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Current density and electric and magnetic multipole-moment operators in quantum mechanics

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Abstract. We define the quantum-mechanical current density operator for general Hamiltonian operators and hence define electric and magnetic multipole-moment operators in close correspondence with the classical case. General Hamiltonian operators are transformed to multipole form by canonical transformation. As examples we treat the charge exchange interaction and relativistic corrections to the magnetic moment of an electron moving in a central potential.

1. Introduction

In the preceding paper (Meister and Felderhof 1980, to be referred to as I) we have presented definitions of the quantum mechanical electric and magnetic multipole-moment operators. For the magnetic moments the correspondence with the classical case could strictly speaking be established only for the Schrödinger Hamiltonian operator. For general Hamiltonian operators the definition of the current density operator was lacking. In this paper we show that the current density operator can be defined uniquely from the first-order interaction with the electromagnetic field. The resulting magnetic multipole-moment operators are in direct correspondence with the classical moments.

We also show that for general Hamiltonian operators one can perform a canonical transformation to multipole form in which the polarisation and magnetisation operators couple to the electric and magnetic fields. The transformation allows a simpler formulation of Siegert's theorem.

As an example we consider the contribution to the current-density operator from charge exchange interactions. We evaluate explicitly the corresponding magnetic dipole and quadrupole moments. We also study relativistic corrections to the magnetic dipole moment of an electron moving in a central potential. Since the corrections appear in the operators rather than in the energy levels, a simpler and more transparent picture emerges than is evident from previous treatments.

2. Definition of the current density operator

We consider a general Hamiltonian operator of the form

$$H = H^{\mathrm{At}}(\{\boldsymbol{p}_k - (e_k/c)\boldsymbol{A}(\boldsymbol{r}_k), \boldsymbol{r}_k, s_k\}) + H^{\mathrm{Rad}} - \int \boldsymbol{\mathcal{M}}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}, \tag{2.1}$$

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where H^{At} is the Hamiltonian for the atom or nucleus in interaction with the radiation field, H^{Rad} is the Hamiltonian for the free radiation field,

$$H^{\mathrm{Rad}} = (1/8\pi) \int (\boldsymbol{E}_{\perp}^2(\boldsymbol{r}) + \boldsymbol{B}^2(\boldsymbol{r}))\, \mathrm{d}\boldsymbol{r} \tag{2.2}$$

and the intrinsic magnetisation $\boldsymbol{\mathcal{M}}(\boldsymbol{r})$ is defined by

$$\boldsymbol{\mathcal{M}}(\boldsymbol{r}) = \sum_j \mu_j \boldsymbol{s}_j \delta(\boldsymbol{r} - \boldsymbol{r}_j), \tag{2.3}$$

where the $\boldsymbol{s}_j$ are spin operators and the μ_j are values of the intrinsic magnetic moments. We use the vector potential $\boldsymbol{A}(\boldsymbol{r})$ in the Coulomb gauge $\nabla \cdot \boldsymbol{A} = 0$, and include the longitudinal Coulomb interaction in (2.1) as a potential energy term. The Hamiltonian operator (2.1) must be regarded as a phenomenological one. The main assumptions involved are that the interactions between particles can be described by potential energy terms, possibly velocity-dependent, and that the interaction with the electromagnetic field is given by a point charge approximation. The Hamiltonian can include spin–orbit interactions, charge exchange coupling terms, etc. The fact that momentum and vector potential appear in the combination $\boldsymbol{p}_k - (e_k/c)\boldsymbol{A}(\boldsymbol{r}_k)$ is an expression of gauge invariance. We could have included isospin, but have omitted it to keep the formalism simple. The difficulties which arise in the definition of charge and current densities when the point charge approximation is dropped have been studied by Foldy (1953).

Since the interaction with the radiation field is weak we can expand H^{At} in powers of $\boldsymbol{A}$. Thus we obtain

$$H = H_0 + V_1 + V_2 + \ldots, \tag{2.4}$$

where

$$H_0 = H_0^{\mathrm{At}}(\{\boldsymbol{p}_k, \boldsymbol{r}_k, \boldsymbol{s}_k\}) + H^{\mathrm{Rad}}, \qquad V_1 = V_1^{\mathrm{orb}} - \int \boldsymbol{\mathcal{M}}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}, \tag{2.5}$$

with

$$V_1^{\mathrm{orb}} = -\sum_{j\alpha} \frac{e_j}{c} H_{1\alpha}^j(\{\boldsymbol{p}_k, \boldsymbol{r}_k, \boldsymbol{s}_k\}, A_\alpha(\boldsymbol{r}_j)). \tag{2.6}$$

By definition the operator $H_{1\alpha}^j$ is linear in $A_\alpha(\boldsymbol{r})$. To make the definition precise it is assumed that in writing out its form no use is made of the commutation relation between $\boldsymbol{r}_j$ and $\boldsymbol{p}_j$.

Writing $\boldsymbol{A}(\boldsymbol{r}_j)$ in (2.6) as

$$\boldsymbol{A}(\boldsymbol{r}_j) = \int \boldsymbol{A}(\boldsymbol{r}) \delta(\boldsymbol{r} - \boldsymbol{r}_j)\, \mathrm{d}\boldsymbol{r}, \tag{2.7}$$

we can put V_1^{orb} in the form

$$V_1^{\mathrm{orb}} = -(1/c) \int \boldsymbol{j}_0(\boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}. \tag{2.8}$$

This defines the zero-order current density operator $\boldsymbol{j}_0(\boldsymbol{r})$. It is assumed that no use is made of the transversality of $\boldsymbol{A}(\boldsymbol{r})$. According to (2.5), the complete perturbation V_1 can also be written in the form (2.8), with current density

$$\boldsymbol{\mathcal{J}}_0(\boldsymbol{r}) = \boldsymbol{j}_0(\boldsymbol{r}) + c\nabla \times \boldsymbol{\mathcal{M}}(\boldsymbol{r}). \tag{2.9}$$

We shall show that the above definition of $j_0(r)$ can be given a more attractive appearance.

The operators $H^j_{1\alpha}$ defined in (2.6) have the property

$$\frac{\mathrm{i}}{\hbar}[H_0, g(r_j)] = \sum_{\alpha=1}^{3} H^j_{1\alpha}\left(X, \frac{\partial g(r_j)}{\partial r_{j\alpha}}\right) \tag{2.10}$$

for any scalar function $g(r)$. We have denoted the complete set of variables $\{p_k, r_k, s_k\}$ by X. The proof of this identity is given in I (4.10). In particular, one has for the zero order particle velocities $\dot{r}_j$,

$$\dot{r}_j \equiv \frac{\mathrm{i}}{\hbar}[H_0, r_j] = \sum_{\alpha=1}^{3} H^j_{1\alpha}(X, 1)e_\alpha, \tag{2.11}$$

where ($e_\alpha = x, y, z$) are unit vectors. We define the super-operator $\dot{r}_j^X$ which can act on any operator F by

$$\dot{r}_j^X F = \sum_{\alpha=1}^{3} H^j_{1\alpha}(X, F)e_\alpha. \tag{2.12}$$

It is clear that $\dot{r}_j^X$ is a linear super-operator. From (2.11) it follows that

$$\dot{r}_j = \dot{r}_j^X 1. \tag{2.13}$$

The charge and current density operators can now be written in the form

$$\rho(r) = \sum_j e_j \delta(r - r_j), \qquad j_0(r) = \sum_j e_j \dot{r}_j^X \delta(r - r_j). \tag{2.14}$$

It is easily shown that these operators satisfy the continuity equation

$$\dot{\rho} + \nabla \cdot j_0 = 0. \tag{2.15}$$

The proof runs as follows:

$$\begin{aligned} \nabla \cdot j_0 &= \sum_j e_j \dot{r}_j^X \cdot \nabla \delta(r - r_j) = \sum_{j\alpha} e_j H^j_{1\alpha}\left(X, \frac{\partial}{\partial r_\alpha}\delta(r - r_j)\right) \\ &= -\sum_{j\alpha} e_j H^j_{1\alpha}\left(X, \frac{\partial}{\partial r_{j\alpha}}\delta(r - r_j)\right) \\ &= -\frac{\mathrm{i}}{\hbar}\sum_j e_j [H_0, \delta(r - r_j)] = -\dot{\rho}. \end{aligned} \tag{2.16}$$

In the last line we have used (2.10).

Note that the continuity equation itself is not sufficient to determine the form of the current density operator, since it can only fix the longitudinal part (Warburton and Weneser 1969). The above rule makes the definition unique. Though we have started out in the Coulomb gauge, the definition of $j_0(r)$ is in fact gauge invariant.

It is clear that the definition works just as well for uncharged particles. In that case the e_k in (2.1) can be regarded as mere parameters and $A(r)$ as an auxiliary vector field. This leads to the number density and flow velocity operators

$$n(r) = \sum_j \delta(r - r_j), \qquad v_0(r) = \sum_j \dot{r}_j^X \delta(r - r_j). \tag{2.17}$$

Using the same reasoning as in (2.16) one shows that these operators satisfy the continuity equation $\dot{n} + \nabla \cdot v_0 = 0$.

3. Examples

In order to illustrate the use of the operators $\boldsymbol{v}_0(\boldsymbol{r})$ and $\boldsymbol{j}_0(\boldsymbol{r})$ defined above we consider some examples for particular Hamiltonian operators.

3.1. Schrödinger Hamiltonian

$$H_0^{\mathrm{At}} = \sum_j \frac{\boldsymbol{p}_j^2}{2m_j} + U(\{\boldsymbol{r}_k, \boldsymbol{s}_k\}). \tag{3.1}$$

In this case

$$H_{1\alpha}^j(\{\boldsymbol{p}_k\}, A_\alpha(\boldsymbol{r}_j)) = (p_{j\alpha}A_\alpha(\boldsymbol{r}_j) + A_\alpha(\boldsymbol{r}_j)p_{j\alpha})/2m_j, \tag{3.2}$$

so that

$$\dot{\boldsymbol{r}}_j^X F = (\boldsymbol{p}_j F + F\boldsymbol{p}_j)/2m_j. \tag{3.3}$$

The flow velocity operator becomes

$$\boldsymbol{v}_0(\boldsymbol{r}) = \sum_j \frac{1}{2m_j}(\boldsymbol{p}_j\delta(\boldsymbol{r}-\boldsymbol{r}_j) + \delta(\boldsymbol{r}-\boldsymbol{r}_j)\boldsymbol{p}_j) = \sum_j \tfrac{1}{2}(\dot{\boldsymbol{r}}_j\delta(\boldsymbol{r}-\boldsymbol{r}_j) + \delta(\boldsymbol{r}-\boldsymbol{r}_j)\dot{\boldsymbol{r}}_j), \tag{3.4}$$

which is of the usual symmetrised form.

3.2. Dirac Hamiltonian

$$H_0^{\mathrm{At}} = \sum_j (c\boldsymbol{\alpha}_j \,.\, \boldsymbol{p}_j + \beta_j m_j c^2) + U(\{\boldsymbol{r}_k\}), \tag{3.5}$$

where $(\boldsymbol{\alpha}_j, \beta_j)$ are Dirac matrices. In this case

$$H_{1\alpha}^j(\{\boldsymbol{p}_k\}, A_\alpha(\boldsymbol{r}_j)) = c\alpha_{j\alpha}A_\alpha(\boldsymbol{r}_j), \tag{3.6}$$

so that

$$\dot{\boldsymbol{r}}_j^X F = c\boldsymbol{\alpha}_j F. \tag{3.7}$$

The flow velocity operator has the usual form,

$$\boldsymbol{v}_0(\boldsymbol{r}) = c\sum_j \boldsymbol{\alpha}_j\delta(\boldsymbol{r}-\boldsymbol{r}_j). \tag{3.8}$$

3.3. Charge exchange interaction

We consider a charge exchange interaction of Majorana type (Sachs 1953),

$$U_0^{\mathrm{exch}} = \sum_{i<j} U_0^{ij}, \qquad U_0^{ij} = J(r_{ij})P_{ij}, \tag{3.9}$$

where P_{ij} is a permutation operator which exchanges the coordinates of particles i and j. It has the explicit representation

$$P_{ij} = \exp[(\mathrm{i}/\hbar)(\boldsymbol{r}_i - \boldsymbol{r}_j) \,.\, (\boldsymbol{p}_j - \boldsymbol{p}_i)] \tag{3.10}$$

with the agreement that $\boldsymbol{p}_j$ and $\boldsymbol{p}_i$ act on wavefunctions but not on the coordinates $\boldsymbol{r}_i$ and

r_j in the exponent. One now has

$$U^{ij} = J(r_{ij}) \exp[(\mathrm{i}/\hbar)(\boldsymbol{r}_i - \boldsymbol{r}_j) \cdot (\boldsymbol{p}_j - (e_j/c)\boldsymbol{A}(\boldsymbol{r}_j) - \boldsymbol{p}_i + (e_i/c)\boldsymbol{A}(\boldsymbol{r}_i))]$$
$$= U_0^{ij} + \sum_{\alpha=1}^{3} \left[-\frac{e_j}{c} U_{1\alpha}^{j}(\{\boldsymbol{p}_k, \boldsymbol{r}_k\}, A_\alpha(\boldsymbol{r}_j)) - \frac{e_i}{c} U_{1\alpha}^{i}(\{\boldsymbol{p}_k, \boldsymbol{r}_k\}, A_\alpha(\boldsymbol{r}_i)) \right] + \ldots, \tag{3.11}$$

where the term linear in $A_\alpha(\boldsymbol{r})$ can be written (Sachs 1948)

$$\sum_{\alpha=1}^{3} \left[-\frac{e_j}{c} U_{1\alpha}^{j}(\{\boldsymbol{p}_k, \boldsymbol{r}_k\}, A_\alpha(\boldsymbol{r}_j)) - \frac{e_i}{c} U_{1\alpha}^{i}(\{\boldsymbol{p}_k, \boldsymbol{r}_k\}, A_\alpha(\boldsymbol{r}_i)) \right]$$
$$= \sum_{\alpha=1}^{3} \frac{\mathrm{i}(e_i - e_j)}{\hbar c} \left(\int_{\boldsymbol{r}_j}^{\boldsymbol{r}_i} A_\alpha(\boldsymbol{s})\, \mathrm{d}s_\alpha \right) J(r_{ij}) P_{ij}, \tag{3.12}$$

where the integral must be taken along the straight line from particle j to particle i. The contribution to the current density operator from U^{exch} is given by

$$\boldsymbol{j}_0^{\mathrm{exch}}(\boldsymbol{r}) = \sum_{i<j} \sum_{\alpha=1}^{3} [e_j U_{1\alpha}^{j}(\{\boldsymbol{p}_k, \boldsymbol{r}_k\}, \delta(\boldsymbol{r} - \boldsymbol{r}_j))\boldsymbol{e}_\alpha + e_i U_{1\alpha}^{i}(\{\boldsymbol{p}_k, \boldsymbol{r}_k\}, \delta(\boldsymbol{r} - \boldsymbol{r}_i))\boldsymbol{e}_\alpha]$$
$$= \sum_{i<j} \frac{\mathrm{i}}{\hbar}(e_i - e_j) \left(\int_{\boldsymbol{r}_i}^{\boldsymbol{r}_j} \delta(\boldsymbol{r} - \boldsymbol{s})\, \mathrm{d}\boldsymbol{s} \right) J(r_{ij}) P_{ij}. \tag{3.13}$$

Clearly only pairs for which the charges differ contribute to this current density. The current density is concentrated on the straight lines between particles with different charges. If we consider protons (π) and neutrons (ν), then the exchange current density can be written

$$\boldsymbol{j}_0^{\mathrm{exch}} = \frac{\mathrm{i}e}{\hbar} \sum_{\pi,\nu} (\boldsymbol{r}_\nu - \boldsymbol{r}_\pi) \int_0^1 \delta(\boldsymbol{r} - \boldsymbol{r}_\pi - \lambda(\boldsymbol{r}_\nu - \boldsymbol{r}_\pi))\, \mathrm{d}\lambda\, J(r_{\pi\nu}) P_{\pi\nu}. \tag{3.14}$$

This form for the current density was also given by Adams (1951) and by Sachs (1953), but after a much more complicated derivation.

3.4. Spin-orbit coupling

We consider a single particle with charge e moving in a central potential. The spin–orbit interaction is of the form

$$U_0^{LS} = J(r_1)(\boldsymbol{r}_1 \times \boldsymbol{p}_1) \cdot \boldsymbol{s}_1. \tag{3.15}$$

Hence it follows that

$$\sum_{\alpha=1}^{3} U_{1\alpha}^{LS}[\boldsymbol{p}_1, \boldsymbol{r}_1, \boldsymbol{s}_1, A_\alpha(\boldsymbol{r}_1)] = \epsilon_{\alpha\beta\gamma} J(r_1) A_\alpha(\boldsymbol{r}_1) s_{1\beta} r_{1\gamma}, \tag{3.16}$$

so that

$$\boldsymbol{j}_0^{LS}(\boldsymbol{r}) = e\epsilon_{\alpha\beta\gamma} J(r_1) \delta(\boldsymbol{r} - \boldsymbol{r}_1) \boldsymbol{e}_\alpha s_{1\beta} r_{1\gamma} = eJ(r_1) \boldsymbol{s}_1 \times \boldsymbol{r}_1 \delta(\boldsymbol{r} - \boldsymbol{r}_1). \tag{3.17}$$

This current density is identical to what one finds by calculating the LS-contribution to $\dot{\boldsymbol{r}}_j$ directly from (3.15). The same is true for any interaction linear in $\boldsymbol{p}$.

4. Electric and magnetic multipole moments

Once the current density operator has been defined, one can derive corresponding polarisation and magnetisation operators by writing

$$\boldsymbol{j}_0(\boldsymbol{r}) = \dot{\boldsymbol{P}}(\boldsymbol{r}) + c\nabla \times \boldsymbol{M}_0(\boldsymbol{r}), \tag{4.1}$$

where the electric polarisation $\boldsymbol{P}(\boldsymbol{r})$ is given by the expansion (cf de Groot 1969 and (I.3.3))

$$\boldsymbol{P}(\boldsymbol{r}) = \int \boldsymbol{r}'\rho(\boldsymbol{r}') \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!}[(\boldsymbol{r}' \cdot \nabla)^n \delta(\boldsymbol{r})]\, \mathrm{d}\boldsymbol{r}', \tag{4.2}$$

and the magnetisation $\boldsymbol{M}_0(\boldsymbol{r})$ by

$$\boldsymbol{M}_0(\boldsymbol{r}) = \frac{1}{c}\int \boldsymbol{r}' \times \boldsymbol{j}_0(\boldsymbol{r}') \sum_{n=0}^{\infty} (-1)^n \frac{n+1}{(n+2)!}[(\boldsymbol{r}' \cdot \nabla)^n \delta(\boldsymbol{r})]\, \mathrm{d}\boldsymbol{r}'. \tag{4.3}$$

Substituting from (2.14), one can write the latter in the form

$$\boldsymbol{M}_0(\boldsymbol{r}) = -\sum_j \frac{e_j}{c} \sum_{n=0}^{\infty} (-1)^n \frac{n+1}{(n+2)!}(\dot{\boldsymbol{r}}_j^X \times \boldsymbol{r}_j)[(\boldsymbol{r}_j \cdot \nabla)^n \delta(\boldsymbol{r})]. \tag{4.4}$$

There is a direct correspondence with the classical expression. One must only be careful to put the super-operators $\dot{\boldsymbol{r}}_j^X$ in the right place. The expression (4.4) is extremely useful in formal calculations, as will be demonstrated in § 6.

The spherical electric and magnetic multipole moment operators can now be written down by direct analogy with the classical definitions. The electric multipole-moment operator $P_{\mathrm{E}}(lm\omega)$ is defined by

$$P_{\mathrm{E}}(lm\omega) = \int \boldsymbol{P}(\boldsymbol{r}) \cdot \boldsymbol{E}_{lm}^{\mathrm{E0}^*}(\boldsymbol{r}, \omega)\, \mathrm{d}\boldsymbol{r}. \tag{4.5}$$

As in the classical case this can be transformed to (Meister and Felderhof 1980)

$$\begin{aligned} P_{\mathrm{E}}(lm\omega) &= \int r\rho(\boldsymbol{r}) \cdot \int_0^1 \boldsymbol{E}_{lm}^{\mathrm{E0}^*}(\lambda \boldsymbol{r}, \omega)\, \mathrm{d}\lambda\, \mathrm{d}\boldsymbol{r} \\ &= \frac{-1}{k[l(l+1)]^{1/2}} \sum_j e_j [(j_l(kr) + krj_l'(kr) + g_l(kr)) Y_{lm}^*]_{\boldsymbol{r}=\boldsymbol{r}_j}. \end{aligned} \tag{4.6}$$

The magnetic E-multipole moment operator $M_{\mathrm{E}}(lm\omega)$ is defined by

$$M_{\mathrm{E}}(lm\omega) = \int \boldsymbol{M}_0(\boldsymbol{r}) \cdot \boldsymbol{B}_{lm}^{\mathrm{E0}^*}(\boldsymbol{r}, \omega)\, \mathrm{d}\boldsymbol{r}. \tag{4.7}$$

This can be transformed to

$$\begin{aligned} M_{\mathrm{E}}(lm\omega) &= \frac{\mathrm{i}}{k^2 c[l(l+1)]^{1/2}} \int \boldsymbol{j}_0(\boldsymbol{r}) \cdot g_l(kr) \nabla Y_{lm}^*\, \mathrm{d}\boldsymbol{r} \\ &= \sum_j e_j \dot{\boldsymbol{r}}_j^X \cdot \frac{\mathrm{i}}{ck^2[l(l+1)]^{1/2}} (g_l(kr) \nabla Y_{lm}^*)_{\boldsymbol{r}=\boldsymbol{r}_j} \\ &= \sum_{j\alpha} \frac{e_j}{c} H_{1\alpha}^j \left[\boldsymbol{X}, \left(\frac{\mathrm{i}}{k^2[l(l+1)]^{1/2}} g_l(kr) \frac{\partial}{\partial r_\alpha} Y_{lm}^* \right)_{\boldsymbol{r}=\boldsymbol{r}_j} \right] \\ &= -V_1^{\mathrm{orb}} \left(\frac{\mathrm{i}}{k^2[l(l+1)]^{1/2}} g_l(kr) \nabla Y_{lm}^* \right). \end{aligned} \tag{4.8}$$

The last expression confirms the conjecture made in § I(4). The magnetic M-multipole moment operator $M_M(lm\omega)$ is defined by

$$M_M(lm\omega) = \int \boldsymbol{M}_0(\boldsymbol{r}) \cdot \boldsymbol{B}_{lm}^{M0*}(\boldsymbol{r}, \omega)\, d\boldsymbol{r}. \tag{4.9}$$

This can be transformed to

$$M_M(lm\omega) = \frac{1}{c}\int j_0(\boldsymbol{r}) \cdot \boldsymbol{A}_{lm}^{M0*}(\boldsymbol{r}, \omega)\, d\boldsymbol{r} = \sum_j \frac{e_j}{c} \dot{\boldsymbol{r}}_j^X \cdot \boldsymbol{A}_{lm}^{M0*}(\boldsymbol{r}_j, \omega)$$

$$= \sum_{j\alpha} \frac{e_j}{c} H_{1\alpha}^j(\boldsymbol{X}, A_{lm,\alpha}^{M0*}(\boldsymbol{r}_j, \omega)) = -V_1^{orb}(\boldsymbol{A}_{lm}^{M0*}(\boldsymbol{r}, \omega)). \tag{4.10}$$

The last expression is again in agreement with the earlier conjecture.

5. Magnetic dipole and quadrupole moments

The general expressions for the frequency-dependent spherical electric and magnetic multipole moments have been given in (4.6), (4.8) and (4.10). Often it suffices to use the frequency-independent dipole or quadrupole moments. These are found more easily from the cartesian expansions (4.2) and (4.3).

As a first example we consider the magnetic dipole and quadrupole moments which follow from the exchange current density derived in § 3. Substituting (3.13) into (4.3) one finds for the magnetic dipole moment

$$\boldsymbol{m}^{exch} = \frac{i}{2\hbar c} \sum_{i<j} (e_i - e_j)(\boldsymbol{r}_i \times \boldsymbol{r}_j) J(r_{ij}) P_{ij}. \tag{5.1}$$

This expression has already been found by Sachs (1948). Similarly one finds for the exchange magnetic quadrupole moment

$$\boldsymbol{Q}^{exch} = \frac{i}{6\hbar c} \sum_{i<j} (e_i - e_j)(\boldsymbol{r}_i \times \boldsymbol{r}_j)(\boldsymbol{r}_i + \boldsymbol{r}_j) J(r_{ij}) P_{ij}. \tag{5.2}$$

As a second example we calculate the relativistic corrections to the magnetic dipole moment of an electron moving in a central potential. We consider the unperturbed Hamiltonian

$$H_0^{At} = H_0^{nr} + W_0, \tag{5.3}$$

where H_0^{nr} is the non-relativistic Hamiltonian operator

$$H_0^{nr} = p^2/2m + V(r) \tag{5.4}$$

and W_0 are the first-order relativistic corrections (Messiah 1972)

$$W_0 = U_0^K + U_0^{LS} + U_0^D = -\frac{p^4}{8m^3c^2} + \frac{\hbar}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}(\boldsymbol{l} \cdot \boldsymbol{s}) + \frac{\hbar^2}{8m^2c^2}\nabla^2 V. \tag{5.5}$$

The first term is the relativistic correction of the kinetic energy, the second is the spin–orbit coupling and the last term is a correction of the potential energy, the so-called Darwin term. In order to find the coupling to the electromagnetic field we form the Hamiltonian operator H as indicated in (2.1). By application of the rules

developed above one finds from U_0^{K} a contribution to the current density operator,

$$\boldsymbol{j}_0^{\mathrm{K}}(\boldsymbol{r}') = (-e/8m^3c^2)[p^2, [\boldsymbol{p}, \delta(\boldsymbol{r}'-\boldsymbol{r})]_+]_+, \tag{5.6}$$

where $[\ ,\ ]_+$ denotes the anti-commutator. By substitution in (4.3) one obtains for the contribution to the magnetic dipole moment

$$\boldsymbol{m}^{\mathrm{K}} = ep^2\boldsymbol{l}/4m^3c^3. \tag{5.7}$$

This is a relativistic mass correction to the usual orbital magnetic moment of the electron. From U_0^{LS} one finds a contribution to the current density operator,

$$\boldsymbol{j}_0^{LS}(\boldsymbol{r}') = \frac{e\hbar}{2m^2c^2}\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\boldsymbol{r}\times\boldsymbol{s}\delta(\boldsymbol{r}'-\boldsymbol{r}), \tag{5.8}$$

where we have used (3.17). The resulting contribution to the magnetic dipole moment is

$$\boldsymbol{m}^{LS} = \frac{e\hbar}{4m^2c^3}\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\boldsymbol{r}\times(\boldsymbol{r}\times\boldsymbol{s}). \tag{5.9}$$

The intrinsic magnetic moment of the electron including its first relativistic correction is given by (Messiah 1972)

$$\boldsymbol{m}^{s} = -(e\hbar g_s/2mc)\boldsymbol{s} + (e\hbar/2m^3c^3)p^2\boldsymbol{s}, \tag{5.10}$$

where g_s is the electron g factor.

If the system is placed in a uniform magnetic field $\boldsymbol{B} = B\boldsymbol{e}_z$, then the complete first-order perturbation to H_0^{nr} is

$$W = W_0 - (\boldsymbol{m}^0 + \boldsymbol{m}^s + \boldsymbol{m}^{\mathrm{K}} + \boldsymbol{m}^{LS})\,.\,\boldsymbol{B}, \tag{5.11}$$

where $\boldsymbol{m}^0 = -(e/2mc)\boldsymbol{l}$ is the non-relativistic orbital magnetic moment of the electron. If we restrict attention to S-states then W is diagonal in the $|nlms_z\rangle$-representation and we find for the fine-structure splitting

$$\Delta E_{\pm} = \langle n00|U_0^{\mathrm{K}} + U_0^{\mathrm{D}}|n00\rangle \pm \frac{e\hbar B}{4mc}\left(g_s - 2\frac{\langle T\rangle}{mc^2} + \frac{2}{3}\frac{\langle T\rangle}{mc^2}\right), \tag{5.12}$$

where $\langle T\rangle = \langle n00|p^2/2m|n00\rangle$ and we have used the virial theorem. The last two terms originate from the relativistic correction to the intrinsic magnetic moment (5.10) and from the spin–orbit magnetic moment (5.9). For the Coulomb potential $V(r) = -Ze^2/r$ one has

$$\langle T\rangle/mc^2 = Z^2\alpha^2/2n^2 = 2{\cdot}66\times10^{-5}\,Z^2/n^2 \tag{5.13}$$

where $\alpha = e^2/\hbar c$ is the fine-structure constant. The result (5.12) was also obtained by Margenau (1940) and by Perl and Hughes (1953) from a direct calculation of the energy levels from the Dirac equation. For alkali atoms the numerical magnitude of the correction terms in (5.12) has been estimated by Perl (1953). The present calculation has the advantage that the physical origin of the correction terms is much clearer, since they are recognised as originating from specific corrections to the magnetic dipole-moment operator. For real atoms nuclear mass corrections must also be taken into account (Hegstrom 1973).

6. Multipole Hamiltonian

By substituting (4.1) in (2.8) and using the spherical wave expansion I(4.4) of the vector potential, one obtains a multipole expansion for the interaction Hamiltonian V_1^{orb} involving the magnetic multipole moments $M_{\text{E}}(lm\omega)$ and $M_{\text{M}}(lm\omega)$ and the time derivative of the electric multipole moment $\dot{P}_{\text{E}}(lm\omega)$. For theoretical and practical purposes it is useful to transform to the so-called multipole Hamiltonian in which the time derivative is eliminated and the vector potential is replaced by the electric and magnetic fields (Power and Zienau 1959, Fiutak 1963, Atkins and Woolley 1970, Woolley 1971, Babiker *et al* 1974, Felderhof and Adu-Gyamfi 1974). We neglect centre-of-mass motion and assume that it makes sense to make a multipole expansion about the origin. One then performs the canonical transformation

$$H' = \Lambda H \Lambda^{-1} \tag{6.1}$$

with

$$\Lambda = \exp\left(-(\mathrm{i}/\hbar c)\int \boldsymbol{P}(\boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\right), \tag{6.2}$$

with $\boldsymbol{P}(\boldsymbol{r})$ as defined in (4.2). The transformed Hamiltonian is

$$\begin{aligned} H' = H^{\text{At}}\left(\left\{p_k - \frac{e_k}{c}\boldsymbol{A}(\boldsymbol{r}_k) + \frac{\partial}{\partial \boldsymbol{r}_k}\frac{1}{c}\int \boldsymbol{P}(\{\boldsymbol{r}_j\}, \boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}, \boldsymbol{r}_k, s_k\right\}\right) \\ + \frac{1}{8\pi}\int (\boldsymbol{E}_\perp^2 + \boldsymbol{B}^2)\,\mathrm{d}\boldsymbol{r} - \int \boldsymbol{P}(\boldsymbol{r}) \cdot \boldsymbol{E}_\perp(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + 2\pi \int \boldsymbol{P}_\perp^2(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} \\ - \int \boldsymbol{\mathcal{M}}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}. \end{aligned} \tag{6.3}$$

Expanding in powers of $\boldsymbol{A}$ one has

$$H' = H_0 + 2\pi \int \boldsymbol{P}_\perp^2(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + V_1' + V_2' + \ldots, \tag{6.4}$$

with

$$V_1' = V_1^{\text{orb}'} - \int \boldsymbol{\mathcal{M}}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}, \tag{6.5}$$

where

$$V_1^{\text{orb}'} = -\int \boldsymbol{P}(\boldsymbol{r}) \cdot \boldsymbol{E}_\perp(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + \sum_{j\alpha} H^j_{1\alpha}\left(\boldsymbol{X}, -\frac{e_j}{c}A_\alpha(\boldsymbol{r}_j) + \frac{\partial}{\partial r_{j\alpha}}\frac{1}{c}\int \boldsymbol{P}(\{\boldsymbol{r}_k\}, \boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\right). \tag{6.6}$$

We show that this last expression can be written as

$$V_1^{\text{orb}'}(\boldsymbol{A}(\boldsymbol{r})) = -\int \boldsymbol{P}(\boldsymbol{r}) \cdot \boldsymbol{E}_\perp(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} - \int \boldsymbol{M}_0(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}, \tag{6.7}$$

with $\boldsymbol{M}_0(\boldsymbol{r})$ as defined in (4.3). Using the identity (Felderhof and Adu-Gyamfi 1974)

$$\frac{\partial}{\partial \boldsymbol{r}_j}\frac{1}{c}\int \boldsymbol{P}(\boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = \frac{e_j}{c}\boldsymbol{A}(\boldsymbol{r}_j) + \frac{e_j}{c}\int \delta(\boldsymbol{r}) \sum_{n=0}^{\infty} \frac{n+1}{(n+2)!}(\boldsymbol{r}_j \cdot \nabla)^n (\boldsymbol{r}_j \times \boldsymbol{B}(\boldsymbol{r}))\,\mathrm{d}\boldsymbol{r}, \tag{6.8}$$

one can rewrite (6.6) as

$$V_1^{\mathrm{orb}'} + \int \boldsymbol{P}(\boldsymbol{r}) \cdot \boldsymbol{E}_\perp(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = \sum_{j\alpha} H'_{1\alpha}\Big(\boldsymbol{X}, \frac{e_j}{c}\int \delta(\boldsymbol{r}) \sum_{n=0}^{\infty} \frac{n+1}{(n+2)!}(\boldsymbol{r}_j \cdot \nabla)^n (\boldsymbol{r}_j \times \boldsymbol{B}(\boldsymbol{r}))_\alpha \, \mathrm{d}\boldsymbol{r}\Big)$$

$$= \sum_j \frac{e_j}{c} \sum_{n=0}^{\infty} \frac{n+1}{(n+2)!} \dot{\boldsymbol{r}}_j^X \cdot \int \delta(\boldsymbol{r})(\boldsymbol{r}_j \cdot \nabla)^n (\boldsymbol{r}_j \times \boldsymbol{B}(\boldsymbol{r}))\, \mathrm{d}\boldsymbol{r}$$

$$= \sum_j \frac{e_j}{c} \sum_{n=0}^{\infty} (-1)^n \frac{n+1}{(n+2)!} (\dot{\boldsymbol{r}}_j^X \times \boldsymbol{r}_j) \cdot \int [(\boldsymbol{r}_j \cdot \nabla)^n \delta(\boldsymbol{r})] \boldsymbol{B}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}. \tag{6.9}$$

This shows that (6.7) is correct.

Substituting the spherical wave expansion I(4.4) in the perturbation V'_1 and using the definitions (4.5) and (4.7), one sees that one can write

$$V'_1 = -\sum_\omega \sum_{lm} (4\pi\hbar\omega^3/Rc^2)^{1/2} \times [(P_{\mathrm{E}}(lm\omega) + M_{\mathrm{E}}(lm\omega) + \mathcal{M}_{\mathrm{E}}(lm\omega))\alpha_{\mathrm{E}}(lm\omega)^\dagger$$

$$+ (M_{\mathrm{M}}(lm\omega) + \mathcal{M}_{\mathrm{M}}(lm\omega))\alpha_{\mathrm{M}}(lm\omega)^\dagger + \mathrm{HC}], \tag{6.10}$$

where $\alpha_{\mathrm{E,M}}(lm\omega)^\dagger$ are creation operators for electric or magnetic multipole radiation and where we have used

$$P_{\mathrm{E}}(lm\omega) + M_{\mathrm{E}}(lm\omega) + \mathcal{M}_{\mathrm{E}}(lm\omega) = -V'_1(\boldsymbol{A}_{lm}^{\mathrm{E0}^*}(\boldsymbol{r}, \omega)), \tag{6.11a}$$

$$M_{\mathrm{M}}(lm\omega) + \mathcal{M}_{\mathrm{M}}(lm\omega) = -V'_1(\boldsymbol{A}_{lm}^{\mathrm{M0}^*}(\boldsymbol{r}, \omega)), \tag{6.11b}$$

which follow from (6.7). The transition probability for emission of electric or magnetic $(lm\omega)$ multipole radiation is determined by the matrix elements of the operators (6.11) between initial and final states $|a\rangle$ and $|b\rangle$ of the atom. The probability for absorption is determined by the matrix elements of the Hermitian conjugate operators.

Comparing with I(4.29), one sees that, on the energy shell, the matrix element for emission of electric multipole radiation found in the conventional theory is identical with that found from the multipole Hamiltonian. Hence in first-order perturbation theory the transition probabilities are the same in the two theories. One can show that if in both Hamiltonian operators one includes the second-order terms V_2 and V'_2, the transition probabilities are the same also in second-order perturbation theory. The multipole Hamiltonian has the advantage that Siegert's theorem (Siegert 1937, Sachs and Austern 1951) takes a simpler form. In practice the eigenstates $|a\rangle$ and $|b\rangle$ and their energies E_a and E_b are not known exactly. It follows from (6.11a) that the uncertainty in the energy does not introduce additional error, as was suggested by I(4.29). Although the transition probabilities are the same whether one uses the conventional or the multipole Hamiltonian, this is not true of the line shape. Power and Zienau (1959) have adduced evidence that experimental line shapes are better described by the multipole Hamiltonian H'.

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