CHAPTER I

Particles: their fields and motion

1 Introduction

The aim of this chapter is to obtain a description of the electromagnetic behaviour of composite particles in the framework of classical, non-relativistic theory. Such composite particles, like atoms, molecules or ions are supposed to consist of charged point particles: the electrons and nuclei. The equations which govern their motion and describe their fields will be derived from the corresponding basic equations valid for charged point particles without structure. The latter microscopic equations are the Maxwell–Lorentz field equations and the Newton equation with the Lorentz force inserted. A series expansion in terms of multipoles leads then to the field equations and the momentum, energy and angular momentum equations for the composite particles.

2 The microscopic field equations

The electric and magnetic fields $\boldsymbol{e}(\boldsymbol{R}, t)$ and $\boldsymbol{b}(\boldsymbol{R}, t)$ at the point with coordinates $\boldsymbol{R}$ and at time t, generated by a collection of point particles $i = 1, 2, \ldots$ with charges e_i, positions $\boldsymbol{R}_i(t)$ and velocities $\dot{\boldsymbol{R}}_i(t)$, satisfy the Maxwell–Lorentz field equations (in the rationalized Gauss system[1])

$$\begin{aligned} \nabla\cdot\boldsymbol{e} &= \sum_i e_i\,\delta(\boldsymbol{R}_i-\boldsymbol{R}),\\ -\partial_0\,\boldsymbol{e}+\nabla\wedge\boldsymbol{b} &= c^{-1}\sum_i e_i\,\dot{\boldsymbol{R}}_i\,\delta(\boldsymbol{R}_i-\boldsymbol{R}),\\ \nabla\cdot\boldsymbol{b} &= 0,\\ \partial_0\,\boldsymbol{b}+\nabla\wedge\boldsymbol{e} &= 0, \end{aligned} \qquad (1)$$

[1] In the Giorgi system different numerical coefficients appear: the factors c^{-1} (both explicitly and in ∂_0) are absent, while in the first two equations $\boldsymbol{e}$ and $\boldsymbol{b}$ are replaced by $\varepsilon_0\boldsymbol{e}$ and $\mu_0^{-1}\boldsymbol{b}$ respectively.

where ∇ and ∂_0 are differentiations with respect to $\boldsymbol{R}$ and ct (with c the speed of light) and the dot and the symbol $\wedge$ scalar and vector products of vectors. The sources contain the three-dimensional delta functions of $\boldsymbol{R}_i - \boldsymbol{R}$.

In non-relativistic theory one is interested in solutions of these equations up to order c^{-1}. To find them it is convenient to introduce potentials. From the third equation it follows that

$$\boldsymbol{b} = \nabla \wedge \boldsymbol{a} \tag{2}$$

with the vector potential $\boldsymbol{a}(\boldsymbol{R}, t)$. Then with the fourth equation one has

$$\boldsymbol{e} = -\nabla\varphi - \partial_0 \boldsymbol{a}, \tag{3}$$

where $\varphi(\boldsymbol{R}, t)$ is the scalar potential. Insertion of these expressions into the first two equations of (1) gives, if one omits terms in c^{-2},

$$\begin{aligned} \Delta\varphi + \partial_0 \nabla\cdot\boldsymbol{a} &= -\sum_i e_i \delta(\boldsymbol{R}_i - \boldsymbol{R}), \\ \Delta\boldsymbol{a} - \nabla(\nabla\cdot\boldsymbol{a} + \partial_0\varphi) &= -c^{-1}\sum_i e_i \dot{\boldsymbol{R}}_i \delta(\boldsymbol{R}_i - \boldsymbol{R}), \end{aligned} \tag{4}$$

where $\Delta = \nabla\cdot\nabla$ is the Laplace operator. The potentials are not fixed in a unique way by the relations (2) and (3). The same electromagnetic fields are described by potentials $\boldsymbol{a}'$ and φ' which are related to the original potentials $\boldsymbol{a}$ and φ by a gauge transformation

$$\begin{aligned} \varphi' &= \varphi - \partial_0 \psi, \\ \boldsymbol{a}' &= \boldsymbol{a} + \nabla\psi \end{aligned} \tag{5}$$

with an arbitrary function ψ. This property is utilized to choose the potentials in such a way that they satisfy

$$\partial_0 \varphi + \nabla\cdot\boldsymbol{a} = 0, \tag{6}$$

the Lorentz condition. The reason for imposing this condition is that then the equations (4) become two uncoupled Poisson equations for φ and $\boldsymbol{a}$:

$$\begin{aligned} \Delta\varphi &= -\sum_i e_i \delta(\boldsymbol{R}_i - \boldsymbol{R}), \\ \Delta\boldsymbol{a} &= -c^{-1}\sum_i e_i \dot{\boldsymbol{R}}_i \delta(\boldsymbol{R}_i - \boldsymbol{R}), \end{aligned} \tag{7}$$

where again a term of order c^{-2} has been dismissed. The solutions follow from the property for the delta function:

$$\Delta \frac{1}{|\boldsymbol{r}|} = -4\pi\delta(\boldsymbol{r}). \tag{8}$$

Using this property, one finds from (7) the non-relativistic potentials in the Lorentz gauge:

$$\begin{aligned} \varphi &= \sum_i \frac{e_i}{4\pi|\boldsymbol{R}_i - \boldsymbol{R}|}, \\ \boldsymbol{a} &= c^{-1}\sum_i \frac{e_i \dot{\boldsymbol{R}}_i}{4\pi|\boldsymbol{R}_i - \boldsymbol{R}|}, \end{aligned} \tag{9}$$

so that the non-relativistic fields (2) and (3) are

$$\begin{aligned} \boldsymbol{e} &= \sum_i \boldsymbol{e}_i, \qquad \boldsymbol{e}_i = -\nabla \frac{e_i}{4\pi|\boldsymbol{R}_i - \boldsymbol{R}|}, \\ \boldsymbol{b} &= \sum_i \boldsymbol{b}_i, \qquad \boldsymbol{b}_i = c^{-1}\nabla \wedge \frac{e_i \dot{\boldsymbol{R}}_i}{4\pi|\boldsymbol{R}_i - \boldsymbol{R}|}. \end{aligned} \tag{10}$$

These formulae show that the non-relativistic electric field is of order c^0 (a term in c^{-1} does not appear), while the non-relativistic magnetic field is of order c^{-1} (no term in c^0 arises). From the first line of (10) it follows that $\boldsymbol{e}$ is irrotational. This is in agreement with the fourth field equation in (1), since $\partial_0 \boldsymbol{b}$ is of order c^{-2} and hence has to be neglected in non-relativistic theory. So strictly spoken one should write in a non-relativistic theory the truncated equation $\nabla \wedge \boldsymbol{e} = 0$ instead of the fourth field equation.

3 *The equation of motion for a point particle*

The equation of motion for a particle with charge e, mass m, position $\boldsymbol{R}_1(t)$, velocity $\dot{\boldsymbol{R}}_1(t)$ and acceleration $\ddot{\boldsymbol{R}}_1(t)$ in an external electromagnetic field $(\boldsymbol{E}_e, \boldsymbol{B}_e)$ is:

$$m\ddot{\boldsymbol{R}}_1 = e\{\boldsymbol{E}_e(\boldsymbol{R}_1, t) + c^{-1}\dot{\boldsymbol{R}}_1 \wedge \boldsymbol{B}_e(\boldsymbol{R}_1, t)\}, \tag{11}$$

where at the right-hand side the Lorentz force appears. The equation of motion of one particle of a set labelled by the index $i = 1, 2, ..., N$ reads

$$m_i \ddot{\boldsymbol{R}}_i = e_i\{\boldsymbol{e}_t(\boldsymbol{R}_i, t) + c^{-1}\dot{\boldsymbol{R}}_i \wedge \boldsymbol{b}_t(\boldsymbol{R}_i, t)\}, \tag{12}$$

where the total electric and magnetic fields are the sums of the external fields and the fields (10) generated by the other particles:

$$\begin{aligned} \boldsymbol{e}_t(\boldsymbol{R}_i, t) &= \sum_{j(\neq i)} \boldsymbol{e}_j(\boldsymbol{R}_i, t) + \boldsymbol{E}_e(\boldsymbol{R}_i, t), \\ \boldsymbol{b}_t(\boldsymbol{R}_i, t) &= \sum_{j(\neq i)} \boldsymbol{b}_j(\boldsymbol{R}_i, t) + \boldsymbol{B}_e(\boldsymbol{R}_i, t). \end{aligned} \tag{13}$$

Since in the equation of motion (12) the magnetic field is accompanied by a factor c^{-1}, one needs there as fields

$$e_t(R_i, t) = -\sum_{j(\neq i)} \nabla_i \frac{e_j}{4\pi|R_i - R_j|} + E_e(R_i, t), \qquad (14)$$
$$b_t(R_i, t) = B_e(R_i, t),$$

instead of the complete expressions (13) with (10).

The equations of motion (12) with (14) may be written in Hamiltonian form

$$\frac{\partial H}{\partial P_i} = \dot{R}_i, \qquad \frac{\partial H}{\partial R_i} = -\dot{P}_i \qquad (15)$$

with the Hamiltonian

$$H = \sum_i \frac{P_i^2}{2m_i} + \sum_{i, j(i\neq j)} \frac{e_i e_j}{8\pi|R_i - R_j|} + \sum_i e_i \left\{\varphi_e(R_i, t) - c^{-1}\frac{P_i}{m_i}\cdot A_e(R_i, t)\right\}, \qquad (16)$$

with φ_e and A_e potentials for the external fields. Indeed insertion of (16) into (15) leads to (12) with (14).

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

a. *The atomic series expansion*

Charged point particles (electrons and nuclei) are often grouped into stable sets, like atoms, molecules or ions. (For convenience we shall sometimes refer to such composite particles simply as 'atoms'.) The starting point for the derivation of the equations for the fields due to such atoms is the set of microscopic field equations (1). It will be convenient in the present case to replace the numbering i of the point particles by a numbering k of the stable groups and i of their constituent particles. The position vector R_i, written as R_{ki} now, can be split into two parts:

$$R_{ki} = R_k + r_{ki}. \qquad (17)$$

Here R_k is the position of some privileged point of the stable group k (e.g. the nucleus of an atom or the centre of mass, etc.), while the r_{ki} ($i = 1, 2, \ldots$) are the internal coordinates, which specify the positions of the constituent particles ki with respect to that of the privileged point of the stable group k.

The case will now be studied in which the solutions e and b of the field equations can be considered as converging series expansions in $|r_{ki}|/|R_k - R|$.

(This situation is realized if the expansion parameter is smaller than unity. Physically this means that the atomic dimension r_{ki} has to be smaller than the distance $|R_k - R|$ from the observation point R of the fields to the central point R_k of the atom. In other words one is now interested in observing the fields outside the stable atomic structure. On the other hand this is also the physical situation in which it is useful to speak of atoms, characterized by a small number of physical quantities which are still to be specified.) Accordingly the delta functions may now be developed in powers of r_{ki} around $R_k - R$. Using (17) one gets then for the field equations (1):

$$\nabla\cdot e = \sum_{k,i} e_{ki} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} (r_{ki}\cdot\nabla)^n \delta(R_k - R),$$
$$-\partial_0 e + \nabla\wedge b = \frac{1}{c}\sum_{k,i} e_{ki}(\dot{R}_k + \dot{r}_{ki}) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} (r_{ki}\cdot\nabla)^n \delta(R_k - R), \qquad (18)$$
$$\nabla\cdot b = 0,$$
$$\partial_0 b + \nabla\wedge e = 0,$$

since $\partial/\partial R_k$ acting on the delta function is the same as $-\nabla$ acting on it. The first of these equations can alternatively be written as

$$\nabla\cdot e = \rho^e - \nabla\cdot p, \qquad (19)$$

if the following abbreviations are used

$$\rho^e = \sum_k \rho_k^e; \qquad \rho_k^e = \sum_i e_{ki}\delta(R_k - R), \qquad (20)$$

$$p = \sum_k p_k; \qquad p_k = \sum_i e_{ki} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n!} r_{ki}(r_{ki}\cdot\nabla)^{n-1}\delta(R_k - R). \qquad (21)$$

The second field equation can be written as

$$-\partial_0 e + \nabla\wedge b = \frac{1}{c}\left\{j - \sum_k \dot{R}_k \nabla\cdot p_k + \sum_{k,i} e_{ki} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \dot{r}_{ki}(r_{ki}\cdot\nabla)^n \delta(R_k - R)\right\} \qquad (22)$$

with the abbreviation

$$j = \sum_k j_k; \qquad j_k = \sum_i e_{ki}\dot{R}_k \delta(R_k - R). \qquad (23)$$

Taking the derivative $\partial_0 = \partial/\partial ct$ of (21), one finds (replacing n by $n+1$)

$$\partial_0 p_k + \frac{1}{c}\dot{R}_k\cdot\nabla p_k - \frac{1}{c}\sum_i e_{ki} \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} (\dot{r}_{ki} r_{ki}\cdot\nabla + n r_{ki}\dot{r}_{ki}\cdot\nabla)(r_{ki}\cdot\nabla)^{n-1} \delta(R_k - R) = 0, \qquad (24)$$

because the time derivative of the delta function is equal to $-\dot{\boldsymbol{R}}_k \cdot \nabla$ acting on it. (In the term $n = 0$ the operator product $\nabla\nabla^{-1}$ should be understood as unity.) Upon adding this (vanishing) expression, summed over k, to the right-hand side of (22), and using the vector identity

$$\nabla \cdot (\boldsymbol{v}\boldsymbol{w} - \boldsymbol{w}\boldsymbol{v}) = \nabla \wedge (\boldsymbol{w} \wedge \boldsymbol{v}), \tag{25}$$

one obtains for the field equation the form

$$-\partial_0 \boldsymbol{e} + \nabla \wedge \boldsymbol{b} = c^{-1}\boldsymbol{j} + \partial_0 \boldsymbol{p} + \nabla \wedge \boldsymbol{m}, \tag{26}$$

where the following abbreviation has been used:

$$\boldsymbol{m} = \sum_k \boldsymbol{m}_k, \tag{27}$$

$$\boldsymbol{m}_k = \frac{1}{c}\,\boldsymbol{p}_k \wedge \dot{\boldsymbol{R}}_k + \frac{1}{c}\sum_i e_{ki} \sum_{n=1}^{\infty} \frac{(-1)^{n-1} n}{(n+1)!}\, \boldsymbol{r}_{ki} \wedge \dot{\boldsymbol{r}}_{ki} (\boldsymbol{r}_{ki} \cdot \nabla)^{n-1} \delta(\boldsymbol{R}_k - \boldsymbol{R}).$$

The forms of the field equations may be further simplified and the abbreviations interpreted, if first physical quantities are introduced, which characterize the internal atomic structure.

b. *Multipole moments*

The stable groups (which were called atoms here) may carry total charges

$$e_k = \sum_i e_{ki}. \tag{28}$$

This is the case for ions and also for single electrons. Other properties which characterize the atoms are the electromagnetic multipole moments. These atomic multipole moments are useful combinations of the internal atomic parameters. The electric dipole and quadrupole moments, for instance, are defined as

$$\overline{\boldsymbol{\mu}}_k^{(1)} = \sum_i e_{ki} \boldsymbol{r}_{ki}, \qquad \overline{\boldsymbol{\mu}}_k^{(2)} = \tfrac{1}{2} \sum_i e_{ki} \boldsymbol{r}_{ki} \boldsymbol{r}_{ki}. \tag{29}$$

These are a vector and a symmetric tensor respectively[1]. The latter is written as a 'dyadic product' $\boldsymbol{r}_{ki}\boldsymbol{r}_{ki}$, which means that it has the Cartesian tensor components $r_{ki}^{\alpha} r_{ki}^{\beta}$ with $\alpha, \beta = 1, 2, 3$. The magnetic dipole and quadrupole moments have the forms

$$\overline{\boldsymbol{\nu}}_k^{(1)} = \tfrac{1}{2} c^{-1} \sum_i e_{ki} \boldsymbol{r}_{ki} \wedge \dot{\boldsymbol{r}}_{ki}, \qquad \overline{\boldsymbol{\nu}}_k^{(2)} = \tfrac{1}{3} c^{-1} \sum_i e_{ki} \boldsymbol{r}_{ki} \boldsymbol{r}_{ki} \wedge \dot{\boldsymbol{r}}_{ki}. \tag{30}$$

[1] Vectors will be denoted by boldface italics; tensors by boldface roman (upright) symbols.

Again the dipole moment is a vector, the quadrupole moment a tensor written here as a dyadic product of the vectors $\boldsymbol{r}_{ki}$ and $\boldsymbol{r}_{ki} \wedge \dot{\boldsymbol{r}}_{ki}$. It should be noticed that $\overline{\boldsymbol{\mu}}_k^{(1)}$ is of the first order in the internal coordinates, but $\overline{\boldsymbol{\mu}}_k^{(2)}$ and $\overline{\boldsymbol{\nu}}_k^{(1)}$ of second order.

The definitions of multipoles of arbitrary order are the following: the electric 2^n-pole moment is

$$\overline{\boldsymbol{\mu}}_k^{(n)} = \frac{1}{n!} \sum_i e_{ki} \boldsymbol{r}_{ki}^n, \qquad (n = 1, 2, \ldots), \tag{31}$$

where the power n stands for a polyad of n vectors $\boldsymbol{r}_{ki}$; the magnetic 2^n-pole moment is

$$\overline{\boldsymbol{\nu}}_k^{(n)} = \frac{n}{(n+1)!} \sum_i e_{ki} \boldsymbol{r}_{ki}^n \wedge \frac{\dot{\boldsymbol{r}}_{ki}}{c}, \qquad (n = 1, 2, \ldots), \tag{32}$$

where again the power is a polyad. The electric 2^n-pole moment is of order n in the internal coordinates, whereas the magnetic 2^n-pole is of order $n+1$ in the internal coordinates.

The values of the multipole moments may depend on the choice of the privileged point $\boldsymbol{R}_k$, but their forms will always be the same combinations of the internal coordinates $\boldsymbol{r}_{ki}$. The electric dipole moment, for instance, depends in general on the choice of $\boldsymbol{R}_k$, but not if the total charge e_k vanishes.

If external electromagnetic fields are acting on the system it may be polarized and thus get induced electromagnetic multipole densities. This is the situation which one studies usually in the theories of the dielectric constant and the magnetic permeability. These theories are however completely independent of the derivation of the Maxwell equations. In the derivation the multipole moments are in fact arbitrary, that is they may be induced by fields exerted on the atoms, they may be permanent moments or they may be sums of both.

If the expansion parameter $|\boldsymbol{r}_{ki}|/|\boldsymbol{R}_k - \boldsymbol{R}|$ is small compared to unity, then only a few terms of the multipole expansion have to be taken into account. Such a situation will occur in diluted systems, where the observation point $\boldsymbol{R}$ of the fields can easily be chosen at a distance $|\boldsymbol{R}_k - \boldsymbol{R}|$ from the atom which is large compared to the atomic dimension $|\boldsymbol{r}_{ki}|$.

c. *The field equations*

With the atomic charges (28) one can now write the expressions (20) and (23) as

$$\rho^e = \sum_k e_k \delta(\boldsymbol{R}_k - \boldsymbol{R}),$$
$$\boldsymbol{j} = \sum_k e_k \boldsymbol{v}_k \delta(\boldsymbol{R}_k - \boldsymbol{R}), \tag{33}$$

where we have written $\boldsymbol{v}_k$ for the velocity $\dot{\boldsymbol{R}}_k$. The quantities (33) are the *atomic charge* and *current* densities. Similarly with (31) and (32) one obtains from (21) and (27) the expressions

$$\boldsymbol{p} = \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} \vdots \sum_k \overline{\boldsymbol{\mu}}_k^{(n)} \delta(\boldsymbol{R}_k - \boldsymbol{R}),$$
$$\boldsymbol{m} = \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} \vdots \sum_k \overline{\boldsymbol{\nu}}_k^{(n)} \delta(\boldsymbol{R}_k - \boldsymbol{R}) + c^{-1} \sum_k \boldsymbol{p}_k \wedge \boldsymbol{v}_k \tag{34}$$
$$= \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} \vdots \sum_k (\overline{\boldsymbol{\nu}}_k^{(n)} + c^{-1} \overline{\boldsymbol{\mu}}_k^{(n)} \wedge \boldsymbol{v}_k) \delta(\boldsymbol{R}_k - \boldsymbol{R}),$$

where the dots stand for $(n-1)$-fold contractions. They may be called the *atomic electric* and *magnetic polarization* densities.

The quantities given here are thus expressed in the internal properties e_k, $\overline{\boldsymbol{\mu}}_k^{(n)}$ and $\overline{\boldsymbol{\nu}}_k^{(n)}$ and the external properties $\boldsymbol{R}_k$ and $\boldsymbol{v}_k \equiv \dot{\boldsymbol{R}}_k$ of the atoms. Since these properties depend themselves on time the atomic densities (33) and (34) are functions of the space and time coordinates $\boldsymbol{R}$ and t. The magnetization vector $\boldsymbol{m}$ contains contributions from the electric multipoles in motion. A similar term, showing the influence of moving magnetic moments on the electric polarization vector $\boldsymbol{p}$ is absent in the present – non-relativistic – treatment.

The atomic charge, current and polarization densities occur in the field equations (19) and (26) so that the total set now reads:

$$\nabla \cdot \boldsymbol{e} = \rho^e - \nabla \cdot \boldsymbol{p},$$
$$-\partial_0 \boldsymbol{e} + \nabla \wedge \boldsymbol{b} = c^{-1} \boldsymbol{j} + \partial_0 \boldsymbol{p} + \nabla \wedge \boldsymbol{m},$$
$$\nabla \cdot \boldsymbol{b} = 0, \tag{35}$$
$$\partial_0 \boldsymbol{b} + \nabla \wedge \boldsymbol{e} = 0.$$

Although they have the same form as the macroscopic Maxwell equations, they are still equations for the microscopic fields $\boldsymbol{e}$ and $\boldsymbol{b}$ in which the existence of atoms (stable groups of point particles) has been taken into account: they will be referred to as *atomic field equations*. Instead of $\boldsymbol{p}$ and $\boldsymbol{m}$ one could alternatively use '*atomic displacement vectors*', defined as

$$\boldsymbol{d} = \boldsymbol{e} + \boldsymbol{p}, \qquad \boldsymbol{h} = \boldsymbol{b} - \boldsymbol{m}. \tag{36}$$

Then the atomic field equations (35) can be written as

$$\nabla \cdot \boldsymbol{d} = \rho^e,$$
$$-\partial_0 \boldsymbol{d} + \nabla \wedge \boldsymbol{h} = c^{-1} \boldsymbol{j},$$
$$\nabla \cdot \boldsymbol{b} = 0, \tag{37}$$
$$\partial_0 \boldsymbol{b} + \nabla \wedge \boldsymbol{e} = 0.$$

The atomic field equations for $\boldsymbol{e}$ and $\boldsymbol{b}$ were derived from the microscopic field equations for these same fields without any averaging or smoothing of the quantities. But while in the microscopic field equations properties of the separate electrons and nuclei occur, in the atomic field equations matter is characterized by parameters pertaining to the atoms (stable groups of electrons and nuclei). The atomic field equations can therefore be said to be valid on the '*kinetic level*' of the theory for electromagnetic fields in the presence of matter.

Finally it may be noted that from (33) follows the law of conservation of atomic charge

$$\partial \rho^e / \partial t = -\nabla \cdot \boldsymbol{j}. \tag{38}$$

It may be derived by taking the time derivative of ρ^e. The fact that $\partial/\partial \boldsymbol{R}_k$ acting on the delta function is the same as minus the nabla operator acting on it, together with the expression for $\boldsymbol{j}$, then leads directly to the right-hand side of (38).

5 *The momentum and energy equations for composite particles*

a. *The equation of motion*

The equation of motion for a constituent particle ki (of the kth atom) with charge e_{ki}, mass m_{ki}, position $\boldsymbol{R}_{ki}(t)$, velocity $\dot{\boldsymbol{R}}_{ki}(t)$ and acceleration $\ddot{\boldsymbol{R}}_{ki}(t)$ in an electromagnetic field $(\boldsymbol{e}_t, \boldsymbol{b}_t)$ has been given in (12):

$$m_{ki} \ddot{\boldsymbol{R}}_{ki} = e_{ki} \{\boldsymbol{e}_t(\boldsymbol{R}_{ki}, t) + c^{-1} \dot{\boldsymbol{R}}_{ki} \wedge \boldsymbol{b}_t(\boldsymbol{R}_{ki}, t)\}. \tag{39}$$

The expressions for the total fields $\boldsymbol{e}_t$ and $\boldsymbol{b}_t$ have been written in (14); they read in the present case:

$$\boldsymbol{e}_t(\boldsymbol{R}_{ki}, t) = -\sum_{j(\neq i)} \nabla_{ki} \frac{e_{kj}}{4\pi |\boldsymbol{R}_{ki} - \boldsymbol{R}_{kj}|} - \sum_{l(\neq k)j} \nabla_{ki} \frac{e_{lj}}{4\pi |\boldsymbol{R}_{ki} - \boldsymbol{R}_{lj}|} + \boldsymbol{E}_e(\boldsymbol{R}_{ki}, t),$$
$$\boldsymbol{b}_t(\boldsymbol{R}_{ki}, t) = \boldsymbol{B}_e(\boldsymbol{R}_{ki}, t). \tag{40}$$

Here ∇_{ki} stands for the space derivative with respect to $\boldsymbol{R}_{ki}$. The fields $(\boldsymbol{e}_t, \boldsymbol{b}_t)$ consist of three parts: the intra-atomic fields due to the other constituent particles kj $(j \neq i)$ of the same atom k, the interatomic fields due to the other atoms and the external fields $(\boldsymbol{E}_e, \boldsymbol{B}_e)$ due to sources outside the system.

The motion of atom k as a whole may be described by introducing as a central point the centre of mass

$$\boldsymbol{R}_k = \sum_i m_{ki} \boldsymbol{R}_{ki} / m_k, \tag{41}$$

where $m_k = \sum_i m_{ki}$. Summation of (39) over the index i, which labels the constituent particles, leads to

$$m_k \ddot{\boldsymbol{R}}_k = \sum_i e_{ki} \{\boldsymbol{e}_t(\boldsymbol{R}_{ki}, t) + c^{-1} \dot{\boldsymbol{R}}_{ki} \wedge \boldsymbol{b}_t(\boldsymbol{R}_{ki}, t)\}. \tag{42}$$

If (40) is inserted into (42) it appears that the contribution of the *intra-atomic* fields drops out, as should be expected for central forces. In this way (42) gets the form

$$m_k \ddot{\boldsymbol{R}}_k = -\sum_{l(\neq k)i,j} \nabla_{ki} \frac{e_{ki} e_{lj}}{4\pi |\boldsymbol{R}_{ki} - \boldsymbol{R}_{lj}|} + \sum_i e_{ki} \left\{ \boldsymbol{E}_e(\boldsymbol{R}_{ki}, t) + \frac{\dot{\boldsymbol{R}}_{ki}}{c} \wedge \boldsymbol{B}_e(\boldsymbol{R}_{ki}, t) \right\}. \tag{43}$$

If the *external* fields are developed in Taylor series in terms of the internal coordinates

$$\boldsymbol{r}_{ki} \equiv \boldsymbol{R}_{ki} - \boldsymbol{R}_k, \tag{44}$$

the last term of (43) gets the form

$$\sum_i e_{ki} \sum_{n=0}^{\infty} \frac{1}{n!} (\boldsymbol{r}_{ki} \cdot \nabla_k)^n \{\boldsymbol{E}_e(\boldsymbol{R}_k, t) + c^{-1} \dot{\boldsymbol{R}}_k \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t) + c^{-1} \dot{\boldsymbol{r}}_{ki} \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t)\}, \tag{45}$$

which might be expressed in terms of the atomic charge (28) and the atomic multipole moments (31), (32). Since the external fields vary slowly over the atoms we shall limit ourselves in (45) to the contributions of the charges and the electric and magnetic dipole moments. (Cf. problem 2 for the general case.) Using the identity

$$\boldsymbol{r}_{ki} \cdot \nabla_k \dot{\boldsymbol{r}}_{ki} = \frac{1}{2} \frac{\mathrm{d}}{\mathrm{d}t} (\boldsymbol{r}_{ki} \boldsymbol{r}_{ki}) \cdot \nabla_k + \tfrac{1}{2} (\boldsymbol{r}_{ki} \wedge \dot{\boldsymbol{r}}_{ki}) \wedge \nabla_k, \tag{46}$$

one gets for (45):

$$(e_k + \bar{\boldsymbol{\mu}}_k^{(1)} \cdot \nabla_k) \{\boldsymbol{E}_e(\boldsymbol{R}_k, t) + c^{-1} \boldsymbol{v}_k \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t)\} + (c^{-1} \dot{\bar{\boldsymbol{\mu}}}_k^{(1)} + \bar{\boldsymbol{\nu}}_k^{(1)} \wedge \nabla_k) \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t), \tag{47}$$

where $\boldsymbol{v}_k$ is the atomic velocity $\dot{\boldsymbol{R}}_k$.

The *interatomic* contribution to the force may likewise be expanded in terms of $\boldsymbol{r}_{ki}$ and $\boldsymbol{r}_{lj}$ if the atoms are outside each other, i.e. if the interatomic distance $|\boldsymbol{R}_k - \boldsymbol{R}_l|$ is greater than the sum of the largest $|\boldsymbol{r}_{ki}|$ and $|\boldsymbol{r}_{lj}|$. In that case the first term at the right-hand side of (43) reads

$$-\sum_{l(\neq k)i,j} \sum_{n,m=0}^{\infty} \frac{1}{n!m!} (\boldsymbol{r}_{ki} \cdot \nabla_k)^n (\boldsymbol{r}_{lj} \cdot \nabla_l)^m \nabla_k \frac{e_{ki} e_{lj}}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|}, \tag{48}$$

or, if the electric multipole moments (31) are used,

$$-\sum_{l(\neq k)} \sum_{n,m=0}^{\infty} \bar{\boldsymbol{\mu}}_k^{(n)} : \nabla_k^n \bar{\boldsymbol{\mu}}_l^{(m)} : \nabla_l^m \nabla_k \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|}. \tag{49}$$

In the general case of arbitrary interatomic distances we may write the right-hand side of (43) as the sum of a long range force $\boldsymbol{f}_k^{\mathrm{L}}$, which consists of (47) and (49) together, and a remaining short range force $\boldsymbol{f}_k^{\mathrm{S}}$. In this way we have

$$m_k \dot{\boldsymbol{v}}_k = \boldsymbol{f}_k^{\mathrm{L}} + \boldsymbol{f}_k^{\mathrm{S}}, \tag{50}$$

$$\begin{aligned} \boldsymbol{f}_k^{\mathrm{L}} = & -\sum_{l(\neq k)} \sum_{n,m=0}^{\infty} \bar{\boldsymbol{\mu}}_k^{(n)} : \nabla_k^n \bar{\boldsymbol{\mu}}_l^{(m)} : \nabla_l^m \nabla_k \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|} \\ & + (e_k + \bar{\boldsymbol{\mu}}_k^{(1)} \cdot \nabla_k) \{\boldsymbol{E}_e(\boldsymbol{R}_k, t) + c^{-1} \boldsymbol{v}_k \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t)\} \\ & + (c^{-1} \dot{\bar{\boldsymbol{\mu}}}_k^{(1)} + \bar{\boldsymbol{\nu}}_k^{(1)} \wedge \nabla_k) \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t), \end{aligned} \tag{51}$$

$$\boldsymbol{f}_k^{\mathrm{S}} = -\sum_{l(\neq k)i,j} \nabla_{ki} \frac{e_{ki} e_{lj}}{4\pi |\boldsymbol{R}_{ki} - \boldsymbol{R}_{lj}|} + \sum_{l(\neq k)} \sum_{n,m=0}^{\infty} \bar{\boldsymbol{\mu}}_k^{(n)} : \nabla_k^n \bar{\boldsymbol{\mu}}_l^{(m)} : \nabla_l^m \nabla_k \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|}. \tag{52}$$

Indeed the contribution $\boldsymbol{f}_k^{\mathrm{S}}$ has short range character, since it vanishes if the atoms are outside each other.

The external fields obey the homogeneous field equations

$$\nabla \cdot \boldsymbol{B}_e = 0, \qquad c^{-1} \partial \boldsymbol{B}_e / \partial t + \nabla \wedge \boldsymbol{E}_e = 0. \tag{53}$$

They permit us to write the long range force (51) as

$$\begin{aligned} \boldsymbol{f}_k^{\mathrm{L}} = & -\sum_{l(\neq k)} \sum_{n,m=0}^{\infty} \bar{\boldsymbol{\mu}}_k^{(n)} : \nabla_k^n \bar{\boldsymbol{\mu}}_l^{(m)} : \nabla_l^m \nabla_k \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|} \\ & + e_k \{\boldsymbol{E}_e(\boldsymbol{R}_k, t) + c^{-1} \boldsymbol{v}_k \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t)\} + \{\nabla_k \boldsymbol{E}_e(\boldsymbol{R}_k, t)\} \cdot \bar{\boldsymbol{\mu}}_k^{(1)} \\ & + \{\nabla_k \boldsymbol{B}_e(\boldsymbol{R}_k, t)\} \cdot (\bar{\boldsymbol{\nu}}_k^{(1)} + c^{-1} \bar{\boldsymbol{\mu}}_k^{(1)} \wedge \boldsymbol{v}_k) + c^{-1} \frac{\mathrm{d}}{\mathrm{d}t} \{\bar{\boldsymbol{\mu}}_k^{(1)} \wedge \boldsymbol{B}_e(\boldsymbol{R}_k, t)\}, \end{aligned} \tag{54}$$

where $\mathrm{d}/\mathrm{d}t$ is the total time derivative. In this way the *equation of motion* (50) with (54) and (52) for an atom in an electromagnetic field of interatomic and external origin is found. If only one atom in an external field is present it gets the simple form:

$$m_k \dot{\boldsymbol{v}}_k = e_k(\boldsymbol{E}_\mathrm{e}+c^{-1}\boldsymbol{v}_k\wedge\boldsymbol{B}_\mathrm{e})+(\nabla_k\boldsymbol{E}_\mathrm{e})\cdot\bar{\boldsymbol{\mu}}_k^{(1)}+(\nabla_k\boldsymbol{B}_\mathrm{e})\cdot(\bar{\boldsymbol{\nu}}_k^{(1)}+c^{-1}\bar{\boldsymbol{\mu}}_k^{(1)}\wedge\boldsymbol{v}_k)$$
$$+c^{-1}\frac{\mathrm{d}}{\mathrm{d}t}(\bar{\boldsymbol{\mu}}_k^{(1)}\wedge\boldsymbol{B}_\mathrm{e}). \quad (55)$$

The first term is the Lorentz force exerted on a charged composite particle, the second is the Kelvin force on an electric dipole moment, the third is the analogous magnetic term which contains the magnetic dipole moment and the electric dipole moment in motion, while the last term describes an electrodynamic effect with a time derivative.

b. *The energy equation*

The energy equation for the constituent particle ki follows if (39) is multiplied by the velocity $\dot{\boldsymbol{R}}_{ki}$:

$$m_{ki}\dot{\boldsymbol{R}}_{ki}\cdot\ddot{\boldsymbol{R}}_{ki} = e_{ki}\dot{\boldsymbol{R}}_{ki}\cdot\boldsymbol{e}_\mathrm{t}(\boldsymbol{R}_{ki},t). \quad (56)$$

Taking the sum over i, introducing the centre of mass (41) and the internal coordinates (44) and inserting the expression (40) for the field $\boldsymbol{e}_\mathrm{t}$ one gets

$$\frac{\mathrm{d}}{\mathrm{d}t}(\tfrac{1}{2}m_k v_k^2+\tfrac{1}{2}\sum_i m_{ki}\dot{r}_{ki}^2) = -\sum_{i,j(i\neq j)}\dot{\boldsymbol{R}}_{ki}\cdot\nabla_{ki}\frac{e_{ki}e_{kj}}{4\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{kj}|}$$
$$-\sum_{l(\neq k)i,j}\dot{\boldsymbol{R}}_{ki}\cdot\nabla_{ki}\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}|}+\sum_i e_{ki}\dot{\boldsymbol{R}}_{ki}\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_{ki},t). \quad (57)$$

The first term at the right-hand side is an *intra-atomic* contribution. It may be transformed into the total time derivative of the intra-atomic Coulomb energy of the atom:

$$-\sum_{i,j(i\neq j)}(\dot{\boldsymbol{R}}_{ki}\cdot\nabla_{ki}+\dot{\boldsymbol{R}}_{kj}\cdot\nabla_{kj})\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{kj}|} = -\frac{\mathrm{d}}{\mathrm{d}t}\sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}_{ki}-\boldsymbol{r}_{kj}|}, \quad (58)$$

where (44) has been used. This term will be shifted to the left-hand side.

The *external* field term of (57) may be expanded in terms of $\boldsymbol{r}_{ki}$. One obtains then

$$\sum_i e_{ki}\sum_{n=0}^{\infty}\frac{1}{n!}(\boldsymbol{r}_{ki}\cdot\nabla_k)^n(\dot{\boldsymbol{R}}_k+\dot{\boldsymbol{r}}_{ki})\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t). \quad (59)$$

Introducing the electric and magnetic multipole moments and confining ourselves to terms with the external fields and their first derivatives we are left with an expression containing charges and dipole moments only:

$$(e_k+\bar{\boldsymbol{\mu}}_k^{(1)}\cdot\nabla_k)\boldsymbol{v}_k\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t)+(\dot{\bar{\boldsymbol{\mu}}}_k^{(1)}+c\bar{\boldsymbol{\nu}}_k^{(1)}\wedge\nabla_k)\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t), \quad (60)$$

where (46) has been used. (Cf. problem 3 for the general expression with all multipole moments.)

The *interatomic* contribution in (57) may also be expanded in terms of $\boldsymbol{r}_{ki}$ and $\boldsymbol{r}_{lj}$ in case the atoms are outside each other:

$$-\sum_{l(\neq k)i,j}\sum_{n,m=0}^{\infty}\frac{1}{n!m!}(\boldsymbol{r}_{ki}\cdot\nabla_k)^n(\boldsymbol{r}_{lj}\cdot\nabla_l)^m(\dot{\boldsymbol{R}}_k+\dot{\boldsymbol{r}}_{ki})\cdot\nabla_k\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}, \quad (61)$$

or, in terms of the multipoles (31),

$$-\sum_{l(\neq k)}\sum_{m=0}^{\infty}\Big(\sum_{n=0}^{\infty}\bar{\boldsymbol{\mu}}_k^{(n)}\vdots\nabla_k^n\boldsymbol{v}_k\cdot\nabla_k+\sum_{n=1}^{\infty}\dot{\bar{\boldsymbol{\mu}}}_k^{(n)}\vdots\nabla_k^n\Big)\bar{\boldsymbol{\mu}}_l^{(m)}\vdots\nabla_l^m\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}. \quad (62)$$

In the general case the second and third term at the right-hand side of (57) may be written as the sum of a long range contribution ψ_k^L, which consists of (60) and (62), and a remaining short range contribution ψ_k^S:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\tfrac{1}{2}m_k v_k^2+\tfrac{1}{2}\sum_i m_{ki}\dot{r}_{ki}^2+\sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}_{ki}-\boldsymbol{r}_{kj}|}\right) = \psi_k^\mathrm{L}+\psi_k^\mathrm{S}, \quad (63)$$

$$\psi_k^\mathrm{L} = -\sum_{l(\neq k)}\sum_{m=0}^{\infty}\Big(\sum_{n=0}^{\infty}\bar{\boldsymbol{\mu}}_k^{(n)}\vdots\nabla_k^n\boldsymbol{v}_k\cdot\nabla_k+\sum_{n=1}^{\infty}\dot{\bar{\boldsymbol{\mu}}}_k^{(n)}\vdots\nabla_k^n\Big)\bar{\boldsymbol{\mu}}_l^{(m)}\vdots\nabla_l^m\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}$$
$$+(e_k+\bar{\boldsymbol{\mu}}_k^{(1)}\cdot\nabla_k)\boldsymbol{v}_k\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t)+(\dot{\bar{\boldsymbol{\mu}}}_k^{(1)}+c\bar{\boldsymbol{\nu}}_k^{(1)}\wedge\nabla_k)\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t), \quad (64)$$

$$\psi_k^\mathrm{S} = -\sum_{l(\neq k)i,j}\dot{\boldsymbol{R}}_{ki}\cdot\nabla_{ki}\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}|}$$
$$+\sum_{l(\neq k)}\sum_{m=0}^{\infty}\Big(\sum_{n=0}^{\infty}\bar{\boldsymbol{\mu}}_k^{(n)}\vdots\nabla_k^n\boldsymbol{v}_k\cdot\nabla_k+\sum_{n=1}^{\infty}\dot{\bar{\boldsymbol{\mu}}}_k^{(n)}\vdots\nabla_k^n\Big)\bar{\boldsymbol{\mu}}_l^{(m)}\vdots\nabla_l^m\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}. \quad (65)$$

With the second equation of (53) one gets for (64)

$$\psi_k^\mathrm{L} = -\sum_{l(\neq k)}\sum_{m=0}^{\infty}\Big(\sum_{n=0}^{\infty}\bar{\boldsymbol{\mu}}_k^{(n)}\vdots\nabla_k^n\boldsymbol{v}_k\cdot\nabla_k+\sum_{n=1}^{\infty}\dot{\bar{\boldsymbol{\mu}}}_k^{(n)}\vdots\nabla_k^n\Big)\bar{\boldsymbol{\mu}}_l^{(m)}\vdots\nabla_l^m\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}$$
$$+e_k\boldsymbol{v}_k\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t)+\boldsymbol{v}_k\cdot\{\nabla_k\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t)\}\cdot\bar{\boldsymbol{\mu}}_k^{(1)}+\dot{\bar{\boldsymbol{\mu}}}_k^{(1)}\cdot\boldsymbol{E}_\mathrm{e}(\boldsymbol{R}_k,t)$$
$$-(\bar{\boldsymbol{\nu}}_k^{(1)}+c^{-1}\bar{\boldsymbol{\mu}}_k^{(1)}\wedge\boldsymbol{v}_k)\cdot\frac{\partial\boldsymbol{B}_\mathrm{e}(\boldsymbol{R}_k,t)}{\partial t}. \quad (66)$$

The *atomic energy equation* (63) is thus completely specified. It contains at the left-hand side kinetic and potential energy terms of which the last two are of intra-atomic character. The right-hand side contains contributions, specified by (66) and (65), in which the fields of interatomic and external origin occur.

For a single atom in an external field the atomic energy equation reduces to

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\tfrac{1}{2}m_k \boldsymbol{v}_k^2+\tfrac{1}{2}\sum_i m_{ki}\dot{\boldsymbol{r}}_{ki}^2+\sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}_{ki}-\boldsymbol{r}_{kj}|}\right)$$
$$= e_k\boldsymbol{v}_k\cdot\boldsymbol{E}_e+\boldsymbol{v}_k\cdot(\nabla_k\boldsymbol{E}_e)\cdot\overline{\boldsymbol{\mu}}_k^{(1)}+\boldsymbol{v}_k\cdot(\nabla_k\boldsymbol{B}_e)\cdot(\overline{\boldsymbol{v}}_k^{(1)}+c^{-1}\overline{\boldsymbol{\mu}}_k^{(1)}\wedge\boldsymbol{v}_k)+\dot{\overline{\boldsymbol{\mu}}}_k^{(1)}\cdot\boldsymbol{E}_e$$
$$-(\overline{\boldsymbol{v}}_k^{(1)}+c^{-1}\overline{\boldsymbol{\mu}}_k^{(1)}\wedge\boldsymbol{v}_k)\cdot\frac{\mathrm{d}\boldsymbol{B}_e}{\mathrm{d}t}, \quad (67)$$

where the total time derivative $\mathrm{d}/\mathrm{d}t \equiv \partial/\partial t+\boldsymbol{v}_k\cdot\nabla_k$ has been introduced in the last term. In this way at the right-hand side the 'power' terms due to the Lorentz and Kelvin forces appear, as well as two terms with total time derivatives. It may be noted that the latter show a remarkable asymmetry: the first contains the derivative of a dipole moment multiplied by a field, while the second contains the derivative of a field multiplied by a dipole moment expression.

6 *The inner angular momentum equation for composite particles*

The inner angular momentum of an atom k may be defined as

$$\overline{\boldsymbol{s}}_k \equiv \sum_i m_{ki}\boldsymbol{r}_{ki}\wedge\dot{\boldsymbol{r}}_{ki} \quad (68)$$

in terms of the masses m_{ki} of the constituent particles and the internal coordinates $\boldsymbol{r}_{ki}$ (44). Its time derivative is

$$\dot{\overline{\boldsymbol{s}}}_k = \sum_i m_{ki}\boldsymbol{r}_{ki}\wedge\ddot{\boldsymbol{r}}_{ki} = \sum_i m_{ki}\boldsymbol{r}_{ki}\wedge\ddot{\boldsymbol{R}}_{ki}, \quad (69)$$

where (41) has been used.

Introducing the equation of motion (39) with the fields (40) we get

$$\dot{\overline{\boldsymbol{s}}}_k = -\sum_{l(\neq k)i,j}\boldsymbol{r}_{ki}\wedge\nabla_{ki}\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}|}$$
$$+\sum_i e_{ki}\boldsymbol{r}_{ki}\wedge\{\boldsymbol{E}_e(\boldsymbol{R}_{ki},t)+c^{-1}\dot{\boldsymbol{R}}_{ki}\wedge\boldsymbol{B}_e(\boldsymbol{R}_{ki},t)\}. \quad (70)$$

The *intra-atomic* contributions to the fields have dropped out in this expression, as should be expected for central forces.

If the *external* fields change slowly, they can be expanded in terms of $\boldsymbol{r}_{ki}$, so that the external field contribution in (70) may then be written as:

$$\sum_i e_{ki}\boldsymbol{r}_{ki}\wedge\sum_{n=0}^{\infty}\frac{1}{n!}(\boldsymbol{r}_{ki}\cdot\nabla_k)^n\{\boldsymbol{E}_e(\boldsymbol{R}_k,t)+c^{-1}(\dot{\boldsymbol{R}}_k+\dot{\boldsymbol{r}}_{ki})\wedge\boldsymbol{B}_e(\boldsymbol{R}_k,t)\}. \quad (71)$$

Assuming that the external fields are sufficiently smooth we limit ourselves to electric and magnetic dipole moments in this expression. We obtain then, with the help of the vector identity

$$\boldsymbol{r}_{ki}\wedge(\dot{\boldsymbol{r}}_{ki}\wedge\boldsymbol{B}_e) = \tfrac{1}{2}(\boldsymbol{r}_{ki}\wedge\dot{\boldsymbol{r}}_{ki})\wedge\boldsymbol{B}_e+\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{r}_{ki}\boldsymbol{r}_{ki})\cdot\boldsymbol{B}_e-\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{r}_{ki}^2)\boldsymbol{B}_e, \quad (72)$$

instead of (71):

$$\overline{\boldsymbol{\mu}}_k^{(1)}\wedge\{\boldsymbol{E}_e(\boldsymbol{R}_k,t)+c^{-1}\boldsymbol{v}_k\wedge\boldsymbol{B}_e(\boldsymbol{R}_k,t)\}+\overline{\boldsymbol{v}}_k^{(1)}\wedge\boldsymbol{B}_e(\boldsymbol{R}_k,t), \quad (73)$$

where we have written $\boldsymbol{v}_k$ for the atomic velocity $\dot{\boldsymbol{R}}_k$.

In case the atoms are outside each other the *interatomic* contribution to the right-hand side of (70) may likewise be expanded, with the result

$$-\sum_{l(\neq k)i,j}\sum_{n,m=0}^{\infty}\frac{1}{n!m!}\boldsymbol{r}_{ki}\wedge\nabla_k(\boldsymbol{r}_{ki}\cdot\nabla_k)^n(\boldsymbol{r}_{lj}\cdot\nabla_l)^m\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}, \quad (74)$$

or, in terms of the electric multipole moments (31),

$$\sum_{l(\neq k)}\sum_{n,m=0}^{\infty}n\nabla_k\wedge\overline{\boldsymbol{\mu}}_k^{(n)}\vdots\nabla_k^{n-1}\overline{\boldsymbol{\mu}}_l^{(m)}\vdots\nabla_l^m\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}. \quad (75)$$

In the general case the right-hand side of (70) may be written as the sum of a long range moment $\boldsymbol{d}_k^{\mathrm{L}}$ and a short range moment $\boldsymbol{d}_k^{\mathrm{S}}$:

$$\dot{\overline{\boldsymbol{s}}}_k = \boldsymbol{d}_k^{\mathrm{L}}+\boldsymbol{d}_k^{\mathrm{S}}, \quad (76)$$

$$\boldsymbol{d}_k^{\mathrm{L}} = \sum_{l(\neq k)}\sum_{n,m=0}^{\infty}n\nabla_k\wedge\overline{\boldsymbol{\mu}}_k^{(n)}\vdots\nabla_k^{n-1}\overline{\boldsymbol{\mu}}_l^{(m)}\vdots\nabla_l^m\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}$$
$$+\overline{\boldsymbol{\mu}}_k^{(1)}\wedge\{\boldsymbol{E}_e(\boldsymbol{R}_k,t)+c^{-1}\boldsymbol{v}_k\wedge\boldsymbol{B}_e(\boldsymbol{R}_k,t)\}+\overline{\boldsymbol{v}}_k^{(1)}\wedge\boldsymbol{B}_e(\boldsymbol{R}_k,t), \quad (77)$$

$$\boldsymbol{d}_k^{\mathrm{S}} = -\sum_{l(\neq k)i,j}\boldsymbol{r}_{ki}\wedge\nabla_{ki}\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}|}$$
$$-\sum_{l(\neq k)}\sum_{n,m=0}^{\infty}n\nabla_k\wedge\overline{\boldsymbol{\mu}}_k^{(n)}\vdots\nabla_k^{n-1}\overline{\boldsymbol{\mu}}_l^{(m)}\vdots\nabla_l^m\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}. \quad (78)$$

For a single atom in an external field the equation (76) with (77–78) reduces to

$$\dot{s}_k = \bar{\mu}_k^{(1)} \wedge (E_e + c^{-1} v_k \wedge B_e) + \bar{\nu}_k^{(1)} \wedge B_e, \tag{79}$$

which shows that in non-relativistic theory the electric dipole moment is coupled to both the electric and the magnetic field, while the magnetic dipole moment is coupled to the magnetic field only.

PROBLEMS

1. Prove by expansion of the non-relativistic field expressions (10) in powers of atomic parameters r_{ki} and introduction of the multipole moments (31–32), that the fields generated by a set of atoms with positions R_k, velocities v_k, charges e_k and multipole moments $\bar{\mu}_k^{(n)}$, $\bar{\nu}_k^{(n)}$ are:

$$e(R, t) = -\sum_k \nabla \frac{e_k}{4\pi |R_k - R|} - \sum_k \sum_{n=1}^{\infty} (-1)^n \bar{\mu}_k^{(n)} \vdots \nabla^n \nabla \frac{1}{4\pi |R_k - R|},$$

$$b(R, t) = c^{-1} \sum_k \nabla \wedge \frac{e_k v_k}{4\pi |R_k - R|} + \sum_k \sum_{n=1}^{\infty} (-1)^n \nabla \wedge (c^{-1} \bar{\mu}_k^{(n)} \vdots \nabla^n v_k$$
$$- c^{-1} \dot{\bar{\mu}}_k^{(n)} \vdots \nabla^{n-1} + \nabla^{n-1} \vdots \bar{\nu}_k^{(n)} \wedge \nabla) \frac{1}{4\pi |R_k - R|}.$$

Show, by adding a delta function $\delta(R' - R_k)$ and an integration over R', that these formulae may be written as:

$$e(R, t) = -\nabla \int \{\rho^e(R', t) - \nabla' \cdot p(R', t)\} \frac{1}{4\pi |R - R'|} \mathrm{d}R',$$

$$b(R, t) = \nabla \wedge \int \{c^{-1} j(R', t) + \partial_0 p(R', t) + \nabla' \wedge m(R', t)\} \frac{1}{4\pi |R - R'|} \mathrm{d}R',$$

with ρ^e, j, p and m given by (33) and (34). Verify, by using (8), that these expressions for the electric and magnetic fields are the solutions of the atomic field equations (35).

2. Prove from (45) that the general expression for the force on a composite particle with position R_k, velocity v_k, charge e_k and multiple moments $\bar{\mu}_k^{(n)}$, $\bar{\nu}_k^{(n)}$ in an external field E_e, B_e is:

$$f_k = (e_k + \sum_{n=1}^{\infty} \bar{\mu}_k^{(n)} \vdots \nabla_k^n)(E_e + c^{-1} v_k \wedge B_e)$$
$$+ \sum_{n=1}^{\infty} (c^{-1} \dot{\bar{\mu}}_k^{(n)} \wedge \nabla_k^{n-1} + \nabla_k^{n-1} \vdots \bar{\nu}_k^{(n)} \wedge \nabla_k) \wedge B_e.$$

This expression is a generalization to all multipoles of (47). By using the field equations (53) for the external field it follows that the equation of motion for a composite particle in an external field may be cast into the form

$$m_k \dot{\boldsymbol{v}}_k = e_k(\boldsymbol{E}_e + c^{-1}\boldsymbol{v}_k \wedge \boldsymbol{B}_e) + \sum_{n=1}^{\infty} \Big[(\boldsymbol{\nabla}_k \boldsymbol{E}_e)\cdot({}^{\leftarrow}\boldsymbol{\nabla}_k^{n-1} \vdots\, \overline{\boldsymbol{\mu}}_k^{(n)})$$
$$+ (\boldsymbol{\nabla}_k \boldsymbol{B}_e)\cdot\{{}^{\leftarrow}\boldsymbol{\nabla}_k^{n-1} \vdots\, (\overline{\boldsymbol{\nu}}_k^{(n)} + c^{-1}\overline{\boldsymbol{\mu}}_k^{(n)} \wedge \boldsymbol{v}_k)\} + c^{-1}\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{\nabla}_k^{n-1} \vdots\, \overline{\boldsymbol{\mu}}_k^{(n)} \wedge \boldsymbol{B}_e)\Big],$$

where ${}^{\leftarrow}\boldsymbol{\nabla}_k$ is the differentiation operator $\partial/\partial \boldsymbol{R}_k$ acting to the left i.e. acting on the external fields. Furthermore the total time derivative $\mathrm{d}/\mathrm{d}t$ is $\partial/\partial t + \boldsymbol{v}_k\cdot\boldsymbol{\nabla}_k$. This second equation is a generalization to all multipoles of (55).

3. Prove from (59) that the work per unit of time exerted on a composite particle in an external field is:

$$\psi_k = (e_k + \sum_{n=1}^{\infty} \overline{\boldsymbol{\mu}}_k^{(n)} \vdots\, \boldsymbol{\nabla}_k^n)\boldsymbol{v}_k\cdot\boldsymbol{E}_e + \sum_{n=1}^{\infty} (\dot{\overline{\boldsymbol{\mu}}}_k^{(n)} \vdots\, \boldsymbol{\nabla}_k^{n-1} + c\boldsymbol{\nabla}_k^{n-1} \vdots\, \overline{\boldsymbol{\nu}}_k^{(n)} \wedge \boldsymbol{\nabla}_k)\cdot\boldsymbol{E}_e,$$

with the same notation as in problem 2. This expression generalizes (60) to all multipole orders. By means of the second field equation (53) it follows that the energy equation for a composite particle in an external field is:

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big(\tfrac{1}{2}m_k \boldsymbol{v}_k^2 + \tfrac{1}{2}\sum_i m_{ki}\dot{\boldsymbol{r}}_{ki}^2 + \sum_{i,\,j(i\neq j)} \frac{e_{ki}e_{kj}}{8\pi|\boldsymbol{r}_{ki} - \boldsymbol{r}_{kj}|}\Big)$$
$$= e_k \boldsymbol{v}_k\cdot\boldsymbol{E}_e + \sum_{n=1}^{\infty} \Big[\boldsymbol{v}_k\cdot(\boldsymbol{\nabla}_k \boldsymbol{E}_e)\cdot({}^{\leftarrow}\boldsymbol{\nabla}_k^{n-1} \vdots\, \overline{\boldsymbol{\mu}}_k^{(n)})$$
$$+ \boldsymbol{v}_k\cdot(\boldsymbol{\nabla}_k \boldsymbol{B}_e)\cdot\{{}^{\leftarrow}\boldsymbol{\nabla}_k^{n-1} \vdots\, (\overline{\boldsymbol{\nu}}_k^{(n)} + c^{-1}\overline{\boldsymbol{\mu}}_k^{(n)} \wedge \boldsymbol{v}_k)\}$$
$$+ \dot{\overline{\boldsymbol{\mu}}}_k^{(n)} \vdots\, \boldsymbol{\nabla}_k^{n-1}\boldsymbol{E}_e - \boldsymbol{\nabla}_k^{n-1} \vdots\, (\overline{\boldsymbol{\nu}}_k^{(n)} + c^{-1}\overline{\boldsymbol{\mu}}_k^{(n)} \wedge \boldsymbol{v}_k)\cdot \frac{\mathrm{d}\boldsymbol{B}_e}{\mathrm{d}t}\Big]$$

as a generalization of equation (67) to all multipole orders.

4. Prove from (71) that the angular momentum equation for a composite particle in an external field is:

$$\dot{\boldsymbol{s}}_k = \sum_{n=1}^{\infty} [n(\boldsymbol{\nabla}_k^{n-1} \vdots\, \overline{\boldsymbol{\mu}}_k^{(n)}) \wedge (\boldsymbol{E}_e + c^{-1}\boldsymbol{v}_k \wedge \boldsymbol{B}_e) + \boldsymbol{\nabla}_k^{n-1} \vdots\, \overline{\boldsymbol{\nu}}_k^{(n)} \wedge \boldsymbol{B}_e$$
$$+ (n-1)(\boldsymbol{\nabla}_k^{n-2} \vdots\, \overline{\boldsymbol{\nu}}_k^{(n)}\cdot\boldsymbol{B}_e) \wedge {}^{\leftarrow}\boldsymbol{\nabla}_k$$
$$+ c^{-1}(n-1)\{\boldsymbol{\nabla}_k^{n-2} \vdots\, \dot{\overline{\boldsymbol{\mu}}}_k^{(n)}\cdot\boldsymbol{B}_e - \boldsymbol{\nabla}_k^{n-2} \vdots\, \dot{\overline{\boldsymbol{\mu}}}_k^{(n)} : \mathbf{U}\boldsymbol{B}_e\}],$$

where $\mathbf{U}$ is the unit tensor of the second rank and where the field equations (53) have been used. Furthermore ${}^{\leftarrow}\boldsymbol{\nabla}_k$ is the nabla operator acting to the left. This equation is the generalization of (79) to all multipole orders.