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Centre of mass motion in non-relativistic quantum electrodynamics

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Abstract. Motion of the centres of mass of stable aggregates of charged particles is allowed for in the non-relativistic quantum theory of radiation by treating the coordinates and momenta of the nuclei along with those of the electrons as dynamical variables. (i) The quantum electrodynamical atomic field equations for the microscopic electric displacement vector \mathbf{d} and magnetic field \mathbf{h} are presented with the effects (ionic, free electronic and Röntgen currents) of arbitrary non-relativistic motion of the centres of mass of the stable aggregates included. The atomic field equations are derived from the Maxwell-Lorentz equations for the microscopic electric field \mathbf{e} and magnetic field \mathbf{b} that follow from use in the Heisenberg equations of motion of the conventional (minimal-coupling) Hamiltonian pertaining to a first-quantized system of electrons and nuclei. Here the stable aggregates may be ions, free electrons, atoms or molecules and, as such, need not be electrically neutral. (ii) For systems composed of molecules (or atoms) that are electrically neutral the multipolar Hamiltonian is obtained by carrying out the Power-Zienau-Woolley transformation on the coordinates and momenta of the nuclei as well as on those of the electrons; terms depending on the motion of the centre of mass of each molecule then appear explicitly in the Hamiltonian. These include a term representing the energy in the magnetic induction field of the polarization- and molecular velocity-dependent magnetization that is associated with the Röntgen current.

It is pointed out that the order of the operators, for example in the expression for the magnetization field, is completely prescribed by the formalism. It is furthermore emphasized that the multipolar Hamiltonian should, irrespectively of the fixity or mobility of the nuclei, be written as a functional of the vector potential \mathbf{a} and its canonically conjugate field $-(1/4\pi c)\mathbf{d}^\perp$, rather than of \mathbf{a} and $-(1/4\pi c)\mathbf{e}^\perp$, as is often done, since this latter procedure leads to incorrect equations of motion.

The relaxation of the fixed-nuclei constraint makes provision for translational motion of all the stable aggregates and for vibrational and rotational degrees of freedom of the nuclear frameworks of the molecules, but for the most part only the centre of mass motion is considered in detail. The separation of the translational motion from the internal motion and the explicit multipolar expansions in terms of internal coordinates and momenta are illustrated, however, by consideration of a two-particle neutral system (hydrogen atom).

1. Introduction and summary

This article contains an exposition of some aspects of the non-relativistic quantum theory of radiation that merit consideration when the coordinates and momenta of all material particles (nuclei as well as electrons) are treated on an equal footing as dynamical variables, so that the coordinates of the centre of mass and the components of the total momentum of each of the distinct stable aggregates into which the whole

collection of particles is supposed to be partitioned are also dynamical variables. The formalism outlined here in addition to giving the complete scheme of atomic field equations for an ensemble of ions, free electrons, atoms or molecules also comprises the multipolar Hamiltonian for systems composed solely of electrically neutral atoms or molecules, and is capable of dealing with effects due specifically to motion of the nuclei, such as the Doppler effect or the recoil of an atom or molecule that occurs when photons are emitted, scattered or absorbed.

The dynamical system consisting of the quantized radiation field in interaction with an arbitrary set of electrons and nuclei may be characterized (Fermi 1932, Heitler 1954, Dirac 1958, Kramers 1964, Power 1964) by the minimal-coupling Hamiltonian

$$\mathcal{H} = \frac{1}{8\pi} \int [(4\pi c \mathcal{P}(\mathbf{r}))^2 + (\text{curl } \mathbf{a}(\mathbf{r}))^2] d^3r + \sum_{\alpha} \frac{1}{2m_{\alpha}} \left(\mathbf{p}_{\alpha} - \frac{e_{\alpha}}{c} \mathbf{a}(\mathbf{q}_{\alpha}) \right)^2 + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{e_{\alpha} e_{\beta}}{|\mathbf{q}_{\alpha} - \mathbf{q}_{\beta}|} \quad (1.1)$$

together with the equal-time canonical commutators, of which only the following are possibly non-vanishing:

$$[q_{\alpha i}, p_{\beta j}] = i\hbar \delta_{\alpha\beta} \delta_{ij} \quad (1.2)$$

$$[a_i(\mathbf{r}), \mathcal{P}_j(\mathbf{r}')] = i\hbar \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{r}'). \quad (1.3)$$

The particle labelled α has charge e_{α} , mass m_{α} , position operator \mathbf{q}_{α} and conjugate momentum \mathbf{p}_{α} , while the vector potential $\mathbf{a}(\mathbf{r})$ is the 'coordinate' of the radiation field and $\mathcal{P}(\mathbf{r})$ is its conjugate momentum. Both \mathbf{a} and \mathcal{P} are transverse fields (Coulomb gauge), in agreement with the appearance of the transverse delta dyadic (Power 1964) on the right-hand side of equation (1.3), and in terms of \mathbf{a} the transverse electric and the magnetic induction fields are given by

$$\mathbf{e}^{\perp}(\mathbf{r}) = -\frac{1}{c} \dot{\mathbf{a}}(\mathbf{r}), \quad \mathbf{b}(\mathbf{r}) = \text{curl } \mathbf{a}(\mathbf{r}). \quad (1.4)$$

The equal-time commutators and the Hamiltonian \mathcal{H} characterize the system in the sense that knowledge of these is sufficient for explicitly deriving the Heisenberg equation of motion

$$\dot{\Omega} = \frac{1}{i\hbar} [\Omega, \mathcal{H}] \quad (1.5)$$

for any dynamical variable Ω , which is a function of the canonical coordinates and momenta. In particular, for the coordinates and momenta themselves the Heisenberg equations lead to the operator form of the Maxwell-Lorentz equations for the microscopic fields \mathbf{e} and \mathbf{b} as well as of Newton's law for the particles under the influence of the Lorentz force. The sources for \mathbf{e} and \mathbf{b} are the total charge and current densities due to all the charged particles. In the classical theory (de Groot 1969, de Groot and Suttrop 1972) those of the Maxwell-Lorentz equations that involve sources can be recast into equations—the so called atomic field equations—for the microscopic electric displacement vector \mathbf{d} and magnetic field \mathbf{h} whose sources are the ionic and free electronic charges and currents only. This is most easily done by relating the bound charge and current densities to the polarization and magnetization fields through the

use of certain distribution identities (Power and Thirunamachandran 1971). Semiclassical treatments of the atomic field equations have been given by de Groot and Suttorp (1972) and by Babiker *et al* (1973). In §2 of this paper an analogous procedure in the context of quantum electrodynamics is carried out. Babiker *et al* (1974) using the fixed-nuclei approximation and a second-quantized formalism to describe the electrons have considered within a quantum electrodynamical framework the atomic field equations for neutral atoms or molecules. The present paper is restricted to first-quantization of the particles but allows for motion of the nuclei. When the particle coordinates are quantum mechanical operators rather than c -numbers, two of the three distribution relations given by Power and Thirunamachandran (1971) are no longer generally valid as kinematical identities. However, they may be shown to hold (in a symmetrized form) as dynamical relations when the time derivatives are calculated as in equation (1.5) and the Hamiltonian is given by equation (1.1), and with their aid are derived the quantum electrodynamical atomic field equations with the effects (ionic, free electronic and Röntgen currents) of arbitrary non-relativistic motion of the centres of mass of the stable aggregates included.

If the material particles can be grouped into non-overlapping and electrically neutral atoms or molecules, then new coordinates and momenta may be introduced so as to render the Hamiltonian \mathcal{H} of equation (1.1) dependent on the electromagnetic fields rather than on the vector potential and so as to eliminate from it the instantaneous intermolecular Coulombic interaction. Each molecule then interacts through its multipole moments with the transverse fields and only through them, and hence in a purely retarded fashion, with the other molecules. The new coordinates and momenta are obtained from the old by a canonical transformation that was first given by Power and Zienau (1959) and has been generalized by Woolley (1971, 1975) and others (Babiker *et al* 1974, Babiker 1975a, b). In most of these works the nuclei have been regarded as being fixed in the observer's reference frame. Woolley (1971), while not regarding the nuclei as fixed, assumed that the centre of mass of each molecule is always stationary. In §3 the Power-Zienau-Woolley transformation is carried out on the coordinates and momenta of the nuclei as well as on those of the electrons and in such a fashion that terms depending on the motion of the centres of mass appear explicitly in the Hamiltonian. These include a term representing the energy in the magnetic induction field of a polarization- and molecular velocity-dependent magnetization whose curl is $1/c$ times the Röntgen current density and which is well known classically (de Groot 1969). Analogous terms arising from a contribution to the electric polarization from a moving magnetization are of order v^2/c^2 (v is the molecular speed) times the usual electric polarization term and, having a purely relativistic origin, do not appear in the treatment given here. The order of the operators in the expression for the multipolar Hamiltonian is prescribed by the canonical transformation. Thus the symmetrization of the magnetization field that makes it Hermitian does not have to be imposed as a separate assumption. Insertion of the multipolar Hamiltonian in the Heisenberg equation (1.5) for the vector potential shows that the new momentum conjugate to \mathbf{a} is $-(1/4\pi c)\mathbf{d}^\perp$ and hence that it is \mathbf{d}^\perp rather than \mathbf{e}^\perp that should appear in this Hamiltonian when written as a functional of the electromagnetic fields. This conclusion is valid generally and has nothing to do with the fixity or mobility of the nuclei. The atomic field equation that connects \mathbf{h} and \mathbf{d}^\perp follows directly, that is without use of the distribution relations, from the Heisenberg equation for the new field momentum. This was the method by which it was derived in the paper by Babiker *et al* (1974) referred to above. Since the multipolar Hamiltonian is applicable only to neutral systems, an

atomic field equation obtained through its use must likewise be restricted to materials from which ions and free electrons are absent, but it may include the effect of the Röntgen current when, as here, each neutral atom or molecule as a whole is movable.

The relaxation of the fixed-nuclei constraint makes provision not only for translational motion of all the stable aggregates but also, insofar as it is meaningful to separate the nuclear and electronic motions, for vibrational and rotational degrees of freedom of the nuclear frameworks of the molecules. The detailed specification of the internal coordinate systems will not be given here. However, a simple illustration of the separation of the centre of mass motion from the internal motion and the explicit multipolar expansions in terms of internal coordinates and momenta is afforded by a two-particle system (hydrogen atom) and this will be discussed in § 3.3.

2. Atomic field equations

To begin the derivation of the atomic field equations the Heisenberg equations for the coordinates and momenta are first written down and are shown to lead to Newton's law with the Lorentz force and to the Maxwell-Lorentz field equations. From the latter the atomic field equations are obtained with the aid of the distribution relations; these are listed and their validity in a quantum mechanical context is commented on in an appendix. The Schrödinger picture will be used throughout, so that, there being no external fields, all operators are constant in time. The time derivative of an operator Ω is then *defined* by equation (1.5) and is such that

$$\langle \psi_1(t) | \dot{\Omega} | \psi_2(t) \rangle = \frac{d}{dt} \langle \psi_1(t) | \Omega | \psi_2(t) \rangle \quad (2.1)$$

for any two solutions of the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \mathcal{H} |\psi(t)\rangle. \quad (2.2)$$

2.1. Heisenberg equations with minimal-coupling Hamiltonian

In the Hamiltonian formalism relations between the operators other than those given in equations (1.1) to (1.3) must be derived from the equations of motion. However, the restrictions $\text{div } \mathbf{a} = 0$ and $\text{div } \mathcal{P} = 0$ can be imposed from the outset, if in application of Hamilton's principle the variations of \mathbf{a} and \mathcal{P} also are circumscribed by the transversality condition (Power 1964). In addition, and as a consequence of the Coulomb gauge, the transverse fields are defined in terms of the vector potential by equations (1.4) and the longitudinal electric field is a definite function of the particle coordinates:

$$\mathbf{e}^{\parallel}(\mathbf{r}) = -\text{grad} \sum_{\alpha} \frac{e_{\alpha}}{|\mathbf{r} - \mathbf{q}_{\alpha}|}. \quad (2.3)$$

For the vector potential evaluated at a field point \mathbf{r} the equation of motion is

$$\dot{\mathbf{a}}_i(\mathbf{r}) = 4\pi c^2 \int \mathcal{P}_j(\mathbf{r}') \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{r}') d^3 r' = 4\pi c^2 \mathcal{P}_i(\mathbf{r}), \quad (2.4)$$

since \mathcal{P} is transverse. Similarly, since \mathbf{a} is transverse, the equation for $\mathcal{P}(\mathbf{r})$ is

$$\dot{\mathcal{P}}_i(\mathbf{r}) = -\frac{1}{4\pi}(\text{curl curl } \mathbf{a}(\mathbf{r}))_i + \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}c} \left(p_{\alpha j} - \frac{e_{\alpha}}{c} a_j(\mathbf{q}_{\alpha}) \right) \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{q}_{\alpha}). \quad (2.5)$$

If \mathbf{a} is evaluated at a particle point \mathbf{q}_{α} , there is an extra term in its time derivative, and then

$$\dot{a}_i(\mathbf{q}_{\alpha}) = 4\pi c^2 \mathcal{P}_i(\mathbf{q}_{\alpha}) + \frac{1}{2m_{\alpha}} \left[\frac{\partial a_i(\mathbf{q}_{\alpha})}{\partial q_{\alpha j}} \left(p_{\alpha j} - \frac{e_{\alpha}}{c} a_j(\mathbf{q}_{\alpha}) \right) + \left(p_{\alpha j} - \frac{e_{\alpha}}{c} a_j(\mathbf{q}_{\alpha}) \right) \frac{\partial a_i(\mathbf{q}_{\alpha})}{\partial q_{\alpha j}} \right]. \quad (2.6)$$

The equations for the particle coordinates and momenta are, respectively,

$$\dot{q}_{\alpha i} = \frac{1}{m_{\alpha}} \left(p_{\alpha i} - \frac{e_{\alpha}}{c} a_i(\mathbf{q}_{\alpha}) \right) \quad (2.7)$$

and

$$\dot{p}_{\alpha i} = \frac{e_{\alpha}}{m_{\alpha}c} \left(p_{\alpha j} - \frac{e_{\alpha}}{c} a_j(\mathbf{q}_{\alpha}) \right) \frac{\partial a_j(\mathbf{q}_{\alpha})}{\partial q_{\alpha i}} + e_{\alpha} \sum_{\beta \neq \alpha} \frac{e_{\beta}(q_{\alpha i} - q_{\beta i})}{|\mathbf{q}_{\alpha} - \mathbf{q}_{\beta}|^3}. \quad (2.8)$$

Finally, the time derivative of the longitudinal electric field evaluated at a field point is, from equation (2.3),

$$\dot{e}_i^{\parallel}(\mathbf{r}) = -4\pi \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \left[\left(p_{\alpha j} - \frac{e_{\alpha}}{c} a_j(\mathbf{q}_{\alpha}) \right) \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_{\alpha}) + \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_{\alpha}) \left(p_{\alpha j} - \frac{e_{\alpha}}{c} a_j(\mathbf{q}_{\alpha}) \right) \right] \quad (2.9)$$

where the expression

$$\delta_{ij}^{\parallel}(\mathbf{r}) = -\frac{1}{4\pi} \partial_i \partial_j \frac{1}{r} \equiv -\frac{1}{4\pi} \frac{\partial^2}{\partial r_i \partial r_j} \frac{1}{r} \quad (2.10)$$

for the longitudinal delta dyadic has been used.

2.2. Maxwell-Lorentz equations and Newton's law

Because of the relations (1.4) and the Coulomb gauge condition the source-free Maxwell-Lorentz equations

$$\text{div } \mathbf{b} = 0, \quad \text{curl } \mathbf{e}^{\perp} = -\frac{1}{c} \dot{\mathbf{b}} \quad (2.11)$$

are identically satisfied. Furthermore, the divergence of the longitudinal electric field is given immediately from equation (2.3) as

$$\text{div } \mathbf{e}^{\parallel}(\mathbf{r}) = 4\pi \sum_{\alpha} e_{\alpha} \delta(\mathbf{r} - \mathbf{q}_{\alpha}). \quad (2.12)$$

The expression (2.9) for the time derivative of this field leads, in view of equation (2.7), to

$$0 = \frac{4\pi}{c} \mathbf{j}^{\parallel} + \frac{1}{c} \dot{\mathbf{e}}^{\parallel} \quad (2.13)$$

where the longitudinal current density is given by

$$j_i^{\parallel}(\mathbf{r}) = \frac{1}{2} \sum_{\alpha} e_{\alpha} \left(\dot{q}_{\alpha j} \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_{\alpha}) + \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_{\alpha}) \dot{q}_{\alpha j} \right). \quad (2.14)$$

The transverse counterpart of equation (2.13) follows from the equations of motion (2.4), (2.5) and (2.7). Thus

$$\frac{1}{2} \ddot{a}_i(\mathbf{r}) = -(\text{curl curl } \mathbf{a}(\mathbf{r}))_i + \frac{4\pi}{c} \sum_{\alpha} e_{\alpha} \dot{q}_{\alpha j} \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{q}_{\alpha}) \quad (2.15)$$

which, in conjunction with equations (1.4), gives

$$\text{curl } \mathbf{b} = \frac{4\pi}{c} \mathbf{j}^{\perp} + \frac{1}{c} \dot{\mathbf{e}}^{\perp} \quad (2.16)$$

where the transverse current density is

$$j_i^{\perp}(\mathbf{r}) = \sum_{\alpha} e_{\alpha} \dot{q}_{\alpha j} \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{q}_{\alpha}). \quad (2.17)$$

In summary, the Maxwell-Lorentz field equations, their longitudinal and transverse parts being written separately, are

$$\text{div } \mathbf{e}^{\parallel} = 4\pi\rho \quad (2.18)$$

$$\text{curl } \mathbf{e}^{\perp} = -\frac{1}{c} \dot{\mathbf{b}} \quad (2.19)$$

$$\text{div } \mathbf{b} = 0 \quad (2.20)$$

$$\text{curl } \mathbf{b} = \frac{4\pi}{c} \mathbf{j}^{\perp} + \frac{1}{c} \dot{\mathbf{e}}^{\perp} \quad (2.21a)$$

$$0 = \frac{4\pi}{c} j^{\parallel} + \frac{1}{c} \dot{\mathbf{e}}^{\parallel} \quad (2.21b)$$

and are valid as operator equations with the charge and current density operators

$$\rho(\mathbf{r}) = \sum_{\alpha} e_{\alpha} \delta(\mathbf{r} - \mathbf{q}_{\alpha}) \quad (2.22)$$

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2} \sum_{\alpha} e_{\alpha} (\dot{\mathbf{q}}_{\alpha} \delta(\mathbf{r} - \mathbf{q}_{\alpha}) + \delta(\mathbf{r} - \mathbf{q}_{\alpha}) \dot{\mathbf{q}}_{\alpha}). \quad (2.23)$$

The operator equation of motion for the material particles under the influence of the electromagnetic fields is obtained from equations (2.6) to (2.8) and is

$$m_{\alpha} \ddot{q}_{\alpha i} = \frac{e_{\alpha}}{c} \dot{q}_{\alpha j} \frac{\partial a_j(\mathbf{q}_{\alpha})}{\partial q_{\alpha i}} + e_{\alpha} e_i^{\parallel}(\mathbf{q}_{\alpha}) - \frac{e_{\alpha}}{2c} \left(\dot{q}_{\alpha j} \frac{\partial a_i(\mathbf{q}_{\alpha})}{\partial q_{\alpha j}} + \frac{\partial a_i(\mathbf{q}_{\alpha})}{\partial q_{\alpha j}} \dot{q}_{\alpha j} \right) + e_{\alpha} e_i^{\perp}(\mathbf{q}_{\alpha}). \quad (2.24)$$

This may be written as

$$m_{\alpha} \ddot{q}_{\alpha} = e_{\alpha} \left[\mathbf{e}(\mathbf{q}_{\alpha}) + \frac{1}{2} \left(\frac{\dot{\mathbf{q}}_{\alpha}}{c} \times \mathbf{b}(\mathbf{q}_{\alpha}) - \mathbf{b}(\mathbf{q}_{\alpha}) \times \frac{\dot{\mathbf{q}}_{\alpha}}{c} \right) \right] \quad (2.25)$$

in which form it is recognizable as Newton's law with the Lorentz force.

The derivation of the equations of motion has been gone into in some detail in order to emphasize that there is no ambiguity in the order of the non-commuting operators $p_{\alpha i}$ and $q_{\alpha i}$. Because of the transverse nature of \mathbf{a} this order is immaterial in the

Hamiltonian itself or in, for example, equation (2.8), and because of the transverse nature of $\delta_{ij}^+(\mathbf{r})$ it is immaterial also in the expression for the transverse current density. In the expressions for the longitudinal current density and for the Lorentz force the order is significant but is completely prescribed by the formalism. There is thus no need here to take a 'symmetric average' as is often done when ambiguities as to the order of operators arise on going over from a classical to a quantum theory.

2.3. Atomic field equations

It is now supposed that the collection of particles can be regarded as being made up of distinct stable aggregates (free electrons, ions, neutral atoms or neutral molecules). The aggregates are labelled ξ and their constituent particles $\alpha(\xi)$. Thus particle $\alpha(\xi)$ has mass $m_{\alpha(\xi)}$, charge $e_{\alpha(\xi)}$, position operator $\mathbf{q}_{\alpha(\xi)}$ and momentum operator $\mathbf{p}_{\alpha(\xi)}$. As mentioned in the introduction, the atomic field equations that involve sources relate the microscopic electric displacement and magnetic field vectors to the ionic and free electronic charges and currents. These charges and currents are associated with a privileged 'central point' $\mathbf{R}(\xi)$ in aggregate ξ and similarly the polarization and magnetization fields, in terms of which the bound charges and currents are incorporated into the scheme, are defined as expansions about $\mathbf{R}(\xi)$. Here this privileged point is consistently taken to be the centre of mass of the aggregate:

$$\mathbf{R}(\xi) = \sum_{\alpha(\xi)} \frac{m_{\alpha(\xi)}}{M(\xi)} \mathbf{q}_{\alpha(\xi)}, \quad (2.26)$$

and, being a function of the dynamical variables $\mathbf{q}_{\alpha(\xi)}$, is itself a dynamical variable. In equation (2.26) $M(\xi)$ is the total mass of aggregate ξ . The total momentum of the aggregate, which is given by

$$\mathbf{P}(\xi) = \sum_{\alpha(\xi)} \mathbf{p}_{\alpha(\xi)}, \quad (2.27)$$

is canonically conjugate to $\mathbf{R}(\xi)$, as may easily be verified from equation (1.2).

The electric polarization field of aggregate ξ is defined (Power and Thirunmachandran 1971) by

$$\mathbf{p}^{(\xi)}(\mathbf{r}) = \sum_{\alpha(\xi)} e_{\alpha(\xi)} (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \int_0^1 \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta. \quad (2.28)$$

Because of the choice of $\mathbf{R}(\xi)$ made here, this field vanishes if the 'aggregate' is merely a free electron or an ion consisting of a single nucleus. For the position and the centre of mass of a point object necessarily coincide. The total polarization field is defined by

$$\mathbf{p}(\mathbf{r}) = \sum_{\xi} \mathbf{p}^{(\xi)}(\mathbf{r}). \quad (2.29)$$

With the aid of the distribution relation (A.1) the first Maxwell-Lorentz equation may now be written

$$\begin{aligned} \operatorname{div} \mathbf{e}^{\parallel}(\mathbf{r}) &= 4\pi \sum_{\xi} \sum_{\alpha(\xi)} e_{\alpha(\xi)} \delta(\mathbf{r} - \mathbf{R}(\xi)) \\ &\quad - 4\pi \partial_i \sum_{\xi} \sum_{\alpha(\xi)} e_{\alpha(\xi)} (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))_j \int_0^1 \delta_{ij}^{\parallel}[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \\ &= 4\pi \sum_{\xi} Q(\xi) \delta(\mathbf{r} - \mathbf{R}(\xi)) - 4\pi \operatorname{div} \mathbf{p}^{\parallel}(\mathbf{r}) \end{aligned} \quad (2.30)$$

where $Q(\xi)$ is the total charge of aggregate ξ . If the microscopic electric displacement vector \mathbf{d} is introduced as

$$\mathbf{d} = \mathbf{e} + 4\pi\mathbf{p}, \quad (2.31)$$

then equation (2.30) becomes

$$\text{div } \mathbf{d}^{\parallel} = 4\pi \sum_{\xi} Q(\xi) \delta(\mathbf{r} - \mathbf{R}(\xi)) = 4\pi(\rho_{\text{ionic}} + \rho_{\text{free}}), \quad (2.32)$$

which shows that the sources of \mathbf{d} are the ‘true’ (ionic and free electronic) charges, whereas those of \mathbf{e} include the polarization charges whose density is $-\text{div } \mathbf{p}^{\parallel}$. Equation (2.32) is the first of the atomic field equations.

In terms of the contributions from the separate aggregates ξ the longitudinal current density of equation (2.14) is

$$\mathbf{j}_i^{\parallel}(\mathbf{r}) = \frac{1}{2} \sum_{\xi} \sum_{\alpha(\xi)} e_{\alpha(\xi)} (\dot{q}_{\alpha(\xi)j} \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_{\alpha(\xi)}) + \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_{\alpha(\xi)}) \dot{q}_{\alpha(\xi)j}). \quad (2.33)$$

The distribution relation (A.2) then gives

$$\begin{aligned} \mathbf{j}_i^{\parallel}(\mathbf{r}) &= \frac{1}{2} \sum_{\xi} Q(\xi) [\dot{\mathbf{R}}_j(\xi) \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{R}(\xi)) + \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{R}(\xi)) \dot{\mathbf{R}}_j(\xi)] \\ &\quad + \frac{\partial}{\partial t} \sum_{\xi} \sum_{\alpha(\xi)} e_{\alpha(\xi)} (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))_j \int_0^1 \delta_{ij}^{\parallel}[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \\ &= (\mathbf{j}_{\text{ionic}}^{\parallel} + \mathbf{j}_{\text{free}}^{\parallel})_i + \dot{\mathbf{p}}_i^{\parallel}. \end{aligned} \quad (2.34)$$

Insertion of this into equation (2.21b) leads to the atomic field equation (2.35) corresponding to the longitudinal part of the fourth Maxwell–Lorentz equation:

$$0 = \frac{4\pi}{c} (\mathbf{j}_{\text{ionic}}^{\parallel} + \mathbf{j}_{\text{free}}^{\parallel}) + \frac{1}{c} \dot{\mathbf{d}}^{\parallel}. \quad (2.35)$$

The transverse part of this equation is obtained with the help of the relation (A.3). Firstly, the transverse current density is

$$\mathbf{j}^{\perp} = \mathbf{j}_{\text{ionic}}^{\perp} + \mathbf{j}_{\text{free}}^{\perp} + \dot{\mathbf{p}}^{\perp} + c \text{curl } \mathbf{m}_{\text{total}} \quad (2.36)$$

where the ‘true’ transverse current density is given by

$$(\mathbf{j}_{\text{ionic}}^{\perp} + \mathbf{j}_{\text{free}}^{\perp})_i = \sum_{\xi} Q(\xi) \dot{\mathbf{R}}_j(\xi) \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{R}(\xi)) \quad (2.37)$$

and the total magnetization field by

$$\begin{aligned} \mathbf{m}_{\text{total}}(\mathbf{r}) &= \sum_{\xi} \sum_{\alpha(\xi)} \frac{e_{\alpha(\xi)}}{2c} \left((\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times (\dot{\mathbf{q}}_{\alpha(\xi)} - \dot{\mathbf{R}}(\xi)) \int_0^1 \theta \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \right. \\ &\quad + \int_0^1 \theta \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times (\dot{\mathbf{q}}_{\alpha(\xi)} - \dot{\mathbf{R}}(\xi)) \\ &\quad + (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \int_0^1 \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \times \dot{\mathbf{R}}(\xi) \\ &\quad \left. - \dot{\mathbf{R}}(\xi) \times (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \int_0^1 \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \right). \end{aligned} \quad (2.38)$$

Substitution of the expression (2.36) for \mathbf{j}^\perp in the transverse part of the fourth Maxwell–Lorentz equation then yields the atomic field equation

$$\text{curl } \mathbf{h} = \frac{4\pi}{c} (\mathbf{j}_{\text{ionic}}^\perp + \mathbf{j}_{\text{free}}^\perp) + \frac{1}{c} \dot{\mathbf{d}}^\perp \quad (2.39)$$

with the auxiliary magnetic field \mathbf{h} being defined (de Groot 1969) by

$$\mathbf{h} = \mathbf{b} - 4\pi \mathbf{m}_{\text{total}}. \quad (2.40)$$

The total current density is given, from equations (2.34) and (2.36), by

$$\mathbf{j} = \mathbf{j}_{\text{ionic}} + \mathbf{j}_{\text{free}} + \dot{\mathbf{p}} + c \text{curl } \mathbf{m}_{\text{total}} \quad (2.41)$$

and is the sum of the ionic, free electronic, polarization and total magnetization current densities. The last of these includes the Röntgen current density

$$\mathbf{j}_{\text{Röntgen}}(\mathbf{r}) = \text{curl } \frac{1}{2} \sum_{\xi} (\mathbf{p}^{(\xi)}(\mathbf{r}) \times \dot{\mathbf{R}}(\xi) - \dot{\mathbf{R}}(\xi) \times \mathbf{p}^{(\xi)}(\mathbf{r})) \quad (2.42)$$

which arises from the contribution to the total magnetization field from the polarization fields of the moving aggregates.

Finally, since the source-free Maxwell–Lorentz equations are unaffected by the introduction of the polarization and magnetization fields, the complete scheme of quantum electrodynamical atomic field equations may now be gathered together to read

$$\text{div } \mathbf{d}^\parallel = 4\pi(\rho_{\text{ionic}} + \rho_{\text{free}}) \quad (2.43)$$

$$\text{curl } \mathbf{e}^\perp = -\frac{1}{c} \dot{\mathbf{b}} \quad (2.44)$$

$$\text{div } \mathbf{b} = 0 \quad (2.45)$$

$$\text{curl } \mathbf{h} = \frac{4\pi}{c} (\mathbf{j}_{\text{ionic}}^\perp + \mathbf{j}_{\text{free}}^\perp) + \frac{1}{c} \dot{\mathbf{d}}^\perp \quad (2.46a)$$

$$0 = \frac{4\pi}{c} (\mathbf{j}_{\text{ionic}}^\parallel + \mathbf{j}_{\text{free}}^\parallel) + \frac{1}{c} \dot{\mathbf{d}}^\parallel. \quad (2.46b)$$

3. Multipolar Hamiltonian

3.1. The Power–Zienau–Woolley transformation

In this section the Power–Zienau–Woolley transformation is carried out on the Hamiltonian of equation (1.1). If, as will now be assumed, the stable aggregates ξ are electrically neutral, then this transformation makes the Hamiltonian depend directly on the electromagnetic fields rather than on the vector potential and also eliminates the instantaneous interaggregate Coulombic interaction. When the labels of the separate aggregates (henceforth called molecules) are explicitly introduced, the Hamiltonian

may be written

$$\mathcal{H} = \frac{1}{8\pi} \int [(4\pi c \mathcal{P}(\mathbf{r}))^2 + (\text{curl } \mathbf{a}(\mathbf{r}))^2] d^3r + \sum_{\xi} \sum_{\alpha(\xi)} \frac{1}{2m_{\alpha(\xi)}} \left(\mathbf{p}_{\alpha(\xi)} - \frac{e_{\alpha(\xi)}}{c} \mathbf{a}(\mathbf{q}_{\alpha(\xi)}) \right)^2 + \frac{1}{2} \sum_{\xi \neq \eta} \sum_{\alpha(\xi)} \sum_{\beta(\eta)} \frac{e_{\alpha(\xi)} e_{\beta(\eta)}}{|\mathbf{q}_{\alpha(\xi)} - \mathbf{q}_{\beta(\eta)}|} + \frac{1}{2} \sum_{\xi} \sum_{\alpha(\xi) \neq \beta(\xi)} \frac{e_{\alpha(\xi)} e_{\beta(\xi)}}{|\mathbf{q}_{\alpha(\xi)} - \mathbf{q}_{\beta(\xi)}|} \quad (3.1)$$

where the last two terms give the intermolecular and intramolecular Coulombic energies, respectively. \mathcal{H} is to be expressed in terms of new variables $\bar{\Omega}$ obtained from the old through the canonical transformation

$$\Omega = U \bar{\Omega} U^{-1} \quad (3.2)$$

with the unitary operator U being given by

$$U = e^{\Gamma} \quad (3.3)$$

and the generating function Γ by

$$\Gamma = -\frac{i}{\hbar c} \int \mathbf{p}(\mathbf{r}) \cdot \mathbf{a}(\mathbf{r}) d^3r. \quad (3.4)$$

The new coordinates and momenta satisfy the same equal-time commutation relations as the old and are Hermitian.

The old coordinates commute with U and so are unaffected by the transformation. Thus

$$\mathbf{a}(\mathbf{r}) = \bar{\mathbf{a}}(\mathbf{r}) \quad (3.5)$$

$$\mathbf{q}_{\alpha(\xi)} = \bar{\mathbf{q}}_{\alpha(\xi)}. \quad (3.6)$$

For the field momentum the commutation relation (1.3) and the operator identity

$$e^{\Gamma} 0 e^{-\Gamma} = 0 + [\Gamma, 0] + \frac{1}{2!} [\Gamma, [\Gamma, 0]] + \dots \quad (3.7)$$

give (Power and Zienau 1959)

$$e^{\Gamma} \bar{\mathcal{P}}_i(\mathbf{r}) e^{-\Gamma} = \bar{\mathcal{P}}_i(\mathbf{r}) + [\Gamma, \bar{\mathcal{P}}_i(\mathbf{r})], \quad (3.8)$$

since

$$[\Gamma, \bar{\mathcal{P}}_i(\mathbf{r})] = \frac{1}{c} p_i^{\perp}(\mathbf{r}), \quad (3.9)$$

which commutes with Γ . Thus

$$\mathcal{P}(\mathbf{r}) = \bar{\mathcal{P}}(\mathbf{r}) + \frac{1}{c} \mathbf{p}^{\perp}(\mathbf{r}). \quad (3.10)$$

To transform the particle momenta the commutator $[\Gamma, \bar{\mathbf{p}}_{\alpha(\xi)}]$ is first computed.

Equations (3.4) and (3.6) together with the expression (2.28) for the polarization field give

$$\begin{aligned}
 [\Gamma, \bar{\mathbf{p}}_{\alpha(\xi)}] &= i\hbar \frac{\partial \Gamma}{\partial \mathbf{q}_{\alpha(\xi)}} \\
 &= \frac{e_{\alpha(\xi)}}{c} \mathbf{a}(\mathbf{q}_{\alpha(\xi)}) + \frac{e_{\alpha(\xi)}}{c} \int_0^1 \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times \text{curl } \mathbf{a}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \\
 &\quad + \frac{m_{\alpha(\xi)}}{M(\xi)} \sum_{\beta(\xi)} \frac{e_{\beta(\xi)}}{c} \int_0^1 (1-\theta)(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi)) \times \text{curl } \mathbf{a}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi))] d\theta \\
 &\quad - \frac{m_{\alpha(\xi)}}{M(\xi)} \frac{Q(\xi)}{c} \mathbf{a}(\mathbf{R}(\xi)) \tag{3.11}
 \end{aligned}$$

where

$$\text{curl } \mathbf{a}(\mathbf{x}) \equiv (\text{curl } \mathbf{a}(\mathbf{r}))_{\mathbf{r}=\mathbf{x}}. \tag{3.12}$$

Since $[\Gamma, \bar{\mathbf{p}}_{\alpha(\xi)}]$ commutes with Γ , it follows from the identity (3.7) that

$$\begin{aligned}
 \mathbf{p}_{\alpha(\xi)} &= \bar{\mathbf{p}}_{\alpha(\xi)} + [\Gamma, \bar{\mathbf{p}}_{\alpha(\xi)}] \\
 &= \bar{\mathbf{p}}_{\alpha(\xi)} + \frac{e_{\alpha(\xi)}}{c} \mathbf{a}(\mathbf{q}_{\alpha(\xi)}) + \frac{e_{\alpha(\xi)}}{c} \int_0^1 \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times \text{curl } \mathbf{a}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \\
 &\quad + \frac{m_{\alpha(\xi)}}{M(\xi)} \sum_{\beta(\xi)} \frac{e_{\beta(\xi)}}{c} \int_0^1 (1-\theta)(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi)) \times \text{curl } \mathbf{a}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi))] d\theta \tag{3.13}
 \end{aligned}$$

where the term proportional to $Q(\xi)$ has, because of the assumed neutrality of the molecules, been omitted. The β sum in equation (3.13) gives the extra terms, over and above those obtained by Woolley (1971), which are due to the motion of $\mathbf{R}(\xi)$ and which vanish if $\mathbf{R}(\xi)$ is a fixed c -number rather than a function of the $\mathbf{q}_{\beta(\xi)}$.

Insertion of the expressions (3.10) and (3.13) into equation (3.1) gives the Hamiltonian in terms of the new variables as

$$\begin{aligned}
 \mathcal{H} &= \frac{1}{8\pi} \int [(4\pi c \bar{\mathcal{P}}(\mathbf{r}))^2 + (\text{curl } \mathbf{a}(\mathbf{r}))^2] d^3r + 4\pi c \int \mathbf{p}^{\perp}(\mathbf{r}) \cdot \bar{\mathcal{P}}(\mathbf{r}) d^3r + 2\pi \int (\mathbf{p}^{\perp}(\mathbf{r}))^2 d^3r \\
 &\quad + \sum_{\xi} \sum_{\alpha(\xi)} \frac{1}{2m_{\alpha(\xi)}} \left(\bar{\mathbf{p}}_{\alpha(\xi)} + \frac{e_{\alpha(\xi)}}{c} \int_0^1 \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times \text{curl } \mathbf{a}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \right. \\
 &\quad \left. + \frac{m_{\alpha(\xi)}}{M(\xi)} \sum_{\beta(\xi)} \frac{e_{\beta(\xi)}}{c} \int_0^1 (1-\theta)(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi)) \times \text{curl } \mathbf{a}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi))] d\theta \right)^2 \\
 &\quad + \frac{1}{2} \sum_{\xi \neq \eta} \sum_{\alpha(\xi)} \sum_{\beta(\eta)} \frac{e_{\alpha(\xi)} e_{\beta(\eta)}}{|\mathbf{q}_{\alpha(\xi)} - \mathbf{q}_{\beta(\eta)}|} + \frac{1}{2} \sum_{\xi} \sum_{\alpha(\xi) \neq \beta(\xi)} \frac{e_{\alpha(\xi)} e_{\beta(\xi)}}{|\mathbf{q}_{\alpha(\xi)} - \mathbf{q}_{\beta(\xi)}|}. \tag{3.14}
 \end{aligned}$$

The fourth term here is, as some long but straightforward manipulation shows, the sum

of a kinetic energy term $\sum_{\xi} \sum_{\alpha(\xi)} \bar{\mathbf{p}}_{\alpha(\xi)}^2 / 2m_{\alpha(\xi)}$ and an interaction energy term

$$\begin{aligned}
 & - \int \mathbf{m}(\mathbf{r}) \cdot \text{curl } \mathbf{a}(\mathbf{r}) \, d^3r - \frac{1}{2} \sum_{\xi} \int \left(\mathbf{p}^{(\xi)}(\mathbf{r}) \times \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} - \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} \times \mathbf{p}^{(\xi)}(\mathbf{r}) \right) \cdot \text{curl } \mathbf{a}(\mathbf{r}) \, d^3r \\
 & + \frac{1}{2} \iint o_{ij}(\mathbf{r}, \mathbf{r}') (\text{curl } \mathbf{a}(\mathbf{r}))_i (\text{curl}' \mathbf{a}(\mathbf{r}'))_j \, d^3r \, d^3r' \\
 & + \sum_{\xi} \frac{1}{2M(\xi)c^2} \left(\int \mathbf{p}^{(\xi)}(\mathbf{r}) \times \text{curl } \mathbf{a}(\mathbf{r}) \, d^3r \right)^2 \\
 & - \sum_{\xi} \frac{1}{2M(\xi)c^2} \left(\int \mathbf{p}'^{(\xi)}(\mathbf{r}) \times \text{curl } \mathbf{a}(\mathbf{r}) \, d^3r \right)^2 \tag{3.15}
 \end{aligned}$$

in which the magnetization field is defined by

$$\begin{aligned}
 \mathbf{m}(\mathbf{r}) = & \sum_{\xi} \sum_{\alpha(\xi)} \frac{e_{\alpha(\xi)}}{2c} \int_0^1 \theta \left[(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times \left(\frac{\bar{\mathbf{p}}_{\alpha(\xi)}}{m_{\alpha(\xi)}} - \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)} \right) \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] \right. \\
 & \left. + \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times \left(\frac{\bar{\mathbf{p}}_{\alpha(\xi)}}{m_{\alpha(\xi)}} - \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)} \right) \right] d\theta, \tag{3.16}
 \end{aligned}$$

the diamagnetic tensor field by

$$\begin{aligned}
 o_{ij}(\mathbf{r}, \mathbf{r}') = & \sum_{\xi} \sum_{\alpha(\xi)} \frac{e_{\alpha(\xi)}^2}{m_{\alpha(\xi)} c^2} [(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))^2 \delta_{ij} - (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))_i (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))_j] \\
 & \times \int_0^1 \theta \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \\
 & \times \int_0^1 \theta' \delta[\mathbf{r}' - \mathbf{R}(\xi) - \theta'(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta' \tag{3.17}
 \end{aligned}$$

and the 'reduced' polarization field by

$$\mathbf{p}'(\mathbf{r}) = \sum_{\xi} \sum_{\alpha(\xi)} e_{\alpha(\xi)} (\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \int_0^1 \theta \delta[\mathbf{r} - \mathbf{R}(\xi) - \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta. \tag{3.18}$$

Here again the order of the operators is prescribed and, analogously to equation (2.27),

$$\bar{\mathbf{P}}(\xi) = \sum_{\alpha(\xi)} \bar{\mathbf{p}}_{\alpha(\xi)}. \tag{3.19}$$

The expression (3.18) for the field $\mathbf{p}'(\mathbf{r})$ is similar to that for the ordinary polarization field $\mathbf{p}(\mathbf{r})$, but the θ integrand has an extra factor of θ , which leads to reduced multipole moments (cf equation (3.48) below). The contribution (3.15) to the Hamiltonian will be shown in the following subsection to represent the energy in the magnetic induction field of the *total* magnetization field defined in equation (2.38).

The longitudinal polarization field $\mathbf{p}^{(\xi)\parallel}(\mathbf{r})$ of a neutral molecule ξ is given, according to equations (2.10) and (2.28), by

$$\mathbf{p}^{(\xi)\parallel}(\mathbf{r}) = \frac{1}{4\pi} \text{grad} \sum_{\alpha(\xi)} \frac{e_{\alpha(\xi)}}{|\mathbf{r} - \mathbf{q}_{\alpha(\xi)}|}. \quad (3.20)$$

This fact may be used (Woolley 1971) to eliminate from the Hamiltonian the intermolecular Coulombic energy, since

$$\frac{1}{2} \sum_{\xi \neq \eta} \sum_{\alpha(\xi)} \sum_{\beta(\eta)} \frac{e_{\alpha(\xi)} e_{\beta(\eta)}}{|\mathbf{q}_{\alpha(\xi)} - \mathbf{q}_{\beta(\eta)}|} = 2\pi \sum_{\xi \neq \eta} \int \mathbf{p}^{(\xi)\parallel}(\mathbf{r}) \cdot \mathbf{p}^{(\eta)\parallel}(\mathbf{r}) d^3r, \quad (3.21)$$

as follows from equation (3.20) and integration by parts. The third term of the expression (3.14) for \mathcal{H} may be decomposed to give

$$2\pi \int (\mathbf{p}^{\perp}(\mathbf{r}))^2 d^3r = 2\pi \sum_{\xi} \int (\mathbf{p}^{(\xi)\perp}(\mathbf{r}))^2 d^3r + 2\pi \sum_{\xi \neq \eta} \int \mathbf{p}^{(\xi)\perp}(\mathbf{r}) \cdot \mathbf{p}^{(\eta)\perp}(\mathbf{r}) d^3r \quad (3.22)$$

and addition of the right-hand side of this to the Coulomb energy (3.21) yields

$$2\pi \sum_{\xi} \int (\mathbf{p}^{(\xi)\perp}(\mathbf{r}))^2 d^3r + 2\pi \sum_{\xi \neq \eta} \int \mathbf{p}^{(\xi)}(\mathbf{r}) \cdot \mathbf{p}^{(\eta)}(\mathbf{r}) d^3r, \quad (3.23)$$

because the integral of the scalar product of a longitudinal and a transverse vector field vanishes, if the fields drop off sufficiently rapidly at infinity. The first part of the expression (3.23) is a sum over self-energies of the individual molecules and its effect is important when the multipolar Hamiltonian is used in carrying out the non-relativistic mass renormalization programme (Power and Zienau 1959). The second part of the expression (3.23) is a contact term which can be neglected unless different molecules overlap significantly, since, in contrast to their transverse or longitudinal parts, the polarization fields $\mathbf{p}^{(\xi)}(\mathbf{r})$ are of a local character.

The Hamiltonian \mathcal{H} may therefore finally be written in its multipolar form as

$$\begin{aligned} \mathcal{H} = & \frac{1}{8\pi} \int [(4\pi c \bar{\mathcal{P}}(\mathbf{r}))^2 + (\text{curl } \mathbf{a}(\mathbf{r}))^2] d^3r + \sum_{\xi} \sum_{\alpha(\xi)} \frac{1}{2m_{\alpha(\xi)}} \bar{\mathbf{p}}_{\alpha(\xi)}^2 + \frac{1}{2} \sum_{\xi} \sum_{\alpha(\xi) \neq \beta(\xi)} \frac{e_{\alpha(\xi)} e_{\beta(\xi)}}{|\mathbf{q}_{\alpha(\xi)} - \mathbf{q}_{\beta(\xi)}|} \\ & + 4\pi c \int \mathbf{p}(\mathbf{r}) \cdot \bar{\mathcal{P}}(\mathbf{r}) d^3r - \int \mathbf{m}(\mathbf{r}) \cdot \text{curl } \mathbf{a}(\mathbf{r}) d^3r \\ & - \frac{1}{2} \sum_{\xi} \int \left(\mathbf{p}^{(\xi)}(\mathbf{r}) \times \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} - \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} \times \mathbf{p}^{(\xi)}(\mathbf{r}) \right) \cdot \text{curl } \mathbf{a}(\mathbf{r}) d^3r \\ & + \frac{1}{2} \iint o_{ij}(\mathbf{r}, \mathbf{r}') (\text{curl } \mathbf{a}(\mathbf{r}))_i (\text{curl}' \mathbf{a}(\mathbf{r}'))_j d^3r d^3r' \\ & + \sum_{\xi} \frac{1}{2M(\xi)c^2} \left(\int \mathbf{p}^{(\xi)}(\mathbf{r}) \times \text{curl } \mathbf{a}(\mathbf{r}) d^3r \right)^2 \\ & - \sum_{\xi} \frac{1}{2M(\xi)c^2} \left(\int \mathbf{p}'^{(\xi)}(\mathbf{r}) \times \text{curl } \mathbf{a}(\mathbf{r}) d^3r \right)^2 \\ & + 2\pi \sum_{\xi} \int (\mathbf{p}^{(\xi)\perp}(\mathbf{r}))^2 d^3r + 2\pi \sum_{\xi \neq \eta} \int \mathbf{p}^{(\xi)}(\mathbf{r}) \cdot \mathbf{p}^{(\eta)}(\mathbf{r}) d^3r \end{aligned} \quad (3.24)$$

with the canonical variables being $\mathbf{q}_{\alpha(\xi)}$ and $\bar{\mathbf{p}}_{\alpha(\xi)}$ for the material particles and $\mathbf{a}(\mathbf{r})$ and $\bar{\mathcal{P}}(\mathbf{r})$ for the transverse electromagnetic field, and where the polarization, magnetization, diamagnetic and reduced polarization fields are defined by equations (2.28), (3.16), (3.17) and (3.18), respectively.

3.2. Heisenberg equations with multipolar Hamiltonian

It is useful to derive the Heisenberg equations of motion for some of the new variables that appear in the multipolar Hamiltonian, as these show how the atomic field equation that connects \mathbf{d}^\perp and \mathbf{h} may be recovered directly (though only for neutral systems) and they clarify the relation between the total magnetization field defined by equation (2.38) and the various matter fields that appear in conjunction with curl \mathbf{a} in the expression (3.24) for \mathcal{H} . In addition, the Heisenberg equation for $\mathbf{a}(\mathbf{r})$ implies, as will firstly be shown, that the new field momentum $\bar{\mathcal{P}}(\mathbf{r})$ is essentially the transverse displacement vector $\mathbf{d}^\perp(\mathbf{r})$, in contrast to the old momentum $\mathcal{P}(\mathbf{r})$ which is, apart from a factor, the transverse electric field $\mathbf{e}^\perp(\mathbf{r})$ (see equations (1.4) and (2.4)). Thus (Babiker *et al* 1974)

$$\begin{aligned} \dot{a}_i(\mathbf{r}) &= 4\pi c^2 \int \bar{\mathcal{P}}_j(\mathbf{r}') \delta_{ij}^\perp(\mathbf{r}-\mathbf{r}') d^3 r' + 4\pi c \int p_j(\mathbf{r}') \delta_{ij}^\perp(\mathbf{r}-\mathbf{r}') d^3 r' \\ &= 4\pi c^2 \bar{\mathcal{P}}_i(\mathbf{r}) + 4\pi c p_i^\perp(\mathbf{r}), \end{aligned} \tag{3.25}$$

since $\bar{\mathcal{P}}$ is transverse. Hence, in view of equations (1.4) and (2.31),

$$\bar{\mathcal{P}}(\mathbf{r}) = -\frac{1}{4\pi c} \mathbf{d}^\perp(\mathbf{r}). \tag{3.26}$$

This may be inferred from equation (3.10) also. It follows that the multipolar Hamiltonian, when written in terms of the electromagnetic fields rather than the vector potential and its conjugate momentum, becomes

$$\begin{aligned} \mathcal{H} &= \frac{1}{8\pi} \int [(\mathbf{d}^\perp(\mathbf{r}))^2 + (\mathbf{b}(\mathbf{r}))^2] d^3 r + \sum_\xi \sum_{\alpha(\xi)} \frac{1}{2m_{\alpha(\xi)}} \bar{\mathbf{p}}_{\alpha(\xi)}^2 + \frac{1}{2} \sum_\xi \sum_{\alpha(\xi) \neq \beta(\xi)} \frac{e_{\alpha(\xi)} e_{\beta(\xi)}}{|\mathbf{q}_{\alpha(\xi)} - \mathbf{q}_{\beta(\xi)}|} \\ &\quad - \int \mathbf{p}(\mathbf{r}) \cdot \mathbf{d}^\perp(\mathbf{r}) d^3 r - \int \mathbf{m}(\mathbf{r}) \cdot \mathbf{b}(\mathbf{r}) d^3 r \\ &\quad - \frac{1}{2} \sum_\xi \int \left(\mathbf{p}^{(\xi)}(\mathbf{r}) \times \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} - \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} \times \mathbf{p}^{(\xi)}(\mathbf{r}) \right) \cdot \mathbf{b}(\mathbf{r}) d^3 r \\ &\quad + \frac{1}{2} \iint o_{ij}(\mathbf{r}, \mathbf{r}') b_i(\mathbf{r}) b_j(\mathbf{r}') d^3 r d^3 r' \\ &\quad + \sum_\xi \frac{1}{2M(\xi)c^2} \left(\int \mathbf{p}^{(\xi)}(\mathbf{r}) \times \mathbf{b}(\mathbf{r}) d^3 r \right)^2 - \sum_\xi \frac{1}{2M(\xi)c^2} \left(\int \mathbf{p}'^{(\xi)}(\mathbf{r}) \times \mathbf{b}(\mathbf{r}) d^3 r \right)^2 \\ &\quad + 2\pi \sum_\xi \int (\mathbf{p}^{(\xi)\perp}(\mathbf{r}))^2 d^3 r + 2\pi \sum_{\xi \neq \eta} \int \mathbf{p}^{(\xi)}(\mathbf{r}) \cdot \mathbf{p}^{(\eta)}(\mathbf{r}) d^3 r. \end{aligned} \tag{3.27}$$

It is noteworthy that it is \mathbf{d}^\perp rather than \mathbf{e}^\perp that appears in this expression. Although it has long been recognized (Power and Zienau 1959, Power 1964) that \mathbf{e}^\perp and \mathbf{d}^\perp are related by the transformation (3.2), the multipolar Hamiltonian has nevertheless often been written with \mathbf{e}^\perp in place of \mathbf{d}^\perp (Woolley 1971, 1975, Babiker *et al* 1974, Healy 1976) and it is stressed here that this procedure is incorrect, since, unless there are no charged particles at all present, \mathbf{d}^\perp and \mathbf{e}^\perp are different field operators and have different equations of motion. This point is further emphasized by the Heisenberg equation for the new momentum \mathcal{P} , which yields the correct atomic field equation connecting \mathbf{d}^\perp and \mathbf{h} only if \mathcal{P} is identified with $-(1/4\pi c)\mathbf{d}^\perp$.

If $\mathbf{m}_{\text{total}}$ is defined by

$$\begin{aligned} m_{\text{total}i}(\mathbf{r}) = & m_i(\mathbf{r}) - \int o_{ij}(\mathbf{r}, \mathbf{r}') b_j(\mathbf{r}') d^3 r' + \left[\frac{1}{2} \sum_{\xi} \left(\mathbf{p}^{(\xi)}(\mathbf{r}) \times \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} - \frac{\bar{\mathbf{P}}(\xi)}{M(\xi)c} \times \mathbf{p}^{(\xi)}(\mathbf{r}) \right) \right. \\ & + \sum_{\xi} \frac{1}{M(\xi)c^2} \mathbf{p}^{(\xi)}(\mathbf{r}) \times \int (\mathbf{p}^{(\xi)}(\mathbf{r}') \times \mathbf{b}(\mathbf{r}')) d^3 r' \\ & \left. - \sum_{\xi} \frac{1}{M(\xi)c^2} \mathbf{p}'^{(\xi)}(\mathbf{r}) \times \int (\mathbf{p}'^{(\xi)}(\mathbf{r}') \times \mathbf{b}(\mathbf{r}')) d^3 r' \right], \end{aligned} \quad (3.28)$$

then the Heisenberg equation for \mathcal{P} takes the form

$$\dot{\mathcal{P}}(\mathbf{r}) = -\frac{1}{4\pi} \text{curl curl } \mathbf{a}(\mathbf{r}) + \text{curl } \mathbf{m}_{\text{total}}(\mathbf{r}), \quad (3.29)$$

as follows from the canonical commutation relations and integration by parts. According to equation (3.26) this may be written

$$\text{curl } \mathbf{h}(\mathbf{r}) = \frac{1}{c} \dot{\mathbf{d}}^\perp(\mathbf{r}) \quad (3.30)$$

where \mathbf{h} is given, as before, by equation (2.40). This agrees with the atomic field equation (2.39), since there are now no ionic or free electronic currents. It remains to be shown, however, that $\mathbf{m}_{\text{total}}$ as defined in terms of the new canonical momenta by equation (3.28) is the same as that defined previously, equation (2.38), in terms of the velocities. This can readily be done by means of the relation (3.31) between the particle velocities and the new momenta,

$$\begin{aligned} \dot{\mathbf{q}}_{\alpha(\xi)} = & \frac{\bar{\mathbf{p}}_{\alpha(\xi)}}{m_{\alpha(\xi)}} + \frac{e_{\alpha(\xi)}}{m_{\alpha(\xi)}c} \int_0^1 \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi)) \times \mathbf{b}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\alpha(\xi)} - \mathbf{R}(\xi))] d\theta \\ & + \frac{1}{M(\xi)} \sum_{\beta(\xi)} \frac{e_{\beta(\xi)}}{c} \int_0^1 (1-\theta)(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi)) \times \mathbf{b}[\mathbf{R}(\xi) + \theta(\mathbf{q}_{\beta(\xi)} - \mathbf{R}(\xi))] d\theta. \end{aligned} \quad (3.31)$$

This relation is the Heisenberg equation of motion for the particle coordinates that results from use of the multipolar form of the Hamiltonian, but it can be deduced more simply by using equations (2.7) and (3.13). From the equality of the two forms (2.38) and (3.28) for $\mathbf{m}_{\text{total}}$ it is now clear that, as mentioned in § 3.1, the expression (3.15) represents the energy in the magnetic induction field of the total magnetization field. It

should be noted, however, that the corresponding Hamiltonian density cannot be written simply as $-\mathbf{m}_{\text{total}}(\mathbf{r}) \cdot \mathbf{b}(\mathbf{r})$, since those terms in $\mathbf{m}_{\text{total}}$ that depend on \mathbf{b} occur in the Hamiltonian with a factor of $\frac{1}{2}$. This is due to their giving rise to the energy of the \mathbf{b} -dependent part of $\mathbf{m}_{\text{total}}$ in the field \mathbf{b} itself.

3.3. Internal variables for a two-particle system

For the purpose of application of the theory it is convenient to introduce a set of internal coordinates and momenta so as to separate the internal motion of each aggregate from that of its centre of mass. This procedure will be illustrated by consideration of a two-particle system (hydrogen atom). The most useful internal coordinate is then (Bethe and Salpeter 1957, Schiff 1968) the relative displacement $\boldsymbol{\rho}$ of the electron (of charge $-e$, mass m_e , position \mathbf{q}_e and conjugate momentum $\bar{\mathbf{p}}_e$) from the proton (of charge $+e$, mass m_p , position \mathbf{q}_p and conjugate momentum $\bar{\mathbf{p}}_p$). The new dynamical variables are the centre of mass and relative coordinates,

$$\mathbf{R} = \frac{m_p}{M} \mathbf{q}_p + \frac{m_e}{M} \mathbf{q}_e \quad (3.32)$$

$$\boldsymbol{\rho} = -\mathbf{q}_p + \mathbf{q}_e, \quad (3.33)$$

and the canonically conjugate momenta,

$$\bar{\mathbf{P}} = \bar{\mathbf{p}}_p + \bar{\mathbf{p}}_e \quad (3.34)$$

$$\bar{\boldsymbol{\pi}} = -\frac{m_e}{M} \bar{\mathbf{p}}_p + \frac{m_p}{M} \bar{\mathbf{p}}_e, \quad (3.35)$$

where now the total mass is $M = m_p + m_e$. Equations (3.32) to (3.35) constitute a further canonical transformation, but one that affects only the particle variables while leaving those of the radiation field unaltered. The inverse of this transformation may be written

$$\mathbf{q}_p - \mathbf{R} = -\frac{m_e}{M} \boldsymbol{\rho} \quad (3.36)$$

$$\mathbf{q}_e - \mathbf{R} = \frac{m_p}{M} \boldsymbol{\rho} \quad (3.37)$$

$$\frac{\bar{\mathbf{p}}_p}{m_p} - \frac{\bar{\mathbf{P}}}{M} = -\frac{\bar{\boldsymbol{\pi}}}{m_p} \quad (3.38)$$

$$\frac{\bar{\mathbf{p}}_e}{m_e} - \frac{\bar{\mathbf{P}}}{M} = \frac{\bar{\boldsymbol{\pi}}}{m_e}. \quad (3.39)$$

Substitution of these expressions in equations (2.28) and (3.16) to (3.18) gives the polarization, magnetization, diamagnetic and reduced polarization fields in terms of the new variables. Thus

$$\mathbf{p}(\mathbf{r}) = -e\rho \left[\frac{m_e}{M} \int_0^1 \delta\left(\mathbf{r} - \mathbf{R} + \theta \frac{m_e}{M} \boldsymbol{\rho}\right) d\theta + \frac{m_p}{M} \int_0^1 \delta\left(\mathbf{r} - \mathbf{R} - \theta \frac{m_p}{M} \boldsymbol{\rho}\right) d\theta \right] \quad (3.40)$$

$$\begin{aligned}
\mathbf{m}(\mathbf{r}) = & \frac{e}{2m_p c} \left[\boldsymbol{\rho} \times \vec{\pi} \int_0^1 \theta \frac{m_e}{M} \delta\left(\mathbf{r} - \mathbf{R} + \theta \frac{m_e}{M} \boldsymbol{\rho}\right) d\theta + \int_0^1 \theta \frac{m_e}{M} \delta\left(\mathbf{r} - \mathbf{R} + \theta \frac{m_e}{M} \boldsymbol{\rho}\right) d\theta \boldsymbol{\rho} \times \vec{\pi} \right] \\
& - \frac{e}{2m_e c} \left[\boldsymbol{\rho} \times \vec{\pi} \int_0^1 \theta \frac{m_p}{M} \delta\left(\mathbf{r} - \mathbf{R} - \theta \frac{m_p}{M} \boldsymbol{\rho}\right) d\theta \right. \\
& \left. + \int_0^1 \theta \frac{m_p}{M} \delta\left(\mathbf{r} - \mathbf{R} - \theta \frac{m_p}{M} \boldsymbol{\rho}\right) d\theta \boldsymbol{\rho} \times \vec{\pi} \right] \quad (3.41)
\end{aligned}$$

$$\begin{aligned}
o_{ij}(\mathbf{r}, \mathbf{r}') = & (\boldsymbol{\rho}^2 \delta_{ij} - \rho_i \rho_j) \\
& \times \left[\frac{e^2}{m_p c^2} \int_0^1 \theta \frac{m_e}{M} \delta\left(\mathbf{r} - \mathbf{R} + \theta \frac{m_e}{M} \boldsymbol{\rho}\right) d\theta \int_0^1 \theta' \frac{m_e}{M} \delta\left(\mathbf{r}' - \mathbf{R} + \theta' \frac{m_e}{M} \boldsymbol{\rho}\right) d\theta' \right. \\
& \left. + \frac{e^2}{m_e c^2} \int_0^1 \theta \frac{m_p}{M} \delta\left(\mathbf{r} - \mathbf{R} - \theta \frac{m_p}{M} \boldsymbol{\rho}\right) d\theta \int_0^1 \theta' \frac{m_p}{M} \delta\left(\mathbf{r}' - \mathbf{R} - \theta' \frac{m_p}{M} \boldsymbol{\rho}\right) d\theta' \right] \quad (3.42)
\end{aligned}$$

$$\mathbf{p}'(\mathbf{r}) = -e\boldsymbol{\rho} \left[\frac{m_e}{M} \int_0^1 \theta \delta\left(\mathbf{r} - \mathbf{R} + \theta \frac{m_e}{M} \boldsymbol{\rho}\right) d\theta + \frac{m_p}{M} \int_0^1 \theta \delta\left(\mathbf{r} - \mathbf{R} - \theta \frac{m_p}{M} \boldsymbol{\rho}\right) d\theta \right]. \quad (3.43)$$

The atomic multipole moments can be obtained by series expansion of the delta functions and by performance of the θ integration. With the self-energy term being omitted, the Hamiltonian for the radiation field interacting with a single atom then takes the form

$$\begin{aligned}
\mathcal{H} = & \frac{1}{8\pi} \int [(\mathbf{d}^\perp(\mathbf{r}))^2 + (\mathbf{b}(\mathbf{r}))^2] d^3r + \frac{\bar{\mathbf{P}}^2}{2M} + \frac{\vec{\pi}^2}{2\mu} - \frac{e^2}{|\boldsymbol{\rho}|} \\
& - \sum_{r=1}^{\infty} p_{i_1 i_2 \dots i_r}^{(r)} \partial_{i_2} \dots \partial_{i_r} d_{i_1}^\perp(\mathbf{R}) - \sum_{r=1}^{\infty} m_{i_1 i_2 \dots i_r}^{(r)} \partial_{i_2} \dots \partial_{i_r} b_{i_1}(\mathbf{R}) \\
& - \frac{1}{2Mc} \epsilon_{ijk} \sum_{r=1}^{\infty} \left(p_{i_1 i_2 \dots i_r}^{(r)} \partial_{i_2} \dots \partial_{i_r} b_k(\mathbf{R}) \bar{P}_j + \bar{P}_j p_{i_1 i_2 \dots i_r}^{(r)} \partial_{i_2} \dots \partial_{i_r} b_k(\mathbf{R}) \right) \\
& + \frac{1}{2} \sum_{r=1}^{\infty} \sum_{s=1}^{\infty} b_{i_1}(\mathbf{R}) \bar{\partial}_{i_2} \dots \bar{\partial}_{i_r} o_{i_1 i_2 \dots i_r, j_1 j_2 \dots j_s}^{(r,s)} \bar{\partial}_{j_2} \dots \bar{\partial}_{j_s} b_{j_1}(\mathbf{R}) \\
& + \frac{1}{2Mc^2} \epsilon_{ikm} \epsilon_{jlm} \sum_{r=1}^{\infty} \sum_{s=1}^{\infty} b_k(\mathbf{R}) \bar{\partial}_{i_2} \dots \bar{\partial}_{i_r} \\
& \times (p_{i_1 i_2 \dots i_r, j_1 j_2 \dots j_s}^{(r)} - p_{i_1 i_2 \dots i_r, j_1 j_2 \dots j_s}^{(s)}) \bar{\partial}_{j_2} \dots \bar{\partial}_{j_s} b_l(\mathbf{R}) \quad (3.44)
\end{aligned}$$

where the multipole moments are defined by

$$p_{i_1 i_2 \dots i_r}^{(r)} = -\frac{e}{r!} \left[\left(\frac{m_p}{M} \right)^r - \left(-\frac{m_e}{M} \right)^r \right] \rho_{i_1} \rho_{i_2} \dots \rho_{i_r} \quad (3.45)$$

$$m_{i_1 i_2 \dots i_r}^{(r)} = -\frac{r}{(r+1)!} \left[\frac{e}{2m_e c} \left(\frac{m_p}{M} \right)^r + \frac{e}{2m_p c} \left(-\frac{m_e}{M} \right)^r \right] (\bar{\lambda}_{i_1} \rho_{i_2} \dots \rho_{i_r} + \rho_{i_2} \dots \rho_{i_r} \bar{\lambda}_{i_1}) \quad (3.46)$$

$$\begin{aligned}
o_{i_1 i_2 \dots i_r, j_1 j_2 \dots j_s}^{(r,s)} \\
= & \frac{rs}{(r+1)!(s+1)!} \left[\frac{e^2}{m_e c^2} \left(\frac{m_p}{M} \right)^{r+s} + \frac{e^2}{m_p c^2} \left(-\frac{m_e}{M} \right)^{r+s} \right] (\boldsymbol{\rho}^2 \delta_{i_1 j_1} - \rho_{i_1} \rho_{j_1}) \rho_{i_2} \dots \rho_{i_r} \rho_{j_2} \dots \rho_{j_s} \quad (3.47)
\end{aligned}$$

$$p_{i_1 i_2 \dots i_r}^{(r)} = -e \frac{r}{(r+1)!} \left[\left(\frac{m_p}{M} \right)^r - \left(-\frac{m_e}{M} \right)^r \right] \rho_{i_1} \rho_{i_2} \dots \rho_{i_r} = \frac{r}{r+1} p_{i_1 i_2 \dots i_r}^{(r)} \quad (3.48)$$

and are all Hermitian. The reduced mass that appears in the atomic part of the Hamiltonian is given by

$$\mu = \frac{m_p m_e}{m_p + m_e} \quad (3.49)$$

and the relative angular momentum that appears in the expression for the magnetic multipole moments by

$$\vec{\lambda} = \boldsymbol{\rho} \times \vec{\pi}. \quad (3.50)$$

The notation used in equation (3.44) for the partial derivatives means that

$$b_i(\mathbf{R}) \vec{\partial}_j = \vec{\partial}_j b_i(\mathbf{R}) = \partial_j b_i(\mathbf{R}) = [\partial_j b_i(\mathbf{r})]_{\mathbf{r}=\mathbf{R}}. \quad (3.51)$$

If m_e remains constant but m_p , and hence M , tends to infinity, the Hamiltonian (3.44) reduces to

$$\begin{aligned} \mathcal{H} = & \frac{1}{8\pi} \int (\mathbf{d}^{\perp 2} + \mathbf{b}^2) d^3r + \frac{\vec{p}_e^2}{2m_e} - \frac{e^2}{|\boldsymbol{\rho}|} \\ & - \sum_{r=1}^{\infty} p_{i_1 i_2 \dots i_r}^{(r)} \partial_{i_2} \dots \partial_{i_r} d_{i_1}^{\perp}(\mathbf{R}) - \sum_{r=1}^{\infty} m_{i_1 i_2 \dots i_r}^{(r)} \partial_{i_2} \dots \partial_{i_r} b_{i_1}(\mathbf{R}) \\ & + \frac{1}{2} \sum_{r=1}^{\infty} \sum_{s=1}^{\infty} b_{i_1}(\mathbf{R}) \vec{\partial}_{i_2} \dots \vec{\partial}_{i_r} o_{i_1 i_2 \dots i_r, j_1 j_2 \dots j_s}^{(r,s)} \vec{\partial}_{j_2} \dots \vec{\partial}_{j_s} b_{j_1}(\mathbf{R}) \end{aligned} \quad (3.52)$$

because, from equations (3.35) and (3.49), $\vec{\pi} \rightarrow \vec{p}_e$ and $\mu \rightarrow m_e$. It follows also from equation (3.37) that now

$$\boldsymbol{\rho} = \mathbf{q}_e - \mathbf{R}. \quad (3.53)$$

\mathcal{H} is then independent of \vec{P} and is of the form appropriate to an electron moving in the Coulomb field of a proton fixed at \mathbf{R} , which is now taken to be a c -number. Moreover, the multipole moment operators then have their familiar forms,

$$p_{i_1 i_2 \dots i_r}^{(r)} = -\frac{e}{r!} \rho_{i_1} \rho_{i_2} \dots \rho_{i_r} \quad (3.54)$$

$$m_{i_1 i_2 \dots i_r}^{(r)} = -\frac{r}{(r+1)!} \frac{e}{2m_e c} (\vec{I}_{i_1} \rho_{i_2} \dots \rho_{i_r} + \rho_{i_2} \dots \rho_{i_r} \vec{I}_{i_1}) \quad (3.55)$$

$$o_{i_1 i_2 \dots i_r, j_1 j_2 \dots j_s}^{(r,s)} = \frac{rs}{(r+1)!(s+1)!} \frac{e^2}{m_e c^2} (\boldsymbol{\rho}^2 \delta_{i_1 j_1} - \rho_{i_1} \rho_{j_1}) \rho_{i_2} \dots \rho_{i_r} \rho_{j_2} \dots \rho_{j_s} \quad (3.56)$$

the operator for the electron's angular momentum about the fixed proton being

$$\vec{I} = (\mathbf{q}_e - \mathbf{R}) \times \vec{p}_e. \quad (3.57)$$

The order of the operators in the expression (3.55) for the magnetic 2^r -pole moments is in agreement with that obtained by Raab (1975), who in a semiclassical treatment used a symmetrized (in $\mathbf{p} \cdot \mathbf{a}$ and $\mathbf{a} \cdot \mathbf{p}$) but non-Coulomb gauged Hamiltonian.

If the masses of the two particles are finite and equal, so that the centre of mass is midway between them, then all the even-order electric and all the odd-order magnetic multipole operators vanish, as do the diamagnetic moment operators $o^{(r,s)}$ with $r+s$ odd.

Appendix

The three distribution relations that were used in § 2.3 to obtain the expressions for the total charge density in terms of the true and the polarization charge densities and for the total current density in terms of the true, the polarization and the total magnetization current densities are listed here for convenience. If the label of the aggregate ξ to which particle α belongs is suppressed, then the three relations are as follows:

$$\delta(\mathbf{r} - \mathbf{q}_\alpha) = \delta(\mathbf{r} - \mathbf{R}) - \partial_i(\mathbf{q}_\alpha - \mathbf{R})_j \int_0^1 \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{R} - \theta(\mathbf{q}_\alpha - \mathbf{R})) d\theta \quad (\text{A.1})$$

$$\begin{aligned} \frac{1}{2}(\dot{q}_{\alpha j} \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_\alpha) + \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{q}_\alpha) \dot{q}_{\alpha i}) \\ = \frac{1}{2}(\dot{\mathbf{R}}_j \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{R}) + \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{R}) \dot{\mathbf{R}}_j) + \frac{\partial}{\partial t}(\mathbf{q}_\alpha - \mathbf{R})_j \int_0^1 \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{R} - \theta(\mathbf{q}_\alpha - \mathbf{R})) d\theta \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} \dot{q}_{\alpha j} \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{q}_\alpha) = \dot{\mathbf{R}}_j \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{R}) + \frac{\partial}{\partial t}(\mathbf{q}_\alpha - \mathbf{R})_j \int_0^1 \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{R} - \theta(\mathbf{q}_\alpha - \mathbf{R})) d\theta \\ + \left[\text{curl} \frac{1}{2} \left((\mathbf{q}_\alpha - \mathbf{R}) \times (\dot{\mathbf{q}}_\alpha - \dot{\mathbf{R}}) \int_0^1 \theta \delta(\mathbf{r} - \mathbf{R} - \theta(\mathbf{q}_\alpha - \mathbf{R})) d\theta \right. \right. \\ + \int_0^1 \theta \delta(\mathbf{r} - \mathbf{R} - \theta(\mathbf{q}_\alpha - \mathbf{R})) d\theta (\mathbf{q}_\alpha - \mathbf{R}) \times (\dot{\mathbf{q}}_\alpha - \dot{\mathbf{R}}) \\ + \int_0^1 \delta(\mathbf{r} - \mathbf{R} - \theta(\mathbf{q}_\alpha - \mathbf{R})) d\theta (\mathbf{q}_\alpha - \mathbf{R}) \times \dot{\mathbf{R}} \\ \left. \left. - \dot{\mathbf{R}} \times (\mathbf{q}_\alpha - \mathbf{R}) \int_0^1 \delta(\mathbf{r} - \mathbf{R} - \theta(\mathbf{q}_\alpha - \mathbf{R})) d\theta \right) \right]_i. \end{aligned} \quad (\text{A.3})$$

In the classical theory, where the \mathbf{q}_α are c -numbers, these relations are quite generally valid as kinematical identities (Power and Thirunamachandran 1971). In the quantum theory the order of the operators as given in equations (A.2) and (A.3) must be adhered to and, even so, the validity of these two equations is more restricted than in the classical case. This is because the usual formula for the derivative of a function of a function is not necessarily true in the operator calculus—not even, except with certain assumptions as to the nature of the commutator of Ω and $\dot{\Omega}$, in the symmetrized form

$$\frac{d}{dt} f(\Omega) = \frac{1}{2}(\dot{\Omega} f'(\Omega) + f'(\Omega) \dot{\Omega}). \quad (\text{A.4})$$

Equations (A.2) and (A.3) can be shown to be consequences of the Heisenberg equation of motion when the 'central point' \mathbf{R} , whose precise definition could be left unspecified in the classical treatment, is taken for definiteness to be the centre of mass of the aggregate to which particle α belongs. The derivations of these equations along these lines are rather lengthy and will not be entered upon here; the proofs are similar to their classical counterparts except that due regard must be had for the order of non-commuting operators and the time derivatives must be calculated from the Heisenberg equation (1.5), it being simplest for this purpose to use the minimal-coupling form (3.1) of the Hamiltonian \mathcal{H} . This method shows that equations (A.2) and (A.3) are valid as dynamical relations for the particular dynamical system under consideration. On the other hand, the proof of equation (A.1) as given by Power and Thirunamachandran (1971) for the classical case holds equally well in the quantum theory and this equation is consequently a kinematical identity.

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