CHAPTER IX

Semi-relativistic description of particles with spin

1 Introduction

For single particles that move in external electromagnetic fields equations of motion and of spin have been derived in a completely covariant way in the preceding chapter. If a set of particles moves under the combined influence of external fields and mutual interactions, a covariant description can be obtained only in the framework of quantum electrodynamics. This would take us outside the scope of the present treatise. However magnetic effects are found already if the non-relativistic theory (in which only electrostatic terms are effectively taken into account) is extended with terms up to and including those of order c^{-2}. Such a description will be the subject of this and the following chapter. In point of fact we shall not even have to consider all terms of order c^{-2}, but only those which contain at least one magnetic multipole term. Such an approximation can alternatively be described by declaring magnetic multipole moments as being of order c^0, and subsequently retaining only terms up to order c^{-1}: the so-called semi-relativistic approximation.

The present chapter will be devoted to the study of the semi-relativistic theory for a set of point particles with spin grouped into stable entities, while the next chapter will contain the corresponding theory of continuous media.

2 The Hamilton operator up to order c^{-2} for a system of Dirac and Klein–Gordon particles in an external field

The wave equation for a single Dirac particle with mass m and charge e in an external electromagnetic field with potentials φ_e and $\boldsymbol{A}_e$ is

$$H_{op}\psi(\boldsymbol{R}, t) = -\frac{\hbar}{i}\frac{\partial\psi(\boldsymbol{R}, t)}{\partial t}, \tag{1}$$

where ψ is a four-component wave function and where the Hamilton operator has the form

$$H_{op} = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi}_{op} + \beta mc^2 + e\varphi_e(\boldsymbol{R}, t). \tag{2}$$

Here we used the 4×4 Dirac matrices $\boldsymbol{\alpha}$ and β, and the abbreviation

$$\boldsymbol{\pi}_{op} \equiv \boldsymbol{P}_{op} - \frac{e}{c}\boldsymbol{A}_e(\boldsymbol{R}, t). \tag{3}$$

(No anomalous magnetic moment term has been included in the Hamiltonian.)

If one wants to describe a system of two Dirac particles one needs a wave function which is an element of the direct product space of the wave functions for particles 1 and 2, and hence a 16-component wave function, labelled by two indices each running from 1 to 4. For such a system the Hamiltonian describing the time behaviour of the wave function will be the sum of two Hamiltonians of the type (2) and an interaction term. An approximate form for the latter (tantamount to taking only terms up to order c^{-2} into account) has been written down by Breit[1] in close analogy to the classical Darwin Hamiltonian (which is valid up to order c^{-2}, see problem 6 of chapter III). It reads

$$H_{int,op} \equiv \frac{e_1 e_2}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|}\{1 - \tfrac{1}{2}\boldsymbol{\alpha}_1\cdot\mathbf{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2)\cdot\boldsymbol{\alpha}_2\}, \tag{4}$$

where e_1 and e_2 are the charges of the two particles, $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ their coordinates and where the three-tensor $\mathbf{T}$ is given by

$$\mathbf{T}(\boldsymbol{s}) \equiv \mathbf{U} + \frac{\boldsymbol{s}\boldsymbol{s}}{s^2}. \tag{5}$$

Furthermore $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$ are Dirac matrices operating on the first and second index of the wave function respectively. (In the direct product notation, they may be written as $\boldsymbol{\alpha}\otimes 1$ and $1\otimes\boldsymbol{\alpha}$ respectively.) The total Hamiltonian of the two-particle system has thus the form

$$H_{op} = \sum_{i=1}^{2}\{c\boldsymbol{\alpha}_i\cdot\boldsymbol{\pi}_{i,op} + \beta_i m_i c^2 + e_i\varphi_e(\boldsymbol{R}_i, t)\} + \frac{e_1 e_2}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|}\{1 - \tfrac{1}{2}\boldsymbol{\alpha}_1\cdot\mathbf{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2)\cdot\boldsymbol{\alpha}_2\} \tag{6}$$

[1] G. Breit, Phys. Rev. **34**(1929)553, **36**(1930)383, **39**(1932)616; for a discussion from the point of view of quantum electrodynamics, see for instance H. A. Bethe and E. E. Salpeter, Quantum mechanics of one- and two-electron atoms (Springer-Verlag, Berlin 1957) p. 170ff, or A. I. Achieser and W. B. Berestezki, Quantenelektrodynamik (Teubner, Leipzig 1962) p. 428ff.

with

$$\pi_{i,\mathrm{op}} = \boldsymbol{P}_{i,\mathrm{op}} - \frac{e}{c}\boldsymbol{A}_{\mathrm{e}}(\boldsymbol{R}_i, t). \tag{7}$$

The Dirac matrices β_1 and β_2 should be understood in the same way as $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$.

The Hamiltonian (6) contains the matrices $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$, which are odd in the Pauli representation of the Dirac matrices that has been used in the preceding chapter. As a consequence the wave equation is in fact a set of 16 coupled wave equations. A similar situation of coupled equations arose for the one-particle system with its four-component wave function. There it turned out to be possible to write the set of four coupled equations as two uncoupled pairs of coupled equations, one for the upper two components and one for the lower two of the wave function. The advantage of this procedure was that then positive and negative energy solutions could be considered separately in a convenient way. In the present case we want to execute a similar programme, again uncoupling the upper-upper part and the lower-lower part from the other components of the wave function[1]. To that end we first transform the wave function by means of a product of two Blount transformations, as for the one-particle case. Then the first two terms of the Hamiltonian get even form, as in (VIII.143), if one considers only terms linear in the external fields (or in the charges) and without derivatives of the fields. If one is not interested in terms of higher order than bilinear in the charges, the last term of the Hamiltonian (6) transforms into an expression which is obtained by utilizing the product of the two Blount transformations up to order e^0, i.e. the product of the P–FW transformation operators (VIII.56) both for particle 1 and particle 2. Then we obtain

$$\hat{H}_{\mathrm{op}} \rightleftarrows \sum_{i=1}^{2}\left\{\beta_i E_{\pi i} + e_i\varphi_{\mathrm{e}}(\boldsymbol{R}_i, t) - \frac{e_i\hbar c}{2E_i}\beta_i\boldsymbol{\sigma}_i\cdot\boldsymbol{B}_{\mathrm{e}}(\boldsymbol{R}_i, t)\right.$$
$$\left. - \frac{e_i\hbar c^2}{2E_i(E_i+m_i c^2)}(\boldsymbol{P}_i\wedge\boldsymbol{\sigma}_i)\cdot\boldsymbol{E}_{\mathrm{e}}(\boldsymbol{R}_i, t)\right\} + \hat{H}_{\mathrm{int}} \equiv \hat{H}, \tag{8}$$

where at the right-hand side the Weyl transform $\hat{H}$ of $\hat{H}_{\mathrm{op}}$ has been written. The first terms represent the two one-particle Hamiltonians of (VIII.143). The last term is the Weyl transform of the transformed interaction Hamiltonian. In view of (4) this interaction Hamiltonian consists of two terms

$$\hat{H}_{\mathrm{int}} = \hat{H}_{\mathrm{I,int}} + \hat{H}_{\mathrm{II,int}}, \tag{9}$$

[1] It is unnecessary to decouple also the upper-lower part and the lower-upper part from each other, v. Z. V. Chraplyvy, Phys. Rev. **91**(1953)388, **92**(1953)1310.

with

$$\hat{H}_{\mathrm{I,int,op}} \equiv U_{\mathrm{op}}(1)U_{\mathrm{op}}(2)\frac{e_1 e_2}{4\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}U^\dagger_{\mathrm{op}}(1)U^\dagger_{\mathrm{op}}(2) \rightleftarrows H_{\mathrm{I,int}}, \tag{10}$$

$$\hat{H}_{\mathrm{II,int.op}} \equiv -U_{\mathrm{op}}(1)U_{\mathrm{op}}(2)\frac{e_1 e_2}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}\boldsymbol{\alpha}_1\cdot\mathbf{T}(\boldsymbol{R}_1-\boldsymbol{R}_2)\cdot\boldsymbol{\alpha}_2\, U^\dagger_{\mathrm{op}}(1)U^\dagger_{\mathrm{op}}(2)$$
$$\rightleftarrows H_{\mathrm{II,int}}. \tag{11}$$

From the rules for Weyl transforms (VIII.132) and the abbreviations (VIII.62)

$$\xi_i \equiv \frac{\hbar}{i}\frac{\partial U(i)}{\partial \boldsymbol{P}_i}U^\dagger(i) = -\frac{\hbar}{i}U(i)\frac{\partial U^\dagger(i)}{\partial \boldsymbol{P}_i}, \tag{12}$$

one finds for (10)

$$\hat{H}_{\mathrm{I,int}} = (1 + \xi_1\cdot\nabla_1 + \xi_2\cdot\nabla_2 + \xi_1\cdot\nabla_1\,\xi_2\cdot\nabla_2 + \tfrac{1}{2}\xi_1\,\xi_1 : \nabla_1\nabla_1$$
$$+ \tfrac{1}{2}\xi_2\,\xi_2 : \nabla_2\nabla_2 + \ldots)\frac{e_1 e_2}{4\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}. \tag{13}$$

Furthermore we find in the same fashion for the second interaction term (11)

$$\hat{H}_{\mathrm{II,int}} = F + \tfrac{1}{2}\xi_1\cdot\nabla_1 F + \tfrac{1}{2}(\nabla_1 F)\cdot\xi_1 + \tfrac{1}{2}\xi_2\cdot\nabla_2 F + \tfrac{1}{2}(\nabla_2 F)\cdot\xi_2$$
$$+ \tfrac{1}{4}\xi_1\cdot\nabla_1\,\xi_2\cdot\nabla_2 F + \tfrac{1}{4}\xi_1\cdot\nabla_1(\nabla_2 F)\cdot\xi_2 + \tfrac{1}{4}\xi_2\cdot\nabla_2(\nabla_1 F)\cdot\xi_1$$
$$+ \tfrac{1}{4}(\nabla_1\nabla_2 F) : \xi_1\,\xi_2 - \tfrac{1}{8}\left(\hbar i\frac{\partial\xi_1}{\partial\boldsymbol{P}_1} - \xi_1\,\xi_1\right) : \nabla_1\nabla_1 F$$
$$- \tfrac{1}{8}(\nabla_1\nabla_1 F) : \left(-\hbar i\frac{\partial\xi_1}{\partial\boldsymbol{P}_1} - \xi_1\,\xi_1\right) + \tfrac{1}{4}\xi_1\cdot\nabla_1(\nabla_1 F)\cdot\xi_1$$
$$- \tfrac{1}{8}\left(\hbar i\frac{\partial\xi_2}{\partial\boldsymbol{P}_2} - \xi_2\,\xi_2\right) : \nabla_2\nabla_2 F - \tfrac{1}{8}(\nabla_2\nabla_2 F) : \left(-\hbar i\frac{\partial\xi_2}{\partial\boldsymbol{P}_2} - \xi_2\,\xi_2\right)$$
$$+ \tfrac{1}{4}\xi_2\cdot\nabla_2(\nabla_2 F)\cdot\xi_2 + \ldots \tag{14}$$

with the abbreviation

$$F \equiv -\frac{e_1 e_2\hat{\boldsymbol{\alpha}}_1\cdot\mathbf{T}(\boldsymbol{R}_1-\boldsymbol{R}_2)\cdot\hat{\boldsymbol{\alpha}}_2}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}, \tag{15}$$

where

$$\hat{\boldsymbol{\alpha}}_i \equiv U(i)\boldsymbol{\alpha}_i U^\dagger(i). \tag{16}$$

In deriving (13) and (14) we employed the identity, which follows from (12),

$$\frac{\partial^2 U(i)}{\partial\boldsymbol{P}_i\partial\boldsymbol{P}_i}U^\dagger(i) = \frac{\partial}{\partial\boldsymbol{P}_i}\left(\frac{i}{\hbar}\xi_i\right) - \frac{1}{\hbar^2}\xi_i\xi_i. \tag{17}$$

The transformed Hamiltonian, given by (8) with (9), (13) and (14) is not in closed form. It contains series in the derivatives of the interparticle potential, occurring in (13) and of the function F (15), occurring in (14). In the case of one single particle in an external field, such series (but there with the derivatives of the external field) also appeared, at least in principle. But there (as well as here for the external field terms) these series could be broken off on the assumption that the external field did not change rapidly (on the scale of the Compton wave length). Here, for the interaction terms (13–14), we are not in such a simple situation, since the interparticle fields may change rapidly. The series may still be broken off if a stronger assumption is adopted namely that only terms up to a certain order in c^{-1} should be taken into account. In fact both (13) and (14) may be seen as series in powers of c^{-1}, if one realizes that ξ_i is of order c^{-1} and $\partial\xi_i/\partial \boldsymbol{P}_i$ of order c^{-2}, as follows from the expressions (VIII.63). Therefore we shall limit ourselves from now on to terms up to and including those of order c^{-2} (terms of higher order in c^{-1} can only be obtained consistently if one starts from an expression of more general validity than (4)). In that case the expression (8) becomes

$$\hat{H}_{\text{op}} \rightleftarrows \sum_{i=1}^{2} \left[\beta_i m_i c^2 + \beta_i \frac{\boldsymbol{P}_i^2}{2m_i} - \beta_i \frac{\boldsymbol{P}_i^4}{8m_i^3 c^2} - \beta_i e_i \frac{\boldsymbol{P}_i}{m_i c} \cdot \boldsymbol{A}_e(\boldsymbol{R}_i, t) \right.$$
$$\left. + e_i \varphi_e(\boldsymbol{R}_i, t) - \frac{e_i \hbar}{2m_i c} \boldsymbol{\sigma}_i \cdot \left\{ \boldsymbol{B}_e(\boldsymbol{R}_i, t)\beta_i - \frac{\boldsymbol{P}_i}{2m_i c} \wedge \boldsymbol{E}_e(\boldsymbol{R}_i, t) \right\} \right] + \hat{H}_{\text{int}}, \quad (18)$$

where only terms up to first order in the external fields have been retained and where now $\hat{H}_{\text{int}}$ is given by (9) with (13–14), the latter without the terms indicated by dots.

The Hamiltonian in (18) contains a number of terms which are already of even-even form, i.e. they do not couple the upper-upper and the lower-lower parts of the wave function with the upper-lower and lower-upper parts. The interaction Hamiltonian $\hat{H}_{\text{int}}$ however contains also parts which are of even-odd, odd-even and odd-odd character and hence do couple the upper-upper and lower-lower components with each other and with the mixed components. The general form of (18) is thus

$$\hat{H}_{\text{op}} \rightleftarrows \mathscr{E}_1 \mathscr{E}_2 + \mathscr{E}_1 \mathscr{O}_2 + \mathscr{O}_1 \mathscr{E}_2 + \mathscr{O}_1 \mathscr{O}_2, \quad (19)$$

where $\mathscr{E}_i$ and $\mathscr{O}_i$ indicate even and odd parts with respect to the matrix indices pertinent to particle i. The odd parts in (19) may be brought into a more convenient form in the following way. Let us transform the Hamiltonian by means of an operator

$$V_{\text{op}} \rightleftarrows 1 + \lambda_1 \beta_2 \mathscr{E}_1 \mathscr{O}_2 + \lambda_2 \beta_1 \mathscr{O}_1 \mathscr{E}_2 + (\lambda_3 \beta_1 + \lambda_4 \beta_2) \mathscr{O}_1 \mathscr{O}_2. \quad (20)$$

Up to order $e_1 e_2$ this operator is unitary, if the λ_i are real coefficients. This is seen by taking into account that the last three parts of the Hamiltonian (19) are of order $e_1 e_2$.

If the Weyl transform of $V_{\text{op}} \hat{H}_{\text{op}} V_{\text{op}}^{-1}$ is calculated, one finds in the first place a term which is simply the product $V\hat{H}V^{-1}$ of the Weyl transforms given by (19) and (20). Up to order $e_1 e_2$ this product is:

$$V\hat{H}V^{-1} = \mathscr{E}_1 \mathscr{E}_2 + \mathscr{E}_1 \mathscr{O}_2 + \mathscr{O}_1 \mathscr{E}_2 + \mathscr{O}_1 \mathscr{O}_2 - 2\lambda_1 E_2 \mathscr{E}_1 \mathscr{O}_2 - 2\lambda_2 E_1 \mathscr{O}_1 \mathscr{E}_2$$
$$- 2\{\lambda_3(E_1 + \beta_1 \beta_2 E_2) + \lambda_4(E_2 + \beta_1 \beta_2 E_1)\} \mathscr{O}_1 \mathscr{O}_2, \quad (21)$$

where we used the (anti)commutation property of β_i with even (odd) matrices $\mathscr{E}_i(\mathscr{O}_i)$ and the fact that the terms independent of e_1 and e_2 in $\hat{H}$ are $\beta_1 E_1 + \beta_2 E_2$. We require that the transformed Hamiltonian, part of which is written in (21), contains no $\mathscr{E}_1 \mathscr{O}_2$ and $\mathscr{O}_1 \mathscr{E}_2$ terms, so we choose $\lambda_1 = 1/2E_2$ and $\lambda_2 = 1/2E_1$. Then the upper-upper terms (and the lower-lower terms) are no longer coupled to the mixed components through terms of the type $\mathscr{E}_1 \mathscr{O}_2$ and $\mathscr{O}_1 \mathscr{E}_2$. In order to achieve that the odd-odd terms do not give rise to unwanted couplings, one may try to make them vanish as well. This gives rise to a unitary operator which is singular and has therefore to be rejected. However the odd-odd terms are harmless[1] already if they are multiplied by $(1 - \beta_1 \beta_2)$, because then this term gives zero if it operates on a wave function which has only upper-upper or only lower-lower components. This is accomplished by choosing λ_3 and λ_4 as $1/\{4(E_1 + E_2)\}$. Hence the unitary operator (20) which we employ is

$$V_{\text{op}} \rightleftarrows 1 + \frac{1}{2E_2} \beta_2 \mathscr{E}_1 \mathscr{O}_2 + \frac{1}{2E_1} \beta_1 \mathscr{O}_1 \mathscr{E}_2 + \frac{\beta_1 + \beta_2}{4(E_1 + E_2)} \mathscr{O}_1 \mathscr{O}_2. \quad (22)$$

Then, up to order c^{-2} and $e_1 e_2$, the transformed Hamiltonian becomes, employing the rule (VIII.132) for the Weyl transform of a product,

$$V_{\text{op}} \hat{H}_{\text{op}} V_{\text{op}}^{-1} \rightleftarrows \mathscr{E}_1 \mathscr{E}_2 + \tfrac{1}{2}(1 - \beta_1 \beta_2) \mathscr{O}_1 \mathscr{O}_2 + \frac{\hbar^2 c^2}{16 E_1 E_2} (1 + \beta_1 \beta_2) \Delta_1 \mathscr{O}_1 \mathscr{O}_2, \quad (23)$$

where we used the fact that the terms with $\mathscr{E}_1 \mathscr{O}_2$ and $\mathscr{O}_1 \mathscr{E}_2$ in (19) are both of order c^{-1}. (The Laplacian operating on the coordinates of particle 1 has been denoted by Δ_1.) Hence in the transformed Hamiltonian again a term (namely the last) appears that is of the unwanted kind discussed above.

[1] Z. V. Chraplyvy, op. cit.

However, in contrast with the $\mathcal{O}_1\mathcal{O}_2$ term of (19) (which is of order c^0) it is only of order c^{-2}. It may be made to disappear by a final unitary transformation with an operator

$$W_{\text{op}} \rightleftarrows 1+\frac{\beta_1+\beta_2}{4(E_1+E_2)}\frac{\hbar^2c^2}{16E_1E_2}(1+\beta_1\beta_2)\Delta_1\mathcal{O}_1\mathcal{O}_2. \tag{24}$$

Then the Hamiltonian gets the form (up to order c^{-2} and e_1e_2):

$$\hat{\hat{H}}_{\text{op}} \equiv W_{\text{op}}V_{\text{op}}\hat{H}_{\text{op}}V_{\text{op}}^{-1}W_{\text{op}}^{-1} \rightleftarrows \mathcal{E}_1\mathcal{E}_2+\tfrac{1}{2}(1-\beta_1\beta_2)\mathcal{O}_1\mathcal{O}_2. \tag{25}$$

If we confine ourselves to positive energy solutions, i.e. to wave functions with only an upper-upper part, we may replace β_1 and β_2 by 1 so that the last term drops out. Then we have for the Weyl transform of the Hamiltonian effectively only the even-even part $\mathcal{E}_1\mathcal{E}_2$ of the right-hand side of (18). The even-even part of (13), up to order c^{-2}, follows by making use of the approximate expressions for the even and odd parts of ξ_i (v. (VIII.63)):

$$\xi_{i,e}=\frac{\hbar\boldsymbol{P}_i\wedge\boldsymbol{\sigma}_i}{4m_i^2c^2}, \qquad \xi_{i,o}=\frac{-\hbar i\beta_i\boldsymbol{\alpha}_i}{2m_ic}. \tag{26}$$

Substituting these expressions into (13) we find

$$\hat{H}_{\text{I,int}}=\left[1+\sum_{i=1}^{2}\left\{\frac{\hbar(\boldsymbol{P}_i\wedge\boldsymbol{\sigma}_i)\cdot\nabla_i}{4m_i^2c^2}+\frac{\hbar^2}{8m_i^2c^2}\Delta_i\right\}\right]\frac{e_1e_2}{4\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}. \tag{27}$$

If we use moreover the approximate expressions for $\hat{\boldsymbol{\alpha}}_i$ (16):

$$\hat{\boldsymbol{\alpha}}_{i,e}=\beta\frac{\boldsymbol{P}_i}{mc}, \qquad \hat{\boldsymbol{\alpha}}_{i,o}=\boldsymbol{\alpha}, \tag{28}$$

we find for (14) with (15), up to order c^{-2},

$$\hat{H}_{\text{II,int}}=-\beta_1\beta_2\{\boldsymbol{P}_1\boldsymbol{P}_2+\tfrac{1}{2}\hbar(\boldsymbol{\sigma}_1\wedge\nabla_1)\boldsymbol{P}_2+\tfrac{1}{2}\hbar(\boldsymbol{\sigma}_2\wedge\nabla_2)\boldsymbol{P}_1$$
$$+\tfrac{1}{4}\hbar^2(\boldsymbol{\sigma}_1\wedge\nabla_1)(\boldsymbol{\sigma}_2\wedge\nabla_2)\}:\frac{e_1e_2\mathbf{T}(\boldsymbol{R}_1-\boldsymbol{R}_2)}{8\pi m_1m_2c^2|\boldsymbol{R}_1-\boldsymbol{R}_2|}. \tag{29}$$

If we replace β_1 and β_2 by 1, we have found now for the complete Hamiltonian for positive-energy solutions, up to terms bilinear in the charges and up to order c^{-2} (omitting from now on the double circumflexes over H_{op}):

$$H_{\text{op}} \rightleftarrows \sum_{i=1}^{2}\left[m_ic^2+\frac{\boldsymbol{P}_i^2}{2m_i}-\frac{\boldsymbol{P}_i^4}{8m_i^3c^2}-e_i\frac{\boldsymbol{P}_i}{m_ic}\cdot\boldsymbol{A}_e(\boldsymbol{R}_i,t)+e_i\varphi_e(\boldsymbol{R}_i,t)\right.$$
$$\left.-\frac{e_i\hbar}{2m_ic}\boldsymbol{\sigma}_i\cdot\left\{\boldsymbol{B}_e(\boldsymbol{R}_i,t)-\frac{\boldsymbol{P}_i}{2m_ic}\wedge\boldsymbol{E}_e(\boldsymbol{R}_i,t)\right\}\right]$$
$$+\left[1+\sum_{i=1}^{2}\left\{\frac{\hbar(\boldsymbol{P}_i\wedge\boldsymbol{\sigma}_i)\cdot\nabla_i}{4m_i^2c^2}+\frac{\hbar^2}{8m_i^2c^2}\Delta_i\right\}\right]\frac{e_1e_2}{4\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}$$
$$-\frac{e_1e_2\boldsymbol{P}_1\cdot\mathbf{T}(\boldsymbol{R}_1-\boldsymbol{R}_2)\cdot\boldsymbol{P}_2}{8\pi m_1m_2c^2|\boldsymbol{R}_1-\boldsymbol{R}_2|}-\{\hbar(\boldsymbol{\sigma}_1\wedge\nabla_1)\cdot\boldsymbol{P}_2+\hbar(\boldsymbol{\sigma}_2\wedge\nabla_2)\cdot\boldsymbol{P}_1$$
$$+\tfrac{1}{2}\hbar^2(\boldsymbol{\sigma}_1\wedge\nabla_1)\cdot(\boldsymbol{\sigma}_2\wedge\nabla_2)\}\frac{e_1e_2}{8\pi m_1m_2c^2|\boldsymbol{R}_1-\boldsymbol{R}_2|}, \tag{30}$$

where in the last term we used the property of the tensor $\mathbf{T}(s)$ (5):

$$(\boldsymbol{a}\wedge\nabla_s)\cdot\frac{\mathbf{T}(s)}{4\pi s}=2(\boldsymbol{a}\wedge\nabla_s)\frac{1}{4\pi s} \tag{31}$$

for an arbitrary vector $\boldsymbol{a}$.

The Hamiltonian[1] obtained contains in the first place the approximation up to order c^{-2} of the one-particle Hamiltonians for particles 1 and 2. It includes, apart from the non-relativistic terms, a kinetic term with the fourth power of the momentum and two terms which couple the spin with the electromagnetic field. Furthermore interaction terms appear, which apart from the Coulomb term, are all of order c^{-2}. One recognizes spin–orbit coupling terms with the vector product of momentum and spin. Next terms with the Laplacians acting on the Coulomb expression appear. They may be written alternatively as[2]

$$-\sum_{i=1}^{2}\frac{\hbar^2}{8m_i^2c^2}e_1e_2\delta(\boldsymbol{R}_1-\boldsymbol{R}_2). \tag{32}$$

Furthermore one encounters the quantum-mechanical analogue of a term in the Darwin Hamiltonian of classical theory (see problem 6 of chapter III). Finally two terms that couple the spin of one particle to the momentum of the other, and a spin–spin interaction term occur. The last term may be

[1] V. e.g. H. A. Bethe and E. E. Salpeter, op. cit. p. 181; A. I. Achieser and W. B. Berestezki, op. cit. p. 431.

[2] In the past confusion about this term existed. Instead of the operator corresponding to (32) one found a non-hermitian operator by employing an elimination procedure for the lower components of the wave function. Then the normalization of the wave function is lost, so that non-hermitian terms appear (cf. A. I. Achieser and W. B. Berestezki, op. cit.).

written in an alternative form by using the ancillary formula

$$\nabla_s \nabla_s \frac{1}{4\pi s} = \mathscr{P}_{\text{sph}} \nabla_s \nabla_s \frac{1}{4\pi s} - \tfrac{1}{3}\mathbf{U}\delta(s), \tag{33}$$

which expresses the double nabla operator acting on $(4\pi s)^{-1}$ in its principal value and a term with the three-dimensional delta function multiplied by the unit tensor $\mathbf{U}$ (v. problem 2 of chapter II). Then the last term of (30) becomes

$$\mathscr{P}_{\text{sph}} \boldsymbol{\sigma}_1 \cdot \nabla_1 \, \boldsymbol{\sigma}_2 \cdot \nabla_2 \frac{e_1 e_2 \hbar^2}{16\pi m_1 m_2 c^2 |\boldsymbol{R}_1 - \boldsymbol{R}_2|} - \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \frac{e_1 e_2}{6 m_1 m_2 c^2} \delta(\boldsymbol{R}_1 - \boldsymbol{R}_2). \tag{34}$$

The Hamilton operator, given in (30) describes a system consisting of two Dirac particles. The generalization to N Dirac particles is obvious. The same procedure may be followed to bring the Hamiltonian into a form which does not couple the upper-...-upper part of the wave function with the other parts. The result is an expression like (30) but now with N one-particle contributions and $\frac{1}{2}N(N-1)$ pair contributions of the type given there.

The physical systems consist usually of electrons and nuclei. The couplings of the electrons with the external field and with each other are described by terms of the form (30). Since the nuclei are much heavier than the electrons, their spin effects can often be neglected: hyperfine splittings are small corrections only. Therefore we shall describe the nuclei from now on as particles without spin, i.e., as Klein–Gordon particles. To find the Hamilton operators for the interaction of a Dirac and a Klein–Gordon particle and of two Klein–Gordon particles in a form comparable to (30) (for the interaction of two Dirac particles) one has to start from an expression that comes instead of (4). Just as the latter formula for two Dirac particles can be derived from quantum electrodynamics, one may obtain for the interaction of two Klein–Gordon particles 1 and 2:

$$\frac{e_1 e_2}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|} - \frac{e_1 e_2 (\tau_3 + i\tau_2)_1 (\tau_3 + i\tau_2)_2}{8c^2} \left\{ \frac{\boldsymbol{P}_{1,\text{op}}}{m_1} \cdot \left\{ \frac{\boldsymbol{P}_{2,\text{op}}}{m_2}, \frac{:\mathbf{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2)}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|} \right\} \right\}, \tag{35}$$

where the Feshbach–Villars representation (chapter VIII, section 4) has been employed. The interaction between a Klein–Gordon particle 1 and a Dirac particle 2 is given by

$$\frac{e_1 e_2}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|} - \frac{e_1 e_2 (\tau_3 + i\tau_2)_1}{4c} \left\{ \frac{\boldsymbol{P}_{1,\text{op}}}{m_1}, \frac{\cdot \mathbf{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{\alpha}_2}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|} \right\}. \tag{36}$$

(As compared to (4) one finds here that the Dirac matrix $\boldsymbol{\alpha}$ for a Dirac

particle is to be replaced by $(\tau_3 + i\tau_2)\boldsymbol{P}_{\text{op}}/mc$ for a Klein–Gordon particle. Moreover anticommutators have to be added for the latter case.) If one takes the same steps as those which led from (4) to (30), one finds from (35) and (36) an expression like (30) for the Klein–Gordon particles but without $\boldsymbol{\sigma}$-terms and the term with the Laplacian. In this way one finds for a collection of electrons and nuclei (described as Dirac and Klein–Gordon particles in the present model) that the Weyl transform of the total Hamiltonian is given by

$$\begin{aligned} H_{\text{op}} \rightleftarrows & \sum_i \frac{\boldsymbol{P}_i^2}{2m_i} + \sum_{i,j(i\neq j)} \frac{e_i e_j}{8\pi|\boldsymbol{R}_i - \boldsymbol{R}_j|} + \sum_i e_i \left\{ \varphi_e(\boldsymbol{R}_i, t) - \frac{\boldsymbol{P}_i}{m_i c} \cdot \boldsymbol{A}_e(\boldsymbol{R}_i, t) \right\} \\ & - \sum_i \frac{\boldsymbol{P}_i^4}{8m_i^3 c^2} - \sum_{i,j(i\neq j)} \frac{e_i e_j}{16\pi c^2 |\boldsymbol{R}_i - \boldsymbol{R}_j|} \frac{\boldsymbol{P}_i}{m_i} \cdot \mathbf{T}(\boldsymbol{R}_i - \boldsymbol{R}_j) \cdot \frac{\boldsymbol{P}_j}{m_j} \\ & + {\sum_{i,j(i\neq j)}}' \frac{e_i e_j \hbar}{4 m_i c^2} \left\{ \left(\frac{\boldsymbol{P}_i}{m_i} \wedge \boldsymbol{\sigma}_i \right) \cdot \nabla_i - 2 \left(\frac{\boldsymbol{P}_j}{m_j} \wedge \boldsymbol{\sigma}_i \right) \cdot \nabla_i \right\} \frac{1}{4\pi|\boldsymbol{R}_i - \boldsymbol{R}_j|} \\ & - {\sum_{i,j(i\neq j)}}'' \frac{e_i e_j \hbar^2}{8 m_i m_j c^2} (\boldsymbol{\sigma}_i \wedge \nabla_i) \cdot (\boldsymbol{\sigma}_j \wedge \nabla_j) \frac{1}{4\pi|\boldsymbol{R}_i - \boldsymbol{R}_j|} \\ & - {\sum_{i,j(i\neq j)}}' \frac{e_i e_j \hbar^2}{8 m_i^2 c^2} \delta(\boldsymbol{R}_i - \boldsymbol{R}_j) - {\sum_i}' \frac{e_i \hbar}{2 m_i c} \boldsymbol{\sigma}_i \cdot \left\{ \boldsymbol{B}_e(\boldsymbol{R}_i, t) - \frac{\boldsymbol{P}_i}{2 m_i c} \wedge \boldsymbol{E}_e(\boldsymbol{R}_i, t) \right\} \\ & = H(1, \ldots, N; t), \end{aligned} \tag{37}$$

where the rest energy terms have been suppressed. The primes indicate that the summations concerned are extended only over the electrons. (One should note that a single prime at a double summation sign means that only the summation over the first index is to be limited to the electrons.)

3 *The field equations and the equations of motion for a set of spin particles*

In this section we shall first study the equations of motion and in connexion with them the field equations. The Hamilton operator that specifies the system is given by expression (37).

The equations of motion for the electrons and nuclei will follow by evaluating the commutators of their position operator with the Hamiltonian. The position operator for electron i reads up to order c^{-2}:

$$\boldsymbol{X}_{i,\text{op}} = \boldsymbol{R}_i + \frac{\hbar \boldsymbol{\sigma}_i \wedge \boldsymbol{P}_{i,\text{op}}}{4 m_i^2 c^2}, \tag{38}$$

as follows from (VIII.68) of the preceding chapter. The position operator found there is valid only for a free particle. However by comparison with (VIII.150) it may be seen that up to order c^{-2} the position operator does not change (at least not with terms in the potentials) if an external field is switched on. For the nuclei the position operator is simply

$$X_{i,\mathrm{op}} = R_i, \tag{39}$$

as follows from (VIII.204).

The equation of motion for an electron i will follow by taking first the commutator of (38) with the Hamiltonian (37). With the rules for Weyl transforms (in particular (VI.A161)) one finds up to order c^{-2}:

$$v_{i,\mathrm{op}} \equiv \frac{\mathrm{d}X_{i,\mathrm{op}}}{\mathrm{d}t} \equiv \frac{i}{\hbar}[H_{\mathrm{op}}, X_{i,\mathrm{op}}] \rightleftarrows \frac{\partial H}{\partial P_i} - \frac{\hbar}{4m_i^2c^2}\sigma_i \wedge \frac{\partial H}{\partial R_i}, \tag{40}$$

or explicitly

$$v_{i,\mathrm{op}} \rightleftarrows \frac{P_i}{m_i} - \frac{e_i}{m_i c}A_e(R_i, t) - \frac{P_i^2 P_i}{2m_i^3c^2}$$
$$- \sum_{j(\neq i)} \frac{e_i e_j P_j\cdot \mathsf{T}(R_i - R_j)}{8\pi m_i m_j c^2 |R_i - R_j|} - \sum_{j(\neq i)}{}' \frac{e_i e_j \hbar}{2m_i m_j c^2}\sigma_j \wedge \nabla_j \frac{1}{4\pi|R_i - R_j|}. \tag{41}$$

The second time derivative is found by taking once more the commutator with the Hamiltonian and adding an explicit time derivative. Then one finds an equation of the form

$$m_i \frac{\mathrm{d}v_{i,\mathrm{op}}}{\mathrm{d}t} \equiv m_i \frac{i}{\hbar}[H_{\mathrm{op}}, v_{i,\mathrm{op}}] + m_i \frac{\partial v_{i,\mathrm{op}}}{\partial t} \rightleftarrows f_i, \tag{42}$$

where f_i is the Weyl transform of the force on the electron. It is convenient to study first its part f_{ie}, which depends on the external fields. Retaining only terms linear in these fields (and linear in the charge e_i) we obtain

$$f_{ie} = e_i E_e(R_i, t) + \frac{e_i}{m_i c} P_i \wedge B_e(R_i, t)$$
$$- \frac{e_i}{m_i^2c^2} P_i P_i\cdot E_e(R_i, t) - \frac{e_i}{2m_i^2c^2} P_i^2 E_e(R_i, t)$$
$$+ \frac{e_i\hbar}{2m_i c}\left[\{\nabla_i B_e(R_i, t)\}\cdot\sigma_i + \tfrac{1}{2}\{\nabla_i E_e(R_i, t)\}\cdot\left(\frac{P_i}{m_i c}\wedge\sigma_i\right)\right]. \tag{43}$$

The total force has a similar structure. It becomes:

$$f_i = e_i e_t(R_i, t) + \frac{e_i}{m_i c} P_i \wedge b_t(R_i, t)$$
$$- \frac{e_i}{m_i^2c^2} P_i P_i\cdot e_t(R_i, t) - \frac{e_i}{2m_i^2c^2} P_i^2 e_t(R_i, t) + \frac{e_i\hbar}{2m_i c}\left[\{\nabla_i b_t(R_i, t)\}\cdot\sigma_i\right.$$
$$\left.+ \tfrac{1}{2}\{\nabla_i e_t(R_i, t)\}\cdot\left(\frac{P_i}{m_i c}\wedge\sigma_i\right)\right] + \frac{e_i\hbar^2}{4m_i^2c^2}\Delta_i e_t(R_i, t), \tag{44}$$

if only terms bilinear in the charges are included. Only the last term of (44) is of a type that did not occur in (43). The other terms contain, instead of the external fields E_e and B_e, the Weyl transforms of quantities e_t and b_t, which will be called the total fields acting on the particle. They are of the form

$$\begin{aligned} e_t(R, t) &= E_e(R, t) + \sum_{j(\neq i)} e_j(R, t), \\ b_t(R, t) &= B_e(R, t) + \sum_{j(\neq i)} b_j(R, t), \end{aligned} \tag{45}$$

with partial fields

$$\begin{aligned} e_j(R, t) = &-e_j\nabla\frac{1}{4\pi|R_j - R|} + \frac{e_j}{2m_j^2c^2}P_j\cdot\nabla\frac{P_j\cdot\mathsf{T}(R_j - R)}{4\pi|R_j - R|} \\ &+ \frac{e_j\hbar}{4m_j^2c^2}\nabla(P_j\wedge\sigma_j)\cdot\nabla\frac{1}{4\pi|R_j - R|} \\ &- \frac{e_j\hbar}{2m_j^2c^2}P_j\cdot\nabla\sigma_j\wedge\nabla\frac{1}{4\pi|R_j - R|} + \frac{e_j\hbar^2}{8m_j^2c^2}\nabla\delta(R_j - R), \\ b_j(R, t) = &\frac{e_j}{m_j c}\nabla\wedge\left(\frac{P_j}{4\pi|R_j - R|}\right) - \frac{e_j\hbar}{2m_j c}\nabla\wedge(\sigma_j\wedge\nabla)\frac{1}{4\pi|R_j - R|}. \end{aligned} \tag{46}$$

The partial fields generated by particle j have been written here for the case that j is an electron. In the sums of (45) all particles occur. For nuclei one has to retain only the first two terms of e_j and the first term of b_j.

The total force (44) on electron i gets a simpler interpretation if one introduces the fields at the position X_i rather than at R_i. Since the difference between these quantities is of order c^{-2}, such a change of arguments of the fields affects only the first term in (44). One has, with (38),

$$e(X_i, t) = e(R_i, t) + \frac{\hbar\sigma_i \wedge P_i}{4m_i^2c^2}\cdot\nabla_i e(R_i, t). \tag{47}$$

Then the equation of motion (42) with (44) may be written as

$$
\begin{aligned}
m_i \frac{\mathrm{d}\boldsymbol{v}_{i,\mathrm{op}}}{\mathrm{d}t} \rightleftarrows \boldsymbol{f}_i = & \ e_i \boldsymbol{e}_\mathrm{t}(\boldsymbol{X}_i, t) + \frac{e_i}{m_i c} \boldsymbol{P}_i \wedge \boldsymbol{b}_\mathrm{t}(\boldsymbol{X}_i, t) - \frac{e_i}{m_i^2 c^2} \boldsymbol{P}_i \boldsymbol{P}_i \cdot \boldsymbol{e}_\mathrm{t}(\boldsymbol{X}_i, t) \\
& - \frac{e_i}{2m_i^2 c^2} \boldsymbol{P}_i^2 \boldsymbol{e}_\mathrm{t}(\boldsymbol{X}_i, t) + \frac{e_i \hbar}{2m_i c} \Big[\{\nabla_i \boldsymbol{b}_\mathrm{t}(\boldsymbol{X}_i, t)\} \cdot \boldsymbol{\sigma}_i \\
& + \{\nabla_i \boldsymbol{e}_\mathrm{t}(\boldsymbol{X}_i, t)\} \cdot \left(\frac{\boldsymbol{P}_i}{m_i c} \wedge \boldsymbol{\sigma}_i \right) \Big] + \frac{e_i \hbar^2}{4m_i^2 c^2} \Delta_i \boldsymbol{e}_\mathrm{t}(\boldsymbol{X}_i, t).
\end{aligned} \tag{48}
$$

The Weyl transform of the force contains in the first place the Lorentz force, present already in non-relativistic theory, supplemented here by two relativistic corrections, connected with the motion of the particle. Then two spin terms appear, which couple the space derivative of the magnetic field with the spin of the particle and the space derivative of the electric field with the spin in motion. One should note that here, in analogy with the classical theory for the orbital magnetic moment, the vector product of the momentum (divided by $m_i c$) and the spin magnetic dipole moment $e_i \hbar \boldsymbol{\sigma}_i / 2m_i c$ occurs and not just half of it as in (44).

The equation of motion for the nuclei may likewise be derived from the Hamiltonian (37). For the velocity operator one finds then the same result as (41). For the second derivative one obtains, after multiplication with m_i, an equation like (48) but without spin terms and with a factor 8 instead of 4 in the denominator of the last term.

In deriving the equations of motion we encountered certain expressions (45) with (46) which have been called the Weyl transforms of the total fields (acting on particle i) and which occurred in the equations of motion (48). The sums $\boldsymbol{e}$ and $\boldsymbol{b}$ of the external fields ($\boldsymbol{E}_\mathrm{e}$, $\boldsymbol{B}_\mathrm{e}$) and all partial fields ($\boldsymbol{e}_j$, $\boldsymbol{b}_j$):

$$
\begin{aligned}
\boldsymbol{e}(\boldsymbol{R}, t) &= \boldsymbol{E}_\mathrm{e}(\boldsymbol{R}, t) + \sum_j \boldsymbol{e}_j(\boldsymbol{R}, t), \\
\boldsymbol{b}(\boldsymbol{R}, t) &= \boldsymbol{B}_\mathrm{e}(\boldsymbol{R}, t) + \sum_j \boldsymbol{b}_j(\boldsymbol{R}, t)
\end{aligned} \tag{49}
$$

satisfy equations that follow from the explicit expressions (46), namely

$$
\begin{aligned}
\nabla \cdot \boldsymbol{e} &= \rho^\mathrm{e} - \nabla \cdot \boldsymbol{p}, \\
-\partial_{0\mathrm{P}} \boldsymbol{e} + \nabla \wedge \boldsymbol{b} &= c^{-1} \boldsymbol{j} + \nabla \wedge \boldsymbol{m}, \\
\nabla \cdot \boldsymbol{b} &= 0, \\
\partial_{0\mathrm{P}} \boldsymbol{b} + \nabla \wedge \boldsymbol{e} &= 0,
\end{aligned} \tag{50}
$$

where $\partial_{0\mathrm{P}} a \equiv c^{-1} \partial_{t\mathrm{P}} a = c^{-1}\{a, H\}_\mathrm{P} + \partial_0 a$ (cf. (VI.72)) with the Hamiltonian H (37) and where the sources have the form

$$
\begin{aligned}
\rho^\mathrm{e} &= \sum_j e_j \delta(\boldsymbol{X}_j - \boldsymbol{R}), \\
c^{-1} \boldsymbol{j} &= \sum_j \frac{e_j}{m_j c} \boldsymbol{P}_j \delta(\boldsymbol{X}_j - \boldsymbol{R}), \\
\boldsymbol{p} &= \sum_j{}' \frac{e_j \hbar}{2m_j^2 c^2} (\boldsymbol{P}_j \wedge \boldsymbol{\sigma}_j - \tfrac{1}{4}\hbar \nabla) \delta(\boldsymbol{X}_j - \boldsymbol{R}), \\
\boldsymbol{m} &= \sum_j{}' \frac{e_j \hbar}{2m_j c} \boldsymbol{\sigma}_j \delta(\boldsymbol{X}_j - \boldsymbol{R}).
\end{aligned} \tag{51}
$$

(The primes at the summation signs indicate that the sum has to be extended over the electrons only.) The delta functions occurring here contain the position $\boldsymbol{X}_j$ (38) of the electrons in their arguments. One should understand them as an abbreviation of the expression (cf. (47))

$$
\delta(\boldsymbol{X}_j - \boldsymbol{R}) = \delta(\boldsymbol{R}_j - \boldsymbol{R}) + \frac{\hbar \boldsymbol{\sigma}_j \wedge \boldsymbol{P}_j}{4m_j^2 c^2} \cdot \nabla_j \delta(\boldsymbol{R}_j - \boldsymbol{R}). \tag{52}
$$

(The use of $\boldsymbol{X}_j$ instead of $\boldsymbol{R}_j$ is only significant in the first expression of (51), since in the others it gives rise to terms of order c^{-3}.) In the derivation of (50) with (51) we retained only terms linear in the charges, as is consistent with the fact that in the Hamiltonian (37) only terms bilinear in the charges have been included.

The equations (50) with (51) contain in their source terms charge and current densities of the same form as the non-relativistic ones (v. (VI.73)), except for the occurrence of $\boldsymbol{X}_j$, and moreover polarization and magnetization densities $\boldsymbol{p}$ and $\boldsymbol{m}$ due to the presence of spin. Terms of this type occur here already at the sub-atomic level in contrast with what was the case for point particles, as treated in chapter VI.

Owing to the use of the position operator $\boldsymbol{X}_j$ (which has covariant character; v. the preceding chapter), the polarization $\boldsymbol{p}$ contains a term due to the spins in motion which has a form similar to that of the relativistic classical expression for a composite particle, namely with the vector product of the velocity $\boldsymbol{P}_j / m_j$ and the magnetic moment $e_j \hbar \boldsymbol{\sigma} / 2m_j c$ [1].

The equations of motion (48) and the field equations (50–51) show – as compared to their non-relativistic counterparts (VI.73) and (VI.81) –

[1] If the non-covariant position $\boldsymbol{R}_j$ had been used one would find only half of this term: cf. J. M. Crowther and D. ter Haar, Proc. Kon. Ned. Akad. Wet. **B74**(1971)341, 351.

which terms have to be added if spin effects are included (up to order c^{-2}).

In addition we have to discuss the equation which describes the change in time of the spin for the electrons. It may be obtained by calculating the commutator of the spin operator with the Hamiltonian. From (VIII.79) of the preceding chapter it follows that up to order c^{-2} the spin operator for electron i is

$$s_{i,\text{op}} = \tfrac{1}{2}\hbar \left\{ \sigma_i + \frac{(P_{i,\text{op}} \wedge \sigma_i) \wedge P_{i,\text{op}}}{2m_i^2 c^2} \right\}. \tag{53}$$

Although the spin operator, given there, pertains to a free particle, it follows by comparison with (VIII.151) that up to order c^{-2} the spin operator does not change if external fields are present.

The spin equation follows by taking the commutator of (53) with the Hamilton operator (37). One finds, with the rule for Weyl transforms, up to order c^{-2},

$$\frac{\mathrm{d}s_{i,\text{op}}}{\mathrm{d}t} \equiv \frac{i}{\hbar}[H_{\text{op}}, s_{i,\text{op}}] \rightleftarrows \frac{e_i \hbar}{2m_i c}\left\{\sigma_i \wedge b_t(R_i, t) + c^{-1}\left(\frac{P_i}{m_i} \wedge \sigma_i\right) \wedge e_t(R_i, t)\right\}. \tag{54}$$

The fields e_t and b_t at the right-hand side are given by (45) with (46). They are taken at the position R_i. Application of formulae like (47) shows that one may write X_i instead of R_i if one wishes: the difference leads to terms of order c^{-3}. For the same reason one may replace $\frac{1}{2}\hbar\sigma_i$ by s_i.

The equation (54) shows that a moment is exerted on the spin if it is not parallel to the magnetic field and if its vector product with the velocity P_i/m_i is not parallel to the electric field.

4 *The semi-relativistic approximation*

To derive equations for stable groups of particles we start from the equations for the Weyl transforms of quantities pertaining to point particles with spin, that have been given in the preceding sections. By making Taylor expansions of quantities occurring in the latter equations, we obtain expressions which contain multipole moments of orbital and spin character that characterize the stable groups as a whole.

In the following not all terms of order c^{-2} will be retained in the multipole expanded quantities, but only those for which at least one of the factors c^{-1} is contained in a magnetic orbital or spin multipole moment. An alternative way to express this procedure consists in considering both the electric and magnetic multipole moments as quantities of order c^0, and subsequently retaining only terms of order c^{-1}. In this way we shall obtain a set of approximate equations, which we shall call the 'semi-relativistic limit' of the theory. (In classical theory (v. chapter IV) we employed a similar approximation.) The reason for considering such a truncated form of the c^{-2}-equations is that in this way all magnetic interaction terms, especially those due to magnetic multipole moments in motion, are taken into account, while effects as the Lorentz contraction of the electric multipole moments are left out. The latter effects are indeed much smaller than the former, since they contain the velocity of the atom as a whole instead of an intra-atomic velocity. As a result one finds then expressions which show an analogy between electric and magnetic contributions (v. sections 5 and 6).

5 *The equations for the fields due to composite particles*

The first pair of sub-atomic field equations (50) with (51) reads, if instead of the summation index j we introduce a double index ki where k labels the stable groups (atoms) and i their constituent particles:

$$\nabla\cdot e = \sum_{k,i} e_{ki}\delta(X_{ki}-R) - \sum_{k,i}{}' \frac{e_{ki}\hbar}{2m_{ki}^2c^2}(P_{ki}\wedge\sigma_{ki})\cdot\nabla\delta(X_{ki}-R) + \sum_{k,i}{}' \frac{e_{ki}\hbar^2}{8m_{ki}^2c^2}\Delta\delta(X_{ki}-R), \tag{55}$$

$$-\partial_{0P} e + \nabla\wedge b = \sum_{k,i}\frac{e_{ki}P_{ki}}{m_{ki}c}\delta(X_{ki}-R) + \sum_{k,i}{}'\frac{e_{ki}\hbar}{2m_{ki}c}\nabla\wedge\sigma_{ki}\delta(X_{ki}-R).$$

The quantity P_{ki}/m_{ki} occurring at the right-hand sides of the equations may be replaced by $\partial_{tP}X_{ki}$, where the symbol ∂_{tP} stands for a Poisson bracket with the Hamiltonian H (37). This is justified since we limited ourselves in the right-hand sides of (55) to terms linear in the charges and up to order c^{-2}.

We now introduce a privileged point R_k for each atom k. The relative coordinates of the particles with respect to this point will be denoted by

$$r_{ki} = X_{ki} - R_k. \tag{56}$$

Then, by making a Taylor expansion of the right-hand sides of (55) one gets the expressions

$$\rho^{\mathrm{e}}-\sum_{n=1}^{\infty}(-1)^{n-1}\nabla^{n}:\sum_{k}(\hat{\mu}_{k}^{(n)}-c^{-1}\hat{\nu}_{k,\mathrm{spin}}^{(n)}\wedge v_{k})\delta(R_{k}-R),$$

$$c^{-1}j+\partial_{0\mathrm{P}}\{\sum_{n=1}^{\infty}(-1)^{n-1}\nabla^{n-1}:\sum_{k}\hat{\mu}_{k}^{(n)}\delta(R_{k}-R)\}$$
$$+\nabla\wedge\{\sum_{n=1}^{\infty}(-1)^{n-1}\nabla^{n-1}:\sum_{k}(\hat{\nu}_{k}^{(n)}+c^{-1}\hat{\mu}_{k}^{(n)}\wedge v_{k})\delta(R_{k}-R)\}, \tag{57}$$

where the definition of the semi-relativistic approximation has been employed to suppress a number of terms. The atomic charge and current densities[1], that occur here, are given by

$$\rho^{\mathrm{e}}=\sum_{k}e_{k}\,\delta(R_{k}-R),$$
$$j=\sum_{k}e_{k}\,v_{k}\,\delta(R_{k}-R) \tag{58}$$

with v_k defined as $\partial_{t\mathrm{P}}R_k$, i.e. by a Poisson bracket of R_k with the Weyl transform of the Hamiltonian plus an explicit time derivative. Furthermore the expressions (57) contain the electric and magnetic multipole moments, defined as

$$\hat{\mu}_{k}^{(n)}=\hat{\mu}_{k,\mathrm{orb}}^{(n)}+\hat{\mu}_{k,\mathrm{spin}}^{(n)},\qquad \hat{\nu}_{k}^{(n)}=\hat{\nu}_{k,\mathrm{orb}}^{(n)}+\hat{\nu}_{k,\mathrm{spin}}^{(n)} \tag{59}$$

with their orbital and spin parts

$$\hat{\mu}_{k,\mathrm{orb}}^{(n)}\equiv\frac{1}{n!}\sum_{i}e_{ki}\,r_{ki}^{n},$$
$$\hat{\mu}_{k,\mathrm{spin}}^{(n)}\equiv\frac{1}{(n-1)!}\,\mathscr{S}\sum_{i}{}'\frac{e_{ki}\hbar}{2m_{ki}c}\,r_{ki}^{n-1}\{(\partial_{0\mathrm{P}}r_{ki})\wedge\sigma_{ki}\},$$
$$\hat{\nu}_{k,\mathrm{orb}}^{(n)}\equiv\frac{n}{(n+1)!}\sum_{i}e_{ki}\,r_{ki}^{n-1}r_{ki}\wedge(\partial_{0\mathrm{P}}r_{ki}),$$
$$\hat{\nu}_{k,\mathrm{spin}}^{(n)}\equiv\frac{1}{(n-1)!}\sum_{i}{}'\frac{e_{ki}\hbar}{2m_{ki}c}\,r_{ki}^{n-1}\sigma_{ki}. \tag{60}$$

The symbol $\mathscr{S}$ indicates that a symmetrization has to be performed on the asymmetric tensor in front of which it appears. The moments are all defined with the help of the internal coordinates r_{ki} (56). We note that here such purely space-like quantities have been employed as internal coordinates, in contrast with what was done in classical semi-relativistic theory. For that reason

[1] These atomic quantities should not be confused with the sub-atomic quantities (51), denoted by the same symbols.

we now want to introduce multipole moments expressed in terms of quantities r'_{ki}. The latter will be defined in terms of r_{ki} and its derivative in a way completely analogous to the classical treatment (v. (IV.A100)):

$$r'_{ki}=r_{ki}+\tfrac{1}{2}c^{-2}(\partial_{t\mathrm{P}}R_k)\cdot r_{ki}(\partial_{t\mathrm{P}}R_k)+c^{-2}(\partial_{t\mathrm{P}}R_k)\cdot r_{ki}\,\partial_{t\mathrm{P}}r_{ki}. \tag{61}$$

Substituting the inverse of this expression (up to order c^{-2}) into (57) with (59) and (60) one finds

$$\rho^{\mathrm{e}}-\nabla\cdot p,$$
$$c^{-1}j+\partial_{0\mathrm{P}}\,p+\nabla\wedge m, \tag{62}$$

with the electric and magnetic polarization densities

$$p=\sum_{n=1}^{\infty}(-1)^{n-1}\nabla^{n-1}:\sum_{k}(\mu_{k}^{(n)}-c^{-1}\nu_{k}^{(n)}\wedge v_{k})\delta(R_{k}-R),$$
$$m=\sum_{n=1}^{\infty}(-1)^{n-1}\nabla^{n-1}:\sum_{k}(\nu_{k}^{(n)}+c^{-1}\mu_{k}^{(n)}\wedge v_{k})\delta(R_{k}-R). \tag{63}$$

The semi-relativistic multipole moments $\mu_k^{(n)}$ and $\nu_k^{(n)}$ that occur here are defined by expressions of the same form as (59–60), but with r'_{ki} instead of r_{ki}:

$$\mu_{k}^{(n)}=\mu_{k,\mathrm{orb}}^{(n)}+\mu_{k,\mathrm{spin}}^{(n)},\qquad \nu_{k}^{(n)}=\nu_{k,\mathrm{orb}}^{(n)}+\nu_{k,\mathrm{spin}}^{(n)}, \tag{64}$$

with orbital and spin parts:

$$\mu_{k,\mathrm{orb}}^{(n)}\equiv\frac{1}{n!}\sum_{i}e_{ki}\,r_{ki}'^{n},$$
$$\mu_{k,\mathrm{spin}}^{(n)}\equiv\frac{1}{(n-1)!}\,\mathscr{S}\sum_{i}{}'\frac{e_{ki}\hbar}{2m_{ki}c}\,r_{ki}'^{n-1}\{(\partial_{0\mathrm{P}}r'_{ki})\wedge\sigma_{ki}\}=\hat{\mu}_{k,\mathrm{spin}}^{(n)},$$
$$\nu_{k,\mathrm{orb}}^{(n)}\equiv\frac{n}{(n+1)!}\sum_{i}e_{ki}\,r_{ki}'^{n-1}r'_{ki}\wedge(\partial_{0\mathrm{P}}r'_{ki})=\hat{\nu}_{k,\mathrm{orb}}^{(n)},$$
$$\nu_{k,\mathrm{spin}}^{(n)}\equiv\frac{1}{(n-1)!}\sum_{i}{}'\frac{e_{ki}\hbar}{2m_{ki}c}\,r_{ki}'^{n-1}\sigma_{ki}=\hat{\nu}_{k,\mathrm{spin}}^{(n)}. \tag{65}$$

Since all terms of order c^{-3} are to be neglected, in fact only the orbital electric multipole moments $\hat{\mu}_{k,\mathrm{orb}}^{(n)}$ and $\mu_{k,\mathrm{orb}}^{(n)}$ are different.

The expressions (63) show a complete symmetry between the electric and magnetic multipole moments, just as the corresponding classical expressions (IV.57) and (IV.58). In particular one finds now a contribution to the electric polarization, due to magnetic multipole moments in motion. The multipole moments that occur here contain contributions due to the occurrence of spin:

the definitions (65) show how multipole moments for spin particles have to be defined such that they add to the orbital multipole moments that occur already in non-relativistic theory (v. (VI.87)).

6 *The laws of motion for composite particles*

a. *The equation of motion*

The equation of motion for a composite particle in a field will be obtained from the equation (48) for its constituent particles, which may carry spin. From the derivation given in (38–48) it follows by inspection that the left-hand side of (48) has as Weyl transform $m_i \partial_{tP}^2 \boldsymbol{X}_i + (e_i \hbar^2/8m_i^2 c^2)\Delta_i e_t(\boldsymbol{X}_i, t)$ so that (replacing i by ki) one may write (48) in the form:

$$\begin{aligned}\partial_{tP}[m_{ki}\{1+\tfrac{1}{2}c^{-2}(\partial_{tP}\boldsymbol{X}_{ki})^2\}\partial_{tP}\boldsymbol{X}_{ki}] &\\ = e_{ki}\boldsymbol{e}_t(\boldsymbol{X}_{ki}, t) + c^{-1}e_{ki}(\partial_{tP}\boldsymbol{X}_{ki}) \wedge \boldsymbol{b}_t(\boldsymbol{X}_{ki}, t) &\\ + \frac{e_{ki}\hbar}{2m_{ki}c}[\{\nabla_{ki}\boldsymbol{b}_t(\boldsymbol{X}_{ki}, t)\}\cdot\boldsymbol{\sigma}_{ki} + c^{-1}\{\nabla_{ki}\boldsymbol{e}_t(\boldsymbol{X}_{ki}, t)\}\cdot\{(\partial_{tP}\boldsymbol{X}_{ki})\wedge\boldsymbol{\sigma}_{ki}\}] &\\ + \frac{e_{ki}\hbar^2}{8m_{ki}^2c^2}\Delta_{ki}\boldsymbol{e}_t(\boldsymbol{X}_{ki}, t),\end{aligned} \quad (66)$$

where the fact has been used that in the right-hand side of (48) $\boldsymbol{P}_{ki}/m_{ki}$ could be replaced by $\partial_{tP}\boldsymbol{X}_{ki}$ (up to terms of order c^{-2} and bilinear in the charges). The fields which occur here are given by the expressions (45) with (46). The equation (66) is valid for the electrons. For the nuclei an equation like (66) but without spin terms and without the last term follows immediately from (48).

The equation (66) bears a close resemblance to the classical equation (IV.A87), the difference being that extra spin terms occur here and that all quantities are Weyl transforms of operators. Just as in chapter IV we want to define a central point that characterizes the composite particle as a whole. To that end we introduce now an operator $\boldsymbol{X}_{k,\mathrm{op}}$ with Weyl transform $\boldsymbol{X}_k$ in such a way that the Weyl transform of the relative position $\boldsymbol{r}_{ki} = \boldsymbol{X}_{ki} - \boldsymbol{X}_k$ satisfies the equation (cf. (IV.A101)):

$$\sum_i \left\{ m_{ki}\boldsymbol{r}_{ki} + \tfrac{1}{2}c^{-2}m_{ki}(\partial_{tP}\boldsymbol{r}_{ki})^2\boldsymbol{r}_{ki} + c^{-2}\sum_{j(\neq i)} \frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{X}_{ki}-\boldsymbol{X}_{kj}|}\boldsymbol{r}_{ki} + c^{-2}m_{ki}(\partial_{tP}\boldsymbol{X}_k)\cdot\boldsymbol{r}_{ki}(\partial_{tP}\boldsymbol{r}_{ki}) \right\} = 0. \quad (67)$$

(The order of the matrices occurring here does not matter, since only terms up to order c^{-2} are to be retained.) The factor $|\boldsymbol{X}_{ki}-\boldsymbol{X}_{kj}|^{-1}$ is defined in a

similar way as in (47). From (67) follows the expression for the central point $\boldsymbol{X}_k$ in terms of $\boldsymbol{X}_{ki}$ (38–39)

$$\boldsymbol{X}_k = \frac{1}{m_k}\sum_i m_{ki}\boldsymbol{X}_{ki} + \frac{1}{m_k c^2}\sum_i \left\{ \tfrac{1}{2}m_{ki}(\partial_{tP}\boldsymbol{r}_{ki})^2\boldsymbol{r}_{ki} + \sum_{j(\neq i)}\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}_{ki}-\boldsymbol{r}_{kj}|}\boldsymbol{r}_{ki} + m_{ki}(\partial_{tP}\boldsymbol{X}_k)\cdot\boldsymbol{r}_{ki}(\partial_{tP}\boldsymbol{r}_{ki}) \right\}. \quad (68)$$

At the right-hand side the relative positions $\boldsymbol{r}_{ki}$ are to be understood as $\boldsymbol{X}_{ki} - m_k^{-1}\sum_i m_{ki}\boldsymbol{X}_{ki}$ (or $\boldsymbol{R}_{ki} - m_k^{-1}\sum_i m_{ki}\boldsymbol{R}_{ki}$), since only terms up to order c^{-2} are to be included.

From (66) one may derive an equation for the atoms as a whole by taking a sum over the electrons and nuclei. If one introduces now quantities $\boldsymbol{r}'_{ki}$, defined in (61) (with $\boldsymbol{X}_k$ instead of $\boldsymbol{R}_k$), one finds as the left-hand side of the equation of motion the Poisson bracket derivation ∂_{tP} of a quantity that has the same form as (IV.A109). The right-hand side of the equation of motion may be split again into three parts: an intra-atomic, an external and an interatomic field contribution. The Weyl transforms of the fields are given by (45) with (46) instead of (IV.A111). In the former spin terms and a derivative of a delta function occur for the electron contributions, which are absent in the latter. Another difference is that the latter contains terms with accelerations, which are missing in the former, because they are effectively quadratic in the charges. As a consequence the intra-atomic contributions to the right-hand side of the equation of motion are the sum of terms that are the counterparts of those of (IV.A112) and an extra spin contribution $-\partial_{tP}\boldsymbol{g}_k$ with $\boldsymbol{g}_k$ given by

$$\boldsymbol{g}_k \equiv \sum_{i,j(i\neq j)}{}' \frac{e_{ki}e_{kj}\hbar}{2m_{ki}c^2}\boldsymbol{\sigma}_{ki}\wedge\nabla_{ki}\frac{1}{4\pi|\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj}|}. \quad (69)$$

For the Weyl transform of the equation of motion for the composite particle as a whole we obtain thus on a par with (IV.A113):

$$\begin{aligned}\partial_{tP}\left[\left\{m_k + \tfrac{1}{2}c^{-2}m_k\boldsymbol{v}_k^2 + \tfrac{1}{2}c^{-2}\sum_i m_{ki}(\partial_{tP}\boldsymbol{r}_{ki})^2 + c^{-2}\sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj}|}\right\}\boldsymbol{v}_k + \boldsymbol{g}_k\right] &\\ = \sum_i e_{ki}\{\boldsymbol{e}(\boldsymbol{X}_{ki}, t) + c^{-1}(\partial_{tP}\boldsymbol{X}_{ki})\wedge\boldsymbol{b}(\boldsymbol{X}_{ki}, t)\} &\\ + c^{-2}\partial_{tP}\left[\sum_i e_{ki}\left\{(\partial_{tP}\boldsymbol{r}_{ki})\cdot\boldsymbol{e}(\boldsymbol{X}_{ki}, t)\boldsymbol{r}_{ki} + (\partial_{tP}\boldsymbol{X}_k)\cdot\boldsymbol{r}_{ki}\,\boldsymbol{e}(\boldsymbol{X}_{ki}, t) + \frac{\bar{\boldsymbol{s}}_k}{m_k}\wedge\boldsymbol{e}(\boldsymbol{X}_{ki}, t)\right\}\right] + \sum_i{}' \frac{e_{ki}\hbar}{2m_{ki}c}\Big[\{\nabla_{ki}\boldsymbol{b}(\boldsymbol{X}_{ki}, t)\}\cdot\boldsymbol{\sigma}_{ki} &\\ + c^{-1}\{\nabla_{ki}\boldsymbol{e}(\boldsymbol{X}_{ki}, t)\}\cdot\{(\partial_{tP}\boldsymbol{X}_{ki})\wedge\boldsymbol{\sigma}_{ki}\} + \frac{\hbar}{4m_{ki}c}\Delta_{ki}\boldsymbol{e}(\boldsymbol{X}_{ki}, t)\Big],\end{aligned} \quad (70)$$

with $\boldsymbol{v}_k \equiv \partial_{tP} \boldsymbol{X}_k$ the Weyl transform of the velocity and $\bar{\boldsymbol{s}}_k \equiv \sum_i m_{ki} \boldsymbol{r}_{ki} \wedge \partial_{tP} \boldsymbol{r}_{ki}$ the (non-relativistic) orbital inner angular momentum. The quantities $\boldsymbol{e}$ and $\boldsymbol{b}$ are the Weyl transforms of the interatomic and external fields.

If the external fields change slowly one may make a multipole expansion of the external field terms at the right-hand side of (70) and retain only the charge and dipole terms. Then one finds, in semi-relativistic approximation, with the definitions (64) and (65) for the semi-relativistic multipole moments defined with respect to $\boldsymbol{X}_k$, for the external field contribution $\boldsymbol{f}_{ke}^{\mathrm{L}}$ of the right-hand side of (70) (cf. (IV.A118)):

$$\begin{aligned} \boldsymbol{f}_{ke}^{\mathrm{L}} = {} & e_k\{\boldsymbol{E}_e(\boldsymbol{X}_k, t) + c^{-1}\boldsymbol{v}_k \wedge \boldsymbol{B}_e(\boldsymbol{X}_k, t)\} \\ & + \{\nabla_k \boldsymbol{E}_e(\boldsymbol{X}_k, t)\}\cdot(\boldsymbol{\mu}_k^{(1)} - c^{-1}\boldsymbol{\nu}_k^{(1)} \wedge \boldsymbol{v}_k) + \{\nabla_k \boldsymbol{B}_e(\boldsymbol{X}_k, t)\}\cdot(\boldsymbol{\nu}_k^{(1)} + c^{-1}\boldsymbol{\mu}_k^{(1)} \wedge \boldsymbol{v}_k) \\ & + c^{-1}\partial_{tP}\{\boldsymbol{\mu}_k^{(1)} \wedge \boldsymbol{B}_e(\boldsymbol{X}_k, t) - \boldsymbol{\nu}_{k,\mathrm{orb}}^{(1)} \wedge \boldsymbol{E}_e(\boldsymbol{X}_k, t)\}, \end{aligned} \tag{71}$$

where the Maxwell equation $\nabla \wedge \boldsymbol{E}_e = -\partial_0 \boldsymbol{B}_e$ for the external fields has been employed. If a single composite particle moves in an external field the semi-relativistic (Weyl-transformed) equation of motion becomes thus:

$$\partial_{tP}(m_k \boldsymbol{v}_k + \boldsymbol{g}_k) = \boldsymbol{f}_{ke}^{\mathrm{L}}, \tag{72}$$

where at the left-hand side only those c^{-2}-terms that contain spin vectors have been retained. As compared to the non-relativistic equation (VI.98–100) one finds here, apart from an extra term $\boldsymbol{g}_k$ at the left-hand side due to the presence of spin, a term that couples the magnetic dipoles in motion with the gradient of the electric field at the right-hand side and moreover a term with the vector product of the orbital magnetic moment and the electric field. The latter is the magnetodynamic effect, from which the spin part is absent here, since the electrons are supposed to carry only normal magnetic moments (v. (VIII.158)). Furthermore both the electric and magnetic dipole moments contain spin contributions. The fields $\boldsymbol{E}_e$ and $\boldsymbol{B}_e$ are taken at the centre $\boldsymbol{X}_k$ of the composite particle.

For a set of composite particles which move in each other's fields, there also exist interatomic contributions to the right-hand side of (70). If the atoms are outside each other one may make a multipole expansion both for the sources of the interatomic fields and for the particles on which the fields act. One finds then in the semi-relativistic approximation a double multipole expansion in terms of electric–electric, magnetic–magnetic and electric–magnetic multipole moments. Only the former two terms are written down here for brevity's sake:

$$\begin{aligned} \boldsymbol{f}_k^{\mathrm{L}} - \boldsymbol{f}_{ke}^{\mathrm{L}} = {} & -\sum_{l(\neq k)} \nabla_k \sum_{n,m=0}^{\infty} \nabla_k^n \vdots \boldsymbol{\mu}_k^{(n)} \nabla_l^m \vdots \boldsymbol{\mu}_l^{(m)} \frac{1}{4\pi|\boldsymbol{X}_k - \boldsymbol{X}_l|} \\ & + \sum_{l(\neq k)} \nabla_k \sum_{n,m=1}^{\infty} (\nabla_k^{n-1} \vdots \boldsymbol{\nu}_k^{(n)} \wedge \nabla_k)\cdot(\nabla_l^{m-1} \vdots \boldsymbol{\nu}_l^{(m)} \wedge \nabla_l) \frac{1}{4\pi|\boldsymbol{X}_k - \boldsymbol{X}_l|}. \end{aligned} \tag{73}$$

In the general case that the atoms are at arbitrary distances of each other one may write the sum of the forces due to the external and interatomic fields as the sum of a long range and a short range part. The long range part $\boldsymbol{f}_k^{\mathrm{L}}$ is given by the sum of (71) and (73). The short range part $\boldsymbol{f}_k^{\mathrm{S}}$ equals the difference of the unexpanded interatomic field contribution and the expanded one (73). We write down only those terms of $\boldsymbol{f}_k^{\mathrm{S}}$ that are the unexpanded counterparts of $\boldsymbol{f}_k^{\mathrm{L}} - \boldsymbol{f}_{ke}^{\mathrm{L}}$. They read

$$\begin{aligned} \boldsymbol{f}_k^{\mathrm{S}} = {} & -\sum_{l(\neq k)} \sum_{i,j} \Big[1 - c^{-2}(\partial_{tP}\boldsymbol{r}_{ki})\cdot(\partial_{tP}\boldsymbol{r}_{lj}) \\ & + c^{-2}\{\partial_{tP}(\boldsymbol{r}_{ki} - \boldsymbol{r}_{lj})\}\cdot\left\{\left(\frac{\hbar}{2m_{ki}}\boldsymbol{\sigma}_{ki} + \frac{\hbar}{2m_{lj}}\boldsymbol{\sigma}_{lj}\right) \wedge \nabla_{ki}\right\} \\ & + c^{-2}\frac{\hbar^2}{4m_{ki}m_{lj}}(\boldsymbol{\sigma}_{ki} \wedge \nabla_{ki})\cdot(\boldsymbol{\sigma}_{lj} \wedge \nabla_{ki})\Big] \nabla_{ki} \frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{X}_{ki} - \boldsymbol{X}_{lj}|} - (\boldsymbol{f}_k^{\mathrm{L}} - \boldsymbol{f}_{ke}^{\mathrm{L}}). \end{aligned} \tag{74}$$

The terms with spin only apply for the electrons, not for the nuclei. The total equation of motion in semi-relativistic approximation becomes

$$\partial_{tP}(m_k \boldsymbol{v}_k + \boldsymbol{g}_k) = \boldsymbol{f}_k^{\mathrm{L}} + \boldsymbol{f}_k^{\mathrm{S}} \tag{75}$$

with both long range and short range forces at the right-hand side.

b. *The energy equation*

The energy equation for a composite particle is obtained by multiplying equation (66) by $\partial_{tP}\boldsymbol{X}_{ki}$ and summing over i. Then one finds, by introducing the relative positions $\boldsymbol{r}_{ki}$ and using (67), for the left-hand side an expression which is the analogue (in fact a Weyl transform) of (IV.A121). If one defines subsequently, just as in (IV.A122), a quantity $\dot{\boldsymbol{r}}'_{ki}$ by means of the definition

$$\begin{aligned} \dot{\boldsymbol{r}}'_{ki} \equiv {} & \partial_{tP}\boldsymbol{r}_{ki} + \tfrac{1}{2}c^{-2}\boldsymbol{v}_k^2 \partial_{tP}\boldsymbol{r}_{ki} + \tfrac{1}{2}c^{-2}\boldsymbol{v}_k\cdot(\partial_{tP}\boldsymbol{r}_{ki})\boldsymbol{v}_k \\ & + c^{-2}\boldsymbol{v}_k\cdot(\partial_{tP}\boldsymbol{r}_{ki})\partial_{tP}\boldsymbol{r}_{ki} + \frac{e_{ki}}{m_{ki}c^2}\boldsymbol{v}_k\cdot\boldsymbol{r}_{ki}\boldsymbol{e}_t(\boldsymbol{X}_{ki}, t), \end{aligned} \tag{76}$$

one finds for the left-hand side of the energy equation the Poisson bracket ∂_{tP} of a quantity that has the form (IV.A124). At the right-hand side of the energy equation appears the sum of an intra-atomic, an interatomic and an external field contribution. For the first of these one gets, by making use of the field expressions (46), a result that is the sum of an expression like (IV.A125) and extra terms depending on spins and on the delta function

$\delta(\boldsymbol{r}_{ki}-\boldsymbol{r}_{kj})$, namely (up to terms bilinear in the charges):

$$-\partial_{tP}\left[u_k+\boldsymbol{v}_k\cdot\boldsymbol{g}_k-\sum_{i,j(i\neq j)}\left\{\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj}|}+\frac{e_{ki}e_{kj}\hbar^2}{8m_{ki}^2c^2}\delta(\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj})\right\}\right] \tag{77}$$

(in the last term the summation over i is confined to the electrons), where we employed the abbreviation u_k given by

$$u_k \equiv \sum_{i,j(i\neq j)}\left\{1+\frac{\hbar}{m_{ki}c^2}\dot{\boldsymbol{r}}'_{ki}\cdot(\boldsymbol{\sigma}_{ki}\wedge\nabla_{ki}) + \frac{\hbar^2}{4m_{ki}m_{kj}c^2}(\boldsymbol{\sigma}_{ki}\wedge\nabla_{ki})\cdot(\boldsymbol{\sigma}_{kj}\wedge\nabla_{ki})\right\}\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj}|} \tag{78}$$

(in the second term the summation over i is confined to the electrons; the same applies to both i and j in the third term) and $\boldsymbol{g}_k$ given in (69). (In (78) we included the Coulomb energy although it drops out in (77); this will turn out to be convenient in the following.) As the energy law, up to order c^{-2}, we find now an equation which is the counterpart of (IV.A126), namely

$$\begin{aligned}
&\partial_{tP}\Bigg[\tfrac{1}{2}m_k\boldsymbol{v}_k^2+\tfrac{3}{8}c^{-2}m_k\boldsymbol{v}_k^4+\sum_i\left(\tfrac{1}{2}m_{ki}\dot{\boldsymbol{r}}'^2_{ki}+\tfrac{1}{4}c^{-2}m_{ki}\dot{\boldsymbol{r}}'^2_{ki}\boldsymbol{v}_k^2+\tfrac{3}{8}c^{-2}m_{ki}\dot{\boldsymbol{r}}'^4_{ki}\right)\\
&\quad+\tfrac{1}{2}c^{-2}\sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj}|}\{\dot{\boldsymbol{r}}'_{ki}\cdot\mathsf{T}(\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj})\cdot\dot{\boldsymbol{r}}'_{kj}+\boldsymbol{v}_k^2\}\\
&\quad-c^{-2}\sum_{i,j(i\neq j)}{}'\frac{e_{ki}e_{kj}\hbar^2}{8m_{ki}^2}\delta(\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj})+u_k+\boldsymbol{v}_k\cdot\boldsymbol{g}_k\Bigg]\\
&=\sum_{k,i}e_{ki}(\partial_{tP}\boldsymbol{X}_{ki})\cdot\boldsymbol{e}(\boldsymbol{X}_{ki},t)+\sum_{k,i}{}'(\partial_{tP}\boldsymbol{X}_{ki})\cdot\Bigg[\frac{e_{ki}\hbar}{2m_{ki}c}\{\nabla_{ki}\boldsymbol{b}(\boldsymbol{X}_{ki},t)\}\cdot\boldsymbol{\sigma}_{ki}\\
&\quad+\frac{e_{ki}\hbar}{2m_{ki}c^2}\{\nabla_{ki}\boldsymbol{e}(\boldsymbol{X}_{ki},t)\}\cdot\{(\partial_{tP}\boldsymbol{X}_{ki})\wedge\boldsymbol{\sigma}_{ki}\}+\frac{e_{ki}\hbar^2}{8m_{ki}^2c^2}\Delta_{ki}\boldsymbol{e}(\boldsymbol{X}_{ki},t)\Bigg]\\
&\quad+c^{-2}\partial_{tP}\Bigg[\sum_i e_{ki}\Bigg\{\frac{\bar{\boldsymbol{s}}_k}{m_k}\wedge\boldsymbol{e}(\boldsymbol{X}_{ki},t)\\
&\qquad+2(\partial_{tP}\boldsymbol{r}_{ki})\cdot\boldsymbol{e}(\boldsymbol{X}_{ki},t)\boldsymbol{r}_{ki}+\boldsymbol{v}_k\cdot\boldsymbol{r}_{ki}\boldsymbol{e}(\boldsymbol{X}_{ki},t)\Bigg\}\cdot\boldsymbol{v}_k\Bigg],
\end{aligned} \tag{79}$$

where the tensor T has been defined in (5) and where $\boldsymbol{e}$ and $\boldsymbol{b}$ are the sums of the external fields and the interatomic fields due to the other atoms.

If the external fields change slowly a multipole expansion of the corresponding terms at the right-hand side of (79) may be performed. The

dipole terms read in the semi-relativistic approximation

$$\begin{aligned}
\psi^{\mathrm{L}}_{k\mathrm{e}} =\ & e_k\boldsymbol{v}_k\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{X}_k,t)+\boldsymbol{v}_k\cdot\{\nabla_k\boldsymbol{E}_\mathrm{e}(\boldsymbol{X}_k,t)\}\cdot(\boldsymbol{\mu}_k^{(1)}-c^{-1}\boldsymbol{v}_k^{(1)}\wedge\boldsymbol{v}_k)\\
&+\partial_{tP}(\boldsymbol{\mu}_k^{(1)}-c^{-1}\boldsymbol{v}_k^{(1)}\wedge\boldsymbol{v}_k)\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{X}_k,t)-(\boldsymbol{v}_k^{(1)}+c^{-1}\boldsymbol{\mu}_k^{(1)}\wedge\boldsymbol{v}_k)\cdot\frac{\partial\boldsymbol{B}_\mathrm{e}(\boldsymbol{X}_k,t)}{\partial t}\\
&+\partial_{tP}\{\boldsymbol{v}^{(1)}_{k,\mathrm{spin}}\cdot\boldsymbol{B}_\mathrm{e}(\boldsymbol{X}_k,t)\}+2c^{-1}\partial_{tP}\{(\boldsymbol{v}^{(1)}_{k,\mathrm{orb}}\wedge\boldsymbol{v}_k)\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{X}_k,t)\},
\end{aligned} \tag{80}$$

where we employed the Maxwell equation $\nabla\wedge\boldsymbol{E}_\mathrm{e}=-\partial_0\boldsymbol{B}_\mathrm{e}$ for the external fields. Only the terms that are linear in the charges are to be retained here. (For convenience terms with $\partial_{tP}(\boldsymbol{v}_k^{(1)}\wedge\boldsymbol{v}_k)$ have been added, although strictly spoken they are negligible in the present approximation.) For the semi-relativistic (Weyl-transformed) energy equation of a single composite particle in a slowly varying external field we found thus

$$\partial_{tP}(\tfrac{1}{2}m_k\boldsymbol{v}_k^2+\boldsymbol{v}_k\cdot\boldsymbol{g}_k+t_k+u_k)=\psi^{\mathrm{L}}_{k\mathrm{e}} \tag{81}$$

with the internal kinetic energy

$$t_k=\tfrac{1}{2}\sum_i m_{ki}\dot{\boldsymbol{r}}'^2_{ki}. \tag{82}$$

At the right-hand side of (81) an expression appears which is equal to (80). From the latter form one finds by comparison with the non-relativistic result (VI.105–106) which additional terms arise in the semi-relativistic theory: in the first place terms due to moving magnetic dipole moments and moreover terms with the spin parts of the electric and magnetic dipoles. Furthermore the fields are taken at the centre $\boldsymbol{X}_k$ instead of $\boldsymbol{R}_k$.

As compared to the semi-relativistic classical result (IV.A127) the present result contains as extra terms with the spin:

$$\boldsymbol{v}_k\cdot(\nabla_k\boldsymbol{E}_\mathrm{e})\cdot(\boldsymbol{\mu}^{(1)}_{k,\mathrm{spin}}-c^{-1}\boldsymbol{v}^{(1)}_{k,\mathrm{spin}}\wedge\boldsymbol{v}_k)+\boldsymbol{v}_k\cdot(\nabla_k\boldsymbol{B}_\mathrm{e})\cdot\boldsymbol{v}^{(1)}_{k,\mathrm{spin}}. \tag{83}$$

(In the semi-relativistic limit the term that couples the spin electric dipole moment in motion with the magnetic field does not contribute, and neither does the Poisson bracket derivative of the spin electric or magnetic dipole moment.) The form of these terms is consistent with the results of chapter VIII: v. problem 6 of that chapter.

If particles forming a set move in each other's fields the energy equation for these particles contains also an interatomic field contribution that may be developed in a double multipole series if the atoms are sufficiently far apart. We write, for brevity's sake, only the terms which couple the electric multipoles with each other and the magnetic ones with each other. They follow by using the expressions (45) and (46) for the Weyl transforms of the fields:

$$\psi_k^{\mathrm{L}}-\psi_{k\mathrm{c}}^{\mathrm{L}} = -\sum_{l(\neq k)}\sum_{n,m=0}^{\infty}\{\boldsymbol{v}_k\cdot\nabla_k\,\boldsymbol{\mu}_k^{(n)} \vdots \nabla_k^n\,\boldsymbol{\mu}_l^{(m)} \vdots \nabla_l^m$$

$$+(\partial_{t\mathrm{P}}\,\boldsymbol{\mu}_k^{(n)}) \vdots \nabla_k^n\,\boldsymbol{\mu}_l^{(m)} \vdots \nabla_l^m\}\frac{1}{4\pi|\boldsymbol{X}_k-\boldsymbol{X}_l|}$$

$$-\sum_{l(\neq k)}\sum_{n,m=1}^{\infty}[(\nabla_k^{n-1} \vdots \boldsymbol{\nu}_k^{(n)}\wedge\nabla_k)\cdot\{\nabla_l^{m-1} \vdots (\partial_{t\mathrm{P}}\,\boldsymbol{\nu}_l^{(m)})\wedge\nabla_l\}$$

$$+\boldsymbol{v}_l\cdot\nabla_l(\nabla_k^{n-1} \vdots \boldsymbol{\nu}_k^{(n)}\wedge\nabla_k)\cdot(\nabla_l^{m-1} \vdots \boldsymbol{\nu}_l^{(m)}\wedge\nabla_l)$$

$$-(\boldsymbol{v}_k-\boldsymbol{v}_l)\cdot\nabla_k(\nabla_k^{n-1} \vdots \boldsymbol{\nu}_{k,\mathrm{spin}}^{(n)}\wedge\nabla_k)\cdot(\nabla_l^{m-1} \vdots \boldsymbol{\nu}_l^{(m)}\wedge\nabla_l)$$

$$-\{\nabla_k^{n-1} \vdots (\partial_{t\mathrm{P}}\,\boldsymbol{\nu}_{k,\mathrm{spin}}^{(n)}\wedge\nabla_k)\}\cdot(\nabla_l^{m-1} \vdots \boldsymbol{\nu}_l^{(m)}\wedge\nabla_l)$$

$$-(\nabla_k^{n-1} \vdots \boldsymbol{\nu}_{k,\mathrm{spin}}^{(n)}\wedge\nabla_k)\cdot\{\nabla_l^{m-1} \vdots (\partial_{t\mathrm{P}}\,\boldsymbol{\nu}_l^{(m)})\wedge\nabla_l\}]\frac{1}{4\pi|\boldsymbol{X}_k-\boldsymbol{X}_l|}. \qquad (84)$$

In the general case of arbitrary separations between the atoms, the inter-atomic contribution to the energy law may be written as a sum of a long range part which is given by (80) with (84) and a short range part ψ_k^{S}. The latter is equal to the difference of the unexpanded and expanded interatomic field contributions. Again we write only those terms that give upon expansion the long range terms (84). One finds for these terms:

$$\psi_k^{\mathrm{S}} = \sum_{l(\neq k)}\sum_{i,j}\Bigg\{-(\boldsymbol{v}_k+\partial_{t\mathrm{P}}\,\boldsymbol{r}_{ki})\cdot\nabla_{ki}-c^{-2}(\partial_{t\mathrm{P}}\,\boldsymbol{r}_{ki})\cdot(\partial_{t\mathrm{P}}\,\boldsymbol{r}_{lj})(\boldsymbol{v}_l+\partial_{t\mathrm{P}}\,\boldsymbol{r}_{lj})\cdot\nabla_{lj}$$

$$-\frac{\hbar}{2m_{lj}c^2}(\boldsymbol{v}_l+\partial_{t\mathrm{P}}\,\boldsymbol{r}_{lj})\cdot\nabla_{ki}(\partial_{t\mathrm{P}}\,\boldsymbol{r}_{ki})\cdot(\boldsymbol{\sigma}_{lj}\wedge\nabla_{ki})$$

$$+\frac{\hbar}{2m_{lj}c^2}(\boldsymbol{v}_k+\partial_{t\mathrm{P}}\,\boldsymbol{r}_{ki})\cdot\nabla_{ki}(\partial_{t\mathrm{P}}\,\boldsymbol{r}_{lj})\cdot(\boldsymbol{\sigma}_{lj}\wedge\nabla_{ki})$$

$$-\frac{\hbar}{2m_{ki}c^2}(\boldsymbol{v}_k+\partial_{t\mathrm{P}}\,\boldsymbol{r}_{ki})\cdot\nabla_{ki}\,\partial_{t\mathrm{P}}(\boldsymbol{r}_{ki}-\boldsymbol{r}_{lj})\cdot(\boldsymbol{\sigma}_{ki}\wedge\nabla_{ki})$$

$$-\frac{\hbar^2}{4m_{ki}m_{lj}c^2}(\boldsymbol{v}_k+\partial_{t\mathrm{P}}\,\boldsymbol{r}_{ki})\cdot\nabla_{ki}(\boldsymbol{\sigma}_{ki}\wedge\nabla_{ki})\cdot(\boldsymbol{\sigma}_{lj}\wedge\nabla_{ki})\Bigg\}$$

$$\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj}|}-(\psi_k^{\mathrm{L}}-\psi_{k\mathrm{c}}^{\mathrm{L}}). \qquad (85)$$

(Again sums of terms in which spins occur are extended only over the electrons.)

The energy equation for an atom that is part of a set of atoms has been found now as:

$$\partial_{t\mathrm{P}}(\tfrac{1}{2}m_k\,v_k^2+\boldsymbol{v}_k\cdot\boldsymbol{g}_k+t_k+u_k) = \psi_k^{\mathrm{L}}+\psi_k^{\mathrm{S}} \qquad (86)$$

with long range and short range power terms at the right-hand side.

c. *The angular momentum equation*

The angular momentum equation for a stable group of spin particles may be derived along similar lines. One finds then an expression for the sum of 1st: the Poisson bracket of the Weyl transform of the orbital angular momentum

$$\boldsymbol{s}_k^{(1)} = \sum_i m_{ki}\,\boldsymbol{r}'_{ki}\wedge\dot{\boldsymbol{r}}'_{ki} \qquad (87)$$

(v. (61) and (76) for the expressions $\boldsymbol{r}'_{ki}$ and $\dot{\boldsymbol{r}}'_{ki}$) with the Weyl transform H of the Hamiltonian, 2nd: a commutator of the spin angular momentum

$$\boldsymbol{s}_k^{(2)} = \sum_i{}'\,\tfrac{1}{2}\hbar\boldsymbol{\sigma}_{ki} \qquad (88)$$

of the particles with H, 3rd: the Poisson bracket with H of a term

$$\boldsymbol{s}_k^{(3)} = \sum_i{}'\,\tfrac{1}{2}\hbar(\boldsymbol{P}_{ki}\wedge\boldsymbol{\sigma}_{ki})\wedge\boldsymbol{P}_{ki}/2m_{ki}^2c^2, \qquad (89)$$

due to the fact that the spins are in motion (v. (53)), and 4th: the Poisson bracket of an intra-atomic field contribution

$$\boldsymbol{s}_k^{(4)} = -\sum_{i,j(i\neq j)}\frac{\hbar}{2m_{kj}c^2}\,\boldsymbol{r}'_{ki}\wedge(\boldsymbol{\sigma}_{kj}\wedge\nabla_{ki})\frac{e_{ki}e_{kj}}{4\pi|\boldsymbol{r}'_{ki}-\boldsymbol{r}'_{kj}|}. \qquad (90)$$

One finds for the special case of a single composite particle in a slowly changing external field $(\boldsymbol{E}_{\mathrm{e}},\boldsymbol{B}_{\mathrm{e}})$:

$$\partial_{t\mathrm{P}}(\boldsymbol{s}_k^{(1)}+\boldsymbol{s}_k^{(3)}+\boldsymbol{s}_k^{(4)})+\frac{i}{\hbar}[H,\boldsymbol{s}_k^{(2)}]$$

$$= \boldsymbol{\mu}_k^{(1)}\wedge(\boldsymbol{E}_{\mathrm{e}}+c^{-1}\boldsymbol{v}_k\wedge\boldsymbol{B}_{\mathrm{e}})+\boldsymbol{\nu}_k^{(1)}\wedge(\boldsymbol{B}_{\mathrm{e}}-c^{-1}\boldsymbol{v}_k\wedge\boldsymbol{E}_{\mathrm{e}})+c^{-1}\boldsymbol{v}_k\wedge(\boldsymbol{\nu}_{k,\mathrm{spin}}^{(1)}\wedge\boldsymbol{E}_{\mathrm{e}})$$

$$-\boldsymbol{v}_k\wedge\boldsymbol{g}_k \qquad (91)$$

(with $\boldsymbol{v}_k \equiv \partial_{t\mathrm{P}}\boldsymbol{X}_k$ and $\boldsymbol{g}_k$ given by (69)) up to dipole terms. As compared to the non-relativistic quantum result (VI.111–112) one finds two extra terms that couple magnetic dipole moments with the external electric field and a term with the spin momentum $\boldsymbol{g}_k$. The fields are taken at the position of the central point $\boldsymbol{X}_k$ with respect to which also the semi-relativistic dipole moments are defined (v. (65)).

Comparison with the classical semi-relativistic equation (IV.A136) shows which spin terms are to be added in the present case. In the first place one has at the left-hand side the spin contributions (88–90) to the inner angular momentum of the composite particle. At the right-hand side four spin terms are added, namely a term $-\boldsymbol{v}_k \wedge \boldsymbol{g}_k$ with the spin momentum $\boldsymbol{g}_k$ (69), and three terms

$$\boldsymbol{\mu}^{(1)}_{k,\mathrm{spin}} \wedge \boldsymbol{E}_{\mathrm{e}} + \boldsymbol{v}^{(1)}_{k,\mathrm{spin}} \wedge \boldsymbol{B}_{\mathrm{e}} + c^{-1}(\boldsymbol{v}_k \wedge \boldsymbol{v}^{(1)}_{k,\mathrm{spin}}) \wedge \boldsymbol{E}_{\mathrm{e}} . \tag{92}$$

The form of the last two terms is the same as that of (54).

The extension to the case of a set of composite particles in each other's fields is straightforward and will not be given here.