$$\langle l'm'| Y_2^q(\hat{\mathbf{r}}) |lm\rangle = (-1)^{m'+l} \sqrt{\frac{3}{4} \frac{l+l'}{l+l'+1}} \sqrt{\max(l,l')} \sqrt{\frac{5}{4\pi}} \begin{pmatrix} l' & 2 & l \\ -m' & q & m \end{pmatrix} \qquad l \neq l \tag{B.39}$$

$$\langle lm| Y_2^0(\hat{\mathbf{r}}) |lm\rangle = \frac{l\,(l+1) - 3m^2}{(2l+3)(2l-1)} \sqrt{\frac{5}{4\pi}} \qquad l = l \tag{B.40}$$

B.9 Hermite polynomials

The Hermite differential equation is given by

$$y'' - 2xy' + 2ny = 0. \tag{B.41}$$

For $n = 0, 1, 2, \ldots$ its solutions satisfy the Rodrigue's formula

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2}). \tag{B.42}$$

The lowest order *Hermite polynomials* are

$$\begin{array}{ll} H_0\,(x) = 1 & H_4\,(x) = 16x^4 - 48x^2 + 12 \\ H_1\,(x) = 2x & H_5\,(x) = 32x^5 - 160x^3 + 120x \\ H_2\,(x) = 4x^2 - 2 & H_6\,(x) = 64x^6 - 480x^4 + 720x^2 - 120 \\ H_3\,(x) = 8x^3 - 12x & H_7\,(x) = 128x^7 - 1344x^5 + 3360x^3 - 1680x \end{array} \tag{B.43}$$

The generating function is

$$e^{2tx-t^2} = \sum_{n=0}^{\infty} H_n\,(x) \frac{t^n}{n!}. \tag{B.44}$$

Useful recurrence relations are

$$H_{n+1}\,(x) = 2xH_n\,(x) - 2nH_{n-1}\,(x) \tag{B.45}$$

$$H_n'\,(x) = 2nH_{n-1}\,(x) \tag{B.46}$$

and the orthogonality relations are given by

$$\int_{-\infty}^{\infty} e^{-x^2} H_m\,(x)\, H_n\,(x) = 2^n n! \sqrt{\pi} \delta_{mn}\,. \tag{B.47}$$

B.10 Laguerre polynomials

Generalized Laguerre polynomials satisfy the following differential equation

$$xy'' + (\alpha + 1 - x)y' + 2ny = 0. \tag{B.48}$$

Its solutions can be represented as[3]

$$L_n^\alpha(x) = \frac{1}{n!} e^x x^{-\alpha} \frac{d^n}{dx^n} (e^{-x} x^{n+\alpha}) \tag{B.49}$$

$$= \sum_{m=0}^{n} (-1)^m \binom{n+\alpha}{n-m} \frac{x^m}{m!}$$

$$= \sum_{m=0}^{n} \frac{\Gamma(\alpha+n+1)}{\Gamma(\alpha+m+1)} \frac{(-1)^m}{(n-m)!} \frac{x^m}{m!} \tag{B.50}$$

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[3] 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*™.

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 lowest order *Laguerre polynomials* are given by

$$L_0^\alpha(x) = 1, \quad L_1^\alpha(x) = \alpha+1-x, \quad L_2^\alpha(x) = \tfrac{1}{2}(\alpha+1)(\alpha+2) - (\alpha+2)x + \tfrac{1}{2}x^2. \tag{B.51}$$

Some special cases for $\alpha = 0$ and $\alpha = -n$ are

$$L_0(x) = 1, \quad L_1(x) = 1-x, \quad L_2(x) = 1-2x+\tfrac{1}{2}x^2, \quad L_n^{-n}(x) = (-1)^n \frac{x^n}{n!}. \tag{B.52}$$

The generating function is

$$\frac{(-1)^m\, t^m}{(1-t)^{m+1}} e^{-x/(1-t)} = \sum_{n=m}^{\infty} L_n^m\,(x)\,\frac{t^n}{n!}$$

The generalized Laguerre polynomials satisfy the orthogonality relation

$$\int_0^\infty x^\alpha e^{-x} L_n^\alpha(x) L_m^\alpha(x)dx = 0 \text{ for } m \neq n \text{ (orthogonality relation)} \tag{B.53}$$

$$\int_0^\infty x^\alpha e^{-x} L_n^\alpha(x)dx = \Gamma(\alpha+1)\delta_{0,n}\,. \tag{B.54}$$

Useful recurrence relations are given by

$$xL_n^\alpha(x) = (2n+\alpha+1)L_n^\alpha(x) - (n+\alpha)L_{n-1}^\alpha(x) - (n+1)L_{n+1}^\alpha \tag{B.55}$$

$$\frac{d}{dx}L_n^\alpha(x) = -L_{n-1}^{\alpha+1}(x) = -[1 + L_1^\alpha(x) + \cdots + L_{n-1}^\alpha(x)] \tag{B.56}$$

Series expansions:

$$L_n^{\alpha+1}(x) = \sum_{m=0}^{n} L_m^\alpha(x) \tag{B.57a}$$

$$\frac{d}{dx}L_n^\alpha(x) = -\sum_{m=0}^{n-1} L_m^\alpha(x) \tag{B.57b}$$

$$\frac{d^2}{dx^2}L_n^\alpha(x) = \sum_{m=0}^{n-2} (n-m-1)\,L_m^\alpha(x) \tag{B.57c}$$

Further, it is practical to introduce a generalized normalization integral

$$J_\nu(m,\alpha) = \int_0^\infty x^{\alpha+\nu} e^{-x} [L_m^\alpha(x)]^2 dx. \tag{B.58}$$

Some special cases are given by

$$J_0(m,\alpha) = \int_0^\infty x^\alpha e^{-x}[L_m^\alpha(x)]^2 dx = \frac{\Gamma(\alpha+m+1)}{m!} \tag{B.59}$$

$$J_1(m,\alpha) = \int_0^\infty x^{\alpha+1} e^{-x}[L_m^\alpha(x)]^2 dx = \frac{\Gamma(\alpha+m+1)}{m!}(2m+\alpha+1) \tag{B.60}$$

$$J_2(m,\alpha) = \int_0^\infty x^{\alpha+2} e^{-x}[L_m^\alpha(x)]^2 dx = \frac{\Gamma(\alpha+m+1)}{m!}[6m(m+\alpha+1)+\alpha^2+3\alpha+2] \tag{B.61}$$

$$J_{-1}(m,\alpha) = \int_0^\infty x^{\alpha-1} e^{-x}[L_m^\alpha(x)]^2 dx = \frac{1}{\alpha}\int_0^\infty x^\alpha e^{-x}[L_m^\alpha(x)]^2 dx = \frac{\Gamma(\alpha+m+1)}{m!}\frac{1}{\alpha} \tag{B.62}$$

The integrals $J_\nu(m,\alpha)$ with $\nu > 0$ are obtained from Eq. (B.59) by repetitive use of the recurrence relation (B.55) and orthogonality relation (B.53); integrals $J_\nu(m,\alpha)$ with $\nu < 0$ are obtained from Eq. (B.59) by partial integration and use of the recurrence relation (B.56), the orthogonality relation (B.53) and the special integral (B.54).

Selected ratios for $m = n - l - 1$ and $\alpha = 2l + 1$

$$J_4/J_1 = \frac{1}{n}[35n^2(n^2-1) - 30n^2(l+2)(l-1) + 3(l+2)(l+1)l(l-1)] \tag{B.63}$$

$$J_3/J_1 = 2\left[5n^2 + 1 - 3l(l+1)\right] \tag{B.64}$$

$$J_2/J_1 = \frac{1}{n}\left[3n^2 - l(l+1)\right] \tag{B.65}$$

$$J_1/J_1 = 1 \tag{B.66}$$

$$J_0/J_1 = \frac{1}{2n} \tag{B.67}$$

$$J_{-1}/J_1 = \frac{1}{2n}\frac{1}{2l+1} \tag{B.68}$$

$$J_{-2}/J_1 = \frac{1}{8}\frac{1}{(l+1)(l+1/2)l} \tag{B.69}$$

$$J_{-3}/J_1 = \frac{1}{32n}\frac{3n^2 - l(l+1)}{(l+3/2)(l+1)(l+1/2)l(l-1/2)} \tag{B.70}$$

B.11 Bessel functions

B.11.1 Spherical Bessel functions

The spherical Bessel differential equation is given by

$$x^2y'' + 2xy' + \left[x^2 - l(l+1)\right]y = 0. \tag{B.71}$$

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).

Some special cases are given by

- Lowest orders:

$$j_0\,(x) = \frac{\sin x}{x}\ , \qquad n_0\,(x) = \frac{\cos x}{x} \tag{B.72a}$$

$$j_1\,(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}, \quad n_1\,(x) = \frac{\cos x}{x^2} + \frac{\sin x}{x}. \tag{B.72b}$$

- Asymptotic forms for $x \to \infty$

$$j_l\,(x) \underset{x\to\infty}{\sim} \frac{1}{x}\sin(x - \tfrac{1}{2}l\pi) \tag{B.73a}$$

$$n_l\,(x) \underset{x\to\infty}{\sim} \frac{1}{x}\cos(x - \tfrac{1}{2}l\pi). \tag{B.73b}$$

- Asymptotic forms for $x \to 0$

$$j_l\,(x) \underset{x\to 0}{\sim} \frac{x^l}{(2l+1)!!}\left[1 - \frac{x^2}{2(2l+3)} + \cdots\right] \tag{B.74a}$$

$$n_l\,(x) \underset{x\to 0}{\sim} \frac{(2l+1)!!}{(2l+1)}\left(\frac{1}{x}\right)^{l+1}\left[1 + \frac{x^2}{2(2l-1)} + \cdots\right]. \tag{B.74b}$$

Relation to Bessel functions:
The spherical Bessel functions are related to half-integer Bessel functions

$$j_l(x) = \sqrt{\frac{\pi}{2x}} J_{l+\frac{1}{2}}(x) \text{ for } l = 0, 1, 2, \ldots \tag{B.75}$$

$$n_l(x) = (-)^l \sqrt{\frac{\pi}{2x}} J_{-l-\frac{1}{2}}(x) \text{ for } l = 0, 1, 2, \ldots \tag{B.76}$$

B.11.2 Bessel functions

The Bessel differential equation is given by

$$x^2 y'' + x y' + \left(x^2 - n^2\right) y = 0. \tag{B.77}$$

The general solution is a linear combination of two particular solutions

$$y = A J_n(x) + B J_{-n}(x) \text{ for } n \neq 0, 1, 2, \cdots \tag{B.78a}$$

$$y = A J_n(x) + B Y_n(x) \text{ for all integer } n \tag{B.78b}$$

where A and B are arbitrary constants and $J_{\pm n}(x)$ are Bessel functions, which are defined by

$$J_{\pm n}(x) = \sum_{p=0}^{\infty} \frac{(-1)^p (x/2)^{2p \pm n}}{p! \Gamma(1 + p \pm n)}. \tag{B.79}$$

The $Y_n(x)$ are Neumann functions and are defined by

$$Y_n(x) = \frac{J_n(x) \cos n\pi - J_{-n}(x)}{\sin n\pi} \text{ for } n \neq 0, 1, 2, \cdots \tag{B.80}$$

$$Y_n(x) = \lim_{p \to n} \frac{J_n(x) \cos p\pi - J_{-n}(x)}{\sin p\pi} \text{ for } n = 0, 1, 2, \cdots . \tag{B.81}$$

Extracting the leading term from the Bessel expansion (B.79) results in

$$J_{\pm n}(x) = \frac{(x/2)^{\pm n}}{\Gamma(1 \pm n)} \left(1 - \frac{(x/2)^2}{(1 \pm n)} + \cdots\right). \tag{B.82}$$

The generating function is of the form

$$e^{x(t-1/t)/2} = \sum_{n=-\infty}^{n=\infty} J_n(x) t^n \tag{B.83}$$

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 $n = 1/4$

$$J_{1/4}(x) = \frac{(x/2)^{1/4}}{\Gamma(5/4)} \left(1 - \frac{(x/2)^2 \Gamma(5/4)}{\Gamma(9/4)} + \cdots\right) \tag{B.84}$$

$$J_{-1/4}(x) = \frac{(x/2)^{-1/4}}{\Gamma(3/4)} \left(1 - \frac{(x/2)^2 \Gamma(3/4)}{\Gamma(7/4)} + \cdots\right) \tag{B.85}$$

Asymptotic expansions:

$$J_n(x) \underset{x\to\infty}{\simeq} \sqrt{\frac{2}{\pi}\frac{1}{x}}\cos\left(x - n\frac{\pi}{2} - \frac{\pi}{4}\right) \tag{B.86}$$

$$Y_n(x) \underset{x\to\infty}{\simeq} \sqrt{\frac{2}{\pi}\frac{1}{x}}\sin\left(x - n\frac{\pi}{2} - \frac{\pi}{4}\right) \tag{B.87}$$

Integral expressions for $\mu + \nu + 1 > \lambda > 0$

$$\int_0^\infty \frac{1}{r^\lambda} J_\mu(kr) J_\nu(kr) dr = \frac{k^{\lambda-1}\Gamma(\lambda)\Gamma\left(\frac{\mu+\nu-\lambda+1}{2}\right)}{2^\lambda\Gamma\left(\frac{\mu-\nu+\lambda+1}{2}\right)\Gamma\left(\frac{\mu+\nu+\lambda+1}{2}\right)\Gamma\left(\frac{\nu-\mu+\lambda+1}{2}\right)}. \tag{B.88}$$

Special cases $2\mu + 1 > \lambda > 0$

$$\int_0^\infty \frac{1}{r^\lambda}\left[J_\mu(kr)\right]^2 dr = \frac{k^{\lambda-1}\Gamma(\lambda)\Gamma\left(\frac{2\mu-\lambda+1}{2}\right)}{2^\lambda\left[\Gamma\left(\frac{\lambda+1}{2}\right)\right]^2\Gamma\left(\frac{2\mu+\lambda+1}{2}\right)}. \tag{B.89}$$

B.11.3 Jacobi-Anger expansion and related expressions

The Jacobi-Anger expansion is given by

$$e^{iz\cos\theta} = \sum_{n=-\infty}^{n=\infty} i^n J_n(z) e^{in\theta}, \tag{B.90}$$

where n assumes only integer values. This relation can be rewritten in several closely related forms

$$e^{iz\sin\theta} = \sum_{n=-\infty}^{n=\infty} i^n J_n(z) e^{in(\theta-\pi/2)} = \sum_{n=-\infty}^{n=\infty} J_n(z) e^{in\theta} \tag{B.91}$$

$$= J_0(z) + \sum_{n=1}^{n=\infty} J_n(z)[e^{in\theta} + (-1)^n e^{-in\theta}] \tag{B.92}$$

$$\cos(z\sin\theta) = \mathrm{Re}(e^{iz\sin\theta}) = J_0(z) + 2\sum_{n=2,4,\cdots}^{n=\infty} J_n(z)\cos(n\theta) \tag{B.93}$$

$$\sin(z\sin\theta) = \mathrm{Im}(e^{iz\sin\theta}) = 2\sum_{n=1,3,\cdots}^{n=\infty} J_n(z)\sin(n\theta). \tag{B.94}$$

B.12 The Wronskian and Wronskian Theorem

Let us consider a second-order differential equation of the following general form

$$\chi'' + F(r)\chi = 0 \tag{B.95}$$

and look for some very 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. (B.95) 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

$$W(\chi_1, \chi_2) \equiv \chi_1\chi_2' - \chi_1'\chi_2. \tag{B.96}$$

Problem B.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 B.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

$$\chi_1'' + F_1(r)\chi_1 = 0 \tag{B.97}$$

$$\chi_2'' + F_2(r)\chi_2 = 0, \tag{B.98}$$

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,*

$$W(\chi_1, \chi_2)|_a^b = \int_a^b [F_1(r) - F_2(r)]\chi_1(r)\chi_2(r)dr. \tag{B.99}$$

The Wronskian theorem expresses the overall variation of the Wronskian of two functions over a given interval of their joint variable.

Problem B.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

$$\chi_1'' + F_1(r)\chi_1 + f_1(r) = 0 \tag{B.100}$$

$$\chi_2'' + F_2(r)\chi_2 + f_2(r) = 0, \tag{B.101}$$

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

$$W(\chi_1, \chi_2)|_a^b = \int_a^b [F_1(r) - F_2(r)]\chi_1\chi_2 dr + \int_a^b [f_1(r)\chi_2 - f_2(r)]\chi_1 dr. \tag{B.102}$$

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 (B.95) on the interval $a < r < b$ for energies ε_1 and ε_2, the Wronskian Theorem takes the form

$$W(\chi_1, \chi_2)|_a^b = (\varepsilon_1 - \varepsilon_2) \int_a^b \chi_1(r)\chi_2(r)dr. \tag{B.103}$$

Similarly, 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 (B.95) with potential $U_1(r)$ and $U_2(r)$, respectively, the Wronskian Theorem takes the form

$$W(\chi_1, \chi_2)|_a^b = \int_a^b \left[U_2(r) - U_1(r)\right] \chi_1(r)\chi_2(r)dr. \tag{B.104}$$

Appendix C

Clebsch-Gordan coefficients

C.1 Relation with the Wigner $3j$ symbols

The Clebsch-Gordan coefficients $\langle j_1 j_2 m_1 m_2 | JM \rangle$ for the coupling $(j_1 \times j_2)$ of two angular momenta j_1 and j_2 are related to the Wigner $3j$ symbols in accordance with

$$\langle j_1 j_2 m_1 m_2 | JM \rangle \equiv (-)^{j_1 - j_2 + M} \sqrt{2J+1} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} \tag{C.1}$$

The Wigner $3j$ symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

have the following properties

Reality:

- the $3j$ symbols are all real

Selection rules:

- the $3j$ symbols satisfy the triangular inequality $\Delta(j_1, j_2, j_3)$

$$|j_1 - j_3| \le j_2 \le |j_1 + j_3| \tag{C.2a}$$

$$\Delta j = 0, \pm 1, \cdots \pm j_2 \qquad (j = 0 \not\leftrightarrow j = 0) \tag{C.2b}$$

- conservation of angular momentum projection

$$m_1 + m_2 + m_3 = 0 \tag{C.3}$$

Symmetries:

- invariant under cyclic permutation
- multiplied by $(-1)^{j_1+j_2+j_3}$ under permutation of two columns
- multiplied by $(-1)^{j_1+j_2+j_3}$ under simultaneous change of sign of m_1, m_2 and m_3.

Orthogonality:

$$\sum_{m_1 m_2} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \delta_{j_3,j_3'} \delta_{m_3,m_3'} \tag{C.4}$$

$$\sum_{j_3=|j_1-j_2|}^{j_1+j_2} \sum_{m_3=-j_3}^{j_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1,m_1'} \delta_{m_2,m_2'} \tag{C.5}$$

In particular:

$$\sum_{m_1} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & (m_3-m_1) & -m_3 \end{pmatrix}^2 = 1 \tag{C.6}$$

$$\sum_{J=0}^{2j} \sum_{M=-J}^{J} (2J+1) \begin{pmatrix} j & j & J \\ m_1 & m_2 & M \end{pmatrix}^2 = 1 \tag{C.7}$$

Special values:

- even and odd summations

$$\sum_{J=\text{even}}^{2j} \sum_{M=-J}^{J} (2J+1) \begin{pmatrix} j & j & J \\ m_1 & m_2 & M \end{pmatrix}^2 = \frac{1}{2} \tag{C.8a}$$

$$\sum_{J=\text{odd}}^{2j} \sum_{M=-J}^{J} (2J+1) \begin{pmatrix} j & j & J \\ m_1 & m_2 & M \end{pmatrix}^2 = \frac{1}{2} \tag{C.8b}$$

- general

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0 \qquad \text{for } m_1+m_2+m_3 \neq 0 \tag{C.9}$$

- J and M taking their maximum value, $\langle j_1 j_2 m_1 m_2 | j_1+j_2 \; j_1+j_2 \rangle = 1$

$$\begin{pmatrix} j_1 & j_2 & j_1+j_2 \\ m_1 & m_2 & -(j_1+j_2) \end{pmatrix} = \frac{1}{\sqrt{2(j_1+j_2)+1}} \tag{C.10}$$

- one of the j null, $\langle j0m0|jm \rangle = 1$ or

$$\begin{pmatrix} j & j & 0 \\ m & -m & 0 \end{pmatrix} = (-)^{j-m} \frac{1}{\sqrt{2j+1}} \tag{C.11}$$

- one of the j is 1 and $m \neq 0$

$$\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix} = (-)^{j-m} \frac{m}{\sqrt{j\,(j+1)\,(2j+1)}} \tag{C.12}$$

- one of the j is 2

$$\begin{pmatrix} j & j & 2 \\ m & -m & 0 \end{pmatrix} = (-)^{j-m} \frac{3m^2 - j\,(j+1)}{\sqrt{j(j+1)(2j+3)\,(2j+1)\,(2j-1)}} \tag{C.13}$$

- one of the $j = 1/2$

$$\begin{pmatrix} l & 1/2 & j = l \pm 1/2 \\ m & \mu & M \end{pmatrix} = (-)^{l+m} \sqrt{\frac{(l - M \pm 1/2)!}{(2j+1)\,(2l+1)\,(l+m)!}}\delta_{m,-(\mu+M)} \tag{C.14}$$

$$\begin{pmatrix} j \pm 1/2 & 1/2 & j \\ m & \mu & M \end{pmatrix} = (-)^{j \pm 1/2 + m} \sqrt{\frac{(j - M)!}{(2j+1)\,(2j+1\pm 1)\,(j+m\pm 1/2)!}}\delta_{m,-(\mu+M)} \tag{C.15}$$

- one of the $j = 1$

$$\begin{pmatrix} j & 1 & j \\ m & 0 & -m \end{pmatrix} = (-)^{-(j-1+m)} \sqrt{\frac{1}{j\,(j+1)\,(2j+1)}}m \tag{C.16}$$

$$\begin{pmatrix} j & 1 & j \\ m & \pm 1 & -(m \pm 1) \end{pmatrix} = (\pm 1)\,(-)^{\mp([j-1+m])} \sqrt{\frac{j(j+1) - m(m \pm 1)}{2j(j+1)(2j+1)}} \tag{C.17}$$

- $m_1 = m_2 = m_3 = 0$ and $j_1 + j_2 + j_3$ is odd

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = 0 \tag{C.18}$$

- $m_1 = m_2 = m_3 = 0$ and $2p = l_1 + l_2 + l_3$ is even

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} = \frac{(-1)^p p! \sqrt{\Delta(l_1 l_2 l_3)}}{(p-l_1)!(p-l_2)!(p-l_3)!}, \tag{C.19}$$

$$\Delta(abc) \equiv \frac{(a+b-c)!(b+c-a)!(c+a-b)!}{(a+b+c+1)!} \tag{C.20}$$

where l_1, l_2, and l_3 are *positive integers* (only an integer angular momentum l can have projection $m_l = 0$) and satisfy the triangular inequalities $|l_1 - l_2| \leq l_3 \leq |l_1 + l_2|$.

- $m_1 = m_2 = m_3 = 0$ and $l, l' =$ integer with $l + l'$ is even

$$\begin{pmatrix} l & l' & 0 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^l \sqrt{\frac{1}{(2l+1)}}\delta_{l,l'} \tag{C.21}$$

- $m_1 = m_2 = m_3 = 0$ and $l, l' =$ integer with $l + l' + 1$ even (this implies $l' = l \pm 1$)

$$\begin{pmatrix} l & l' & 1 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^l \sqrt{\frac{\max(l, l')}{(2l+1)(2l'+1)}} \tag{C.22}$$

- $m_1 = m_2 = m_3 = 0$ and $l, l' =$ integer with $l + l'$ even (this implies $l' = l, l \pm 2$)

$$\begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^l \sqrt{\frac{3}{4}\frac{l + l'}{l + l' + 1}} \sqrt{\frac{\max(l, l')}{(2l+1)(2l'+1)}} \tag{C.23}$$

$$\begin{pmatrix} l & l & 2 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{l+1} \sqrt{\frac{l\,(l+1)}{(2l+3)\,(2l+1)\,(2l-1)}} \tag{C.24}$$

C.2 Relation with the Wigner $6j$ symbols

The Wigner $6j$ symbols are defined by the relation

$$\langle j',(jj'')\,g_2;JM|\,(j'j)\,g_1,j'',;J'M'\rangle=\delta_{JJ'}\delta_{MM'}(-)^{j+j'+j''+J}\sqrt{(2g_1+1)\,(2g_2+1)}\begin{Bmatrix} j' & j & g_1 \\ j'' & J & g_2 \end{Bmatrix} \tag{C.25}$$

The Wigner $6j$ symbols $\begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix}$ have the following properties:

Reality:

The $6j$ symbols are all real.

Selection rules:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix}=0 \qquad \text{unless the triads } (j_1,j_2,j_3)\,(j_1,J_2,J_3)\,(J_1,j_2,J_3)\,(J_1,J_2,j_3)$$

- satisfy the triangular inequalities
- have an integral sum

Symmetry:

- invariant under permutation,

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix}=\begin{Bmatrix} j_2 & j_1 & j_3 \\ J_2 & J_1 & J_3 \end{Bmatrix} \tag{C.26}$$

- invariant under simultaneous exchange of two elements from the first line with the corresponding elements from the second line,

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix}=\begin{Bmatrix} J_1 & J_2 & j_3 \\ j_1 & j_2 & J_3 \end{Bmatrix} \tag{C.27}$$

Orthogonality:

$$\sum_j (2j+1)\begin{Bmatrix} j_1 & j_2 & j \\ J_1 & J_2 & J \end{Bmatrix}\begin{Bmatrix} j_1 & j_2 & j \\ J_1 & J_2 & J' \end{Bmatrix}=\frac{\delta_{J'J}}{(2J+1)} \tag{C.28}$$

Fundamental relations:

- summation over the product of three $3j$ symbols

$$\sum_{m_1m_2m_3}(-)^{j_1+j_2+j_3+m_1+m_2+m_3}\begin{pmatrix} j_1 & j_2 & j \\ m_1 & -m_2 & m \end{pmatrix}\begin{pmatrix} j_2 & j_3 & j' \\ m_2 & -m_3 & m' \end{pmatrix}\begin{pmatrix} j_3 & j_1 & J \\ m_3 & -m_1 & M \end{pmatrix}=$$

$$=\begin{Bmatrix} j' & J & j \\ j_1 & j_2 & j_3 \end{Bmatrix}\begin{pmatrix} j' & J & j \\ m' & M & m \end{pmatrix} \tag{C.29}$$

Note that $m_1=m_2-m$ and $m_3=m_2+m'$. Hence, the sum runs over a single independent index.

C.3 Tables of Clebsch-Gordan coefficients

The Glebsch-Gordan coefficients $\langle j_1 j_2 m_1 m_2 | JM\rangle$ for the coupling of two arbitrary angular momenta $\mathbf{j}_1$ and $\mathbf{j}_2$ to the total angular momentum $\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$ is given below for various important cases (note that this holds in general and does not depend on the type of

$\|m\|=1$	$\|1,1\rangle$	$\|1,-1\rangle$
$\langle j_1 j_2,1/2,1/2\|$	1	0
$\langle j_1 j_2,-1/2,-1/2\|$	0	1

$m=0$	$\|1,0\rangle$	$\|0,0\rangle$
$\langle j_1 j_2,1/2,-1/2\|$	$\sqrt{1/2}$	$\sqrt{1/2}$
$\langle j_1 j_2,-1/2,1/2\|$	$\sqrt{1/2}$	$-\sqrt{1/2}$

$(1/2 \times 1/2)$

$\|m\|=3/2$	$\|3/2,3/2\rangle$	$\|3/2,-3/2\rangle$
$\langle j_1 j_2,1,1/2\|$	1	0
$\langle j_1 j_2,-1,-1/2\|$	0	1

$m=1/2$	$\|3/2,1/2\rangle$	$\|1/2,1/2\rangle$
$\langle j_1 j_2,1,-1/2\|$	$\sqrt{1/3}$	$\sqrt{2/3}$
$\langle j_1 j_2,0,1/2\|$	$\sqrt{2/3}$	$-\sqrt{1/3}$

$m=-1/2$	$\|3/2,-1/2\rangle$	$\|1/2,-1/2\rangle$
$\langle j_1 j_2,0,-1/2\|$	$\sqrt{2/3}$	$\sqrt{1/3}$
$\langle j_1 j_2,-1,1/2\|$	$\sqrt{1/3}$	$-\sqrt{2/3}$

$(1 \times 1/2)$

$\|m\|=2$	$\|2,2\rangle$	$\|2,-2\rangle$
$\langle j_1 j_2,3/2,1/2\|$	1	
$\langle j_1 j_2,-3/2,-1/2\|$	0	1

$m=1$	$\|2,1\rangle$	$\|1,1\rangle$
$\langle j_1 j_2,3/2,-1/2\|$	$\sqrt{1/4}$	$\sqrt{3/4}$
$\langle j_1 j_2,1/2,1/2\|$	$\sqrt{3/4}$	$-\sqrt{1/4}$

$m=-1$	$\|2,-1\rangle$	$\|1,-1\rangle$
$\langle j_1 j_2,-1/2,-1/2\|$	$\sqrt{3/4}$	$\sqrt{1/4}$
$\langle j_1 j_2,-3/2,1/2\|$	$\sqrt{1/4}$	$-\sqrt{3/4}$

$m=0$	$\|2,0\rangle$	$\|1,0\rangle$
$\langle j_1 j_2,1/2,-1/2\|$	$\sqrt{1/2}$	$\sqrt{1/2}$
$\langle j_1 j_2,-1/2,1/2\|$	$\sqrt{1/2}$	$-\sqrt{1/2}$

$(3/2 \times 1/2)$

$\|m\|=5/2$	$\|5/2,5/2\rangle$	$\|5/2,-5/2\rangle$
$\langle j_1 j_2,2,1/2\|$	1	0
$\langle j_1 j_2,-2,-1/2\|$	0	1

$m=3/2$	$\|5/2,3/2\rangle$	$\|3/2,3/2\rangle$
$\langle j_1 j_2,2,-1/2\|$	$\sqrt{1/5}$	$\sqrt{4/5}$
$\langle j_1 j_2,1,1/2\|$	$\sqrt{4/5}$	$-\sqrt{1/5}$

$m=-3/2$	$\|5/2,-3/2\rangle$	$\|3/2,-3/2\rangle$
$\langle j_1 j_2,-1,-1/2\|$	$\sqrt{4/5}$	$\sqrt{1/5}$
$\langle j_1 j_2,-2,1/2\|$	$\sqrt{1/5}$	$-\sqrt{4/5}$

$m=1/2$	$\|5/2,1/2\rangle$	$\|3/2,1/2\rangle$
$\langle j_1 j_2,1,-1/2\|$	$\sqrt{2/5}$	$\sqrt{3/5}$
$\langle j_1 j_2,0,1/2\|$	$\sqrt{3/5}$	$-\sqrt{2/5}$

$m=-1/2$	$\|5/2,-1/2\rangle$	$\|3/2,-1/2\rangle$
$\langle j_1 j_2,0,-1/2\|$	$\sqrt{3/5}$	$\sqrt{2/5}$
$\langle j_1 j_2,-1,1/2\|$	$\sqrt{2/5}$	$-\sqrt{3/5}$

$(2 \times 1/2)$

(5/2 × 1/2)

$\lvert m\rvert=3$	$\lvert 3,3\rangle$	$\lvert 3,-3\rangle$
$\langle j_1j_2,5/2,1/2\rvert$	1	0
$\langle j_1j_2,-5/2,-1/2\rvert$	0	1

$m=2$	$\lvert 3,2\rangle$	$\lvert 2,1\rangle$
$\langle j_1j_2,5/2,-1/2\rvert$	$\sqrt{1/6}$	$\sqrt{5/6}$
$\langle j_1j_2,3/2,1/2\rvert$	$\sqrt{5/6}$	$-\sqrt{1/6}$

$m=-2$	$\lvert 3,-1\rangle$	$\lvert 2,-1\rangle$
$\langle j_1j_2,-3/2,-1/2\rvert$	$\sqrt{5/6}$	$\sqrt{1/6}$
$\langle j_1j_2,-5/2,1/2\rvert$	$\sqrt{1/6}$	$-\sqrt{5/6}$

$m=1$	$\lvert 3,1\rangle$	$\lvert 1,1\rangle$
$\langle j_1j_2,3/2,-1/2\rvert$	$\sqrt{1/3}$	$\sqrt{2/3}$
$\langle j_1j_2,1/2,1/2\rvert$	$\sqrt{2/3}$	$-\sqrt{1/3}$

$m=-1$	$\lvert 2,-1\rangle$	$\lvert 1,-1\rangle$
$\langle j_1j_2,-1/2,-1/2\rvert$	$\sqrt{2/3}$	$\sqrt{1/3}$
$\langle j_1j_2,-3/2,1/2\rvert$	$\sqrt{1/3}$	$-\sqrt{2/3}$

$m=0$	$\lvert 3,0\rangle$	$\lvert 1,0\rangle$
$\langle j_1j_2,1/2,-1/2\rvert$	$\sqrt{1/2}$	$\sqrt{1/2}$
$\langle j_1j_2,-1/2,1/2\rvert$	$\sqrt{1/2}$	$-\sqrt{1/2}$

(3 × 1/2)

$\lvert m\rvert=7/2$	$\lvert 7/2,7/2\rangle$	$\lvert 7/2,-7/2\rangle$
$\langle j_1j_2,3,1/2\rvert$	1	0
$\langle j_1j_2,-3,-1/2\rvert$	0	1

$m=5/2$	$\lvert 7/2,5/2\rangle$	$\lvert 5/2,5/2\rangle$
$\langle j_1j_2,3,-1/2\rvert$	$\sqrt{1/7}$	$\sqrt{6/7}$
$\langle j_1j_2,2,1/2\rvert$	$\sqrt{6/7}$	$-\sqrt{1/7}$

$m=-5/2$	$\lvert 7/2,-5/2\rangle$	$\lvert 5/2,-5/2\rangle$
$\langle j_1j_2,-2,-1/2\rvert$	$\sqrt{6/7}$	$\sqrt{1/7}$
$\langle j_1j_2,-3,1/2\rvert$	$\sqrt{1/7}$	$-\sqrt{6/7}$

$m=3/2$	$\lvert 7/2,3/2\rangle$	$\lvert 5/2,3/2\rangle$
$\langle j_1j_2,2,-1/2\rvert$	$\sqrt{2/7}$	$\sqrt{5/7}$
$\langle j_1j_2,1,1/2\rvert$	$\sqrt{5/7}$	$-\sqrt{2/7}$

$m=-3/2$	$\lvert 7/2,-3/2\rangle$	$\lvert 5/2,-3/2\rangle$
$\langle j_1j_2,-1,-1/2\rvert$	$\sqrt{5/7}$	$\sqrt{2/7}$
$\langle j_1j_2,-2,1/2\rvert$	$\sqrt{2/7}$	$-\sqrt{5/7}$

$m=1/2$	$\lvert 7/2,1/2\rangle$	$\lvert 5/2,1/2\rangle$
$\langle j_1j_2,1,-1/2\rvert$	$\sqrt{3/7}$	$\sqrt{4/7}$
$\langle j_1j_2,0,1/2\rvert$	$\sqrt{4/7}$	$-\sqrt{3/7}$

$m=-1/2$	$\lvert 7/2,-1/2\rangle$	$\lvert 5/2,-1/2\rangle$
$\langle j_1j_2,0,-1/2\rvert$	$\sqrt{4/7}$	$\sqrt{3/7}$
$\langle j_1j_2,-1,1/2\rvert$	$\sqrt{3/7}$	$-\sqrt{4/7}$

(4 × 1/2)

$\lvert m\rvert=9/2$	$\lvert 9/2,9/2\rangle$	$\lvert 9/2,-9/2\rangle$
$\langle j_1j_2,4,1/2\rvert$	1	0
$\langle j_1j_2,-4,-1/2\rvert$	0	1

$m=7/2$	$\lvert 9/2,7/2\rangle$	$\lvert 7/2,7/2\rangle$
$\langle j_1j_2,4,-1/2\rvert$	$\sqrt{1/9}$	$\sqrt{8/9}$
$\langle j_1j_2,3,1/2\rvert$	$\sqrt{8/9}$	$-\sqrt{1/9}$

$m=-7/2$	$\lvert 9/2,-7/2\rangle$	$\lvert 7/2,-7/2\rangle$
$\langle j_1j_2,-3,-1/2\rvert$	$\sqrt{8/9}$	$\sqrt{1/9}$
$\langle j_1j_2,-4,1/2\rvert$	$\sqrt{1/9}$	$-\sqrt{8/9}$

$m=5/2$	$\lvert 9/2,5/2\rangle$	$\lvert 7/2,5/2\rangle$
$\langle j_1j_2,3,-1/2\rvert$	$\sqrt{2/9}$	$\sqrt{7/9}$
$\langle j_1j_2,2,1/2\rvert$	$\sqrt{7/9}$	$-\sqrt{2/9}$

$m=-5/2$	$\lvert 9/2,-5/2\rangle$	$\lvert 7/2,-5/2\rangle$
$\langle j_1j_2,-2,-1/2\rvert$	$\sqrt{7/9}$	$\sqrt{2/9}$
$\langle j_1j_2,-3,1/2\rvert$	$\sqrt{2/9}$	$-\sqrt{7/9}$

$m=3/2$	$\lvert 9/2,3/2\rangle$	$\lvert 7/2,3/2\rangle$
$\langle j_1j_2,2,-1/2\rvert$	$\sqrt{1/3}$	$\sqrt{2/3}$
$\langle j_1j_2,1,1/2\rvert$	$\sqrt{2/3}$	$-\sqrt{1/3}$

$m=-3/2$	$\lvert 9/2,-3/2\rangle$	$\lvert 7/2,-3/2\rangle$
$\langle j_1j_2,-1,-1/2\rvert$	$\sqrt{2/3}$	$\sqrt{1/3}$
$\langle j_1j_2,-2,1/2\rvert$	$\sqrt{1/3}$	$-\sqrt{2/3}$

$m=1/2$	$\lvert 9/2,1/2\rangle$	$\lvert 7/2,1/2\rangle$
$\langle j_1j_2,1,-1/2\rvert$	$\sqrt{4/9}$	$\sqrt{5/9}$
$\langle j_1j_2,0,1/2\rvert$	$\sqrt{5/9}$	$-\sqrt{4/9}$

$m=-1/2$	$\lvert 9/2,-1/2\rangle$	$\lvert 7/2,-1/2\rangle$
$\langle j_1j_2,0,-1/2\rvert$	$\sqrt{5/9}$	$\sqrt{4/9}$
$\langle j_1j_2,-1,1/2\rvert$	$\sqrt{4/9}$	$-\sqrt{5/9}$

Appendix D

Vector relations

D.1 Inner and outer products

$$(\mathbf{u},\mathbf{v},\mathbf{w}) = \mathbf{u}\cdot(\mathbf{v}\times\mathbf{w}) = \mathbf{v}\cdot(\mathbf{w}\times\mathbf{u}) = \mathbf{w}\cdot(\mathbf{u}\times\mathbf{v}) \tag{D.1}$$

$$\mathbf{u}\times(\mathbf{v}\times\mathbf{w}) = (\mathbf{u}\cdot\mathbf{w})\mathbf{v} - (\mathbf{u}\cdot\mathbf{v})\mathbf{w} \tag{D.2}$$

$$\mathbf{u}\times(\mathbf{v}\times\mathbf{w}) = -\,(\mathbf{v}\times\mathbf{w})\times\mathbf{u} \tag{D.3}$$

$$(\mathbf{u}\times\mathbf{v})\cdot(\mathbf{w}\times\mathbf{z}) = (\mathbf{u}\cdot\mathbf{w})(\mathbf{v}\cdot\mathbf{z}) - (\mathbf{u}\cdot\mathbf{z})(\mathbf{v}\cdot\mathbf{w}) \tag{D.4}$$

D.2 Gradient, divergence and curl

D.2.1 Expressions with a single derivative

$$\boldsymbol{\nabla}\cdot(\mathbf{A}\phi) = (\mathbf{A}\cdot\boldsymbol{\nabla}\phi) + \phi(\boldsymbol{\nabla}\cdot\mathbf{A}) \tag{D.5}$$

$$\boldsymbol{\nabla}\times(\mathbf{A}\phi) = -(\mathbf{A}\times\boldsymbol{\nabla}\phi) + \phi(\boldsymbol{\nabla}\times\mathbf{A}) \tag{D.6}$$

$$\boldsymbol{\nabla}\cdot(\mathbf{A}\times\mathbf{B}) = \mathbf{B}\cdot(\boldsymbol{\nabla}\times\mathbf{A}) + \mathbf{A}\cdot(\boldsymbol{\nabla}\times\mathbf{B}) \tag{D.7}$$

$$\boldsymbol{\nabla}\times(\mathbf{A}\times\mathbf{B}) = (\mathbf{B}\cdot\boldsymbol{\nabla})\mathbf{A} - \mathbf{B}(\boldsymbol{\nabla}\cdot\mathbf{A}) - (\mathbf{A}\cdot\boldsymbol{\nabla})\mathbf{B} + \mathbf{A}(\boldsymbol{\nabla}\cdot\mathbf{B}) \tag{D.8}$$

$$\boldsymbol{\nabla}(\mathbf{A}\cdot\mathbf{B}) = (\mathbf{B}\cdot\boldsymbol{\nabla})\mathbf{A} + (\mathbf{A}\cdot\boldsymbol{\nabla})\mathbf{B} + \mathbf{B}\times(\boldsymbol{\nabla}\times\mathbf{A}) + \mathbf{A}\times(\boldsymbol{\nabla}\times\mathbf{B}) \tag{D.9}$$

Special cases:

$$\boldsymbol{\nabla}\cdot\mathbf{r} = 3 \tag{D.10}$$

$$\boldsymbol{\nabla}\times\mathbf{r} = \mathbf{0} \tag{D.11}$$

$$(\mathbf{A}\cdot\boldsymbol{\nabla})\mathbf{r} = \mathbf{A} \tag{D.12}$$

$$\boldsymbol{\nabla}\cdot\dot{\mathbf{r}} = \boldsymbol{\nabla}\times\dot{\mathbf{r}} = (\mathbf{A}\cdot\boldsymbol{\nabla})\dot{\mathbf{r}} = \mathbf{0} \tag{D.13}$$

$$\boldsymbol{\nabla}r^n = nr^{n-1}\,(\mathbf{r}/r) = nr^{n-1}\hat{\mathbf{r}} \tag{D.14}$$

Combining Eqs.(D.9), (D.11) and (D.12) we find

$$\boldsymbol{\nabla}(\mathbf{r}\cdot\mathbf{A}) = \mathbf{A} + (\mathbf{r}\cdot\boldsymbol{\nabla})\mathbf{A} + \mathbf{r}\times(\boldsymbol{\nabla}\times\mathbf{A}). \tag{D.15}$$

Similarly we find by combining Eqs.(D.9) with Eq.(D.8)

$$\boldsymbol{\nabla}(\dot{\mathbf{r}} \cdot \mathbf{A}) = (\dot{\mathbf{r}} \cdot \boldsymbol{\nabla})\mathbf{A} + \dot{\mathbf{r}} \times (\boldsymbol{\nabla} \times \mathbf{A}). \tag{D.16}$$

$$\frac{d}{dt}\mathbf{A} = \frac{\partial}{\partial t}\mathbf{A} + (\dot{\mathbf{r}} \cdot \nabla)\mathbf{A} \tag{D.17}$$

D.2.2 Expressions with second derivatives

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla}\phi) = 0 \tag{D.18}$$

$$\boldsymbol{\nabla} \cdot (\boldsymbol{\nabla} \times \mathbf{A}) = 0 \tag{D.19}$$

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{A}) = \boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \mathbf{A}) - \boldsymbol{\nabla}^2\mathbf{A} \tag{D.20}$$

Special case:

$$\boldsymbol{\nabla}^2(1/r) = -4\pi\delta(\mathbf{r}) \tag{D.21}$$

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