

## Chapter 2

# Non-relativistic QED

**Abstract** A brief presentation is given of the construction of the theory of molecular QED. This is done by first writing a classical Lagrangian function for a collection of non-relativistic charged particles coupled to an electromagnetic field. After selecting the Coulomb gauge, Hamilton's principle is invoked and the Lagrangian is substituted into the Euler-Lagrange equations of motion and shown to lead to the correct dynamical equations. These are Newton's second law of motion with added Lorentz force law electric and magnetic field dependent terms, and the wave equation for the vector potential in the presence of sources. Canonically conjugate particle and field momenta are then evaluated, from which the Hamiltonian is derived. Elevation of classical variables to quantum operators finally yields the molecular QED Hamiltonian, which is expressed in minimal-coupling and multipolar forms. In the QED formulation, the electromagnetic field is described as a set of independent simple harmonic oscillators. Elementary excitations of the field, the photons, emerge automatically on quantisation.

**Keywords** Lagrangian · Polarisation · Magnetisation · Minimal-coupling Hamiltonian · Canonical transformation · Multipolar Hamiltonian · Perturbation theory

## 2.1 Classical Mechanics and Electrodynamics

As implied by its name, quantum electrodynamics (QED) [1] concerns the quantum mechanical description of charged particles in motion. Newton's Laws of Motion adequately treat the vast majority of kinematical situations encountered by macroscopic objects [2]. If these bodies move with velocities that are appreciable relative to that of light, however, then a Lorentz transformation may be applied, resulting in a relativistic treatment of the dynamics, as formulated by Einstein in his Special and General Theories of Relativity. A particularly elegant and advantageous form of classical mechanics, from the viewpoint of development of a quantum mechanical theory [3], is through the utilisation of the Lagrangian function,  $L$ ,

which is defined for a conservative system as the difference between kinetic and potential energies,  $T - V$ , along with the invocation of Hamilton's principle. This states that the path taken by an object as it moves in configuration space from space-time point  $(q_1, t_1)$  to  $(q_2, t_2)$ , where  $q$  is the generalised coordinate and  $t$  is the time, is the one for which the action,  $S$ , is a variational minimum.  $S$  is defined as the time integral of  $L$ , so that the extremum condition is

$$\delta S = \delta \int_{t_1}^{t_2} L(q, \dot{q}, t) dt = 0, \quad (2.1)$$

where  $\delta$  denotes the variation, and the velocity,  $\dot{q} = dq/dt$ . Standard calculus of variations [4] leads to the Euler-Lagrange equations of motion

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_\alpha} \right) - \frac{\partial L}{\partial q_\alpha} = 0, \quad \alpha = 1, 2, \dots, N, \quad (2.2)$$

for a system with  $N$  degrees of freedom. Selection of a suitable coordinate system for a specific dynamical problem often prevents the wider exploitation of Eq. (2.2) in classical mechanics when compared to applications of Newton's Second Law of Motion.

Since charged particles, protons and electrons are constituents of all matter—from the atoms of elements to the chemical compounds they form, any theory of the dynamics of such sources must also include a correct description of the electromagnetic fields that necessarily ensue, or which may be applied. These are expressed beautifully by Maxwell's equations, which encapsulate the properties and behaviour of all electromagnetic phenomena [5]. Hence classical mechanics and classical electrodynamics form two key ingredients in any theory of radiation-matter interaction. Unfortunately, these classical laws do not apply to microscopic entities. Elementary particles are instead governed according to quantum mechanical principles. This is the third, and obviously the most crucial element in the construction of QED theory. Slow or fast moving sub-atomic species, with energies that are significantly less than or comparable to  $mc^2$ , where  $m$  is the mass and  $c$  is the speed of light, may then be appropriately tackled by using non-relativistic or relativistic formulations of quantum mechanics, respectively.

To facilitate the application of quantum mechanical rules to the coupled charged particle-electromagnetic field system, Maxwell's equations are written in their microscopic form:

$$\epsilon_0 \text{div} \vec{E} = \rho \quad (2.3)$$

$$\text{div} \vec{B} = 0 \quad (2.4)$$

$$\text{curl} \vec{e} = -\frac{\partial \vec{b}}{\partial t} \quad (2.5)$$

$$\text{curl} \vec{b} = \frac{1}{c^2} \frac{\partial \vec{e}}{\partial t} + \frac{1}{\epsilon_0 c^2} \vec{j}, \quad (2.6)$$

with  $\epsilon_0$  the permittivity of the vacuum, which along with the permeability of the vacuum,  $\mu_0$ , are related to the speed of light via  $c^2 = (\epsilon_0 \mu_0)^{-1}$ .

Maxwell's equations may be converted to their more familiar macroscopic counterparts after performing a spatial average over the fundamental microscopic electric field  $\vec{e}(\vec{r}, t)$ , and the magnetic induction field  $\vec{b}(\vec{r}, t)$ , which are both functions of position  $\vec{r}$ , and time,  $t$ . These fields are related to the sources via the charge and current densities,  $\rho(\vec{r})$  and  $\vec{j}(\vec{r})$ , respectively. In a microscopic description these densities are defined as follows for a collection of point particles that give rise to continuous distributions of electric charge and current:

$$\rho(\vec{r}) = \sum_{\alpha} e_{\alpha} \delta(\vec{r} - \vec{q}_{\alpha}) \quad (2.7)$$

and

$$\vec{j}(\vec{r}) = \sum_{\alpha} e_{\alpha} \dot{\vec{q}}_{\alpha} \delta(\vec{r} - \vec{q}_{\alpha}). \quad (2.8)$$

In the last two relations,  $e_{\alpha}$  is the charge of particle  $\alpha$  positioned at  $\vec{q}_{\alpha}$ , and  $\delta(\vec{r})$  is the Dirac delta function [3].

Auxiliary fields are absent from the microscopic Maxwell equations since all charges present in the system contribute to  $\rho(\vec{r})$  and  $\vec{j}(\vec{r})$ . From the perspective of facilitating the quantisation of the electromagnetic field, it is beneficial to recast Maxwell's equations in terms of potentials rather than fields. This is done through the introduction of the scalar potential,  $\phi(\vec{r}, t)$ , and the vector potential,  $\vec{a}(\vec{r}, t)$ , on making use of the fact that a potential function is obtainable by integrating a field of force. Whence  $\vec{b} = \text{curl} \vec{a}$ , and  $-\nabla \phi = \vec{e} + \frac{\partial \vec{a}}{\partial t}$ . Substituting these last two relations into the inhomogeneous Maxwell Eqs. (2.3) and (2.6) enable the potentials to be related to the sources. The potentials are themselves subject to transformation by the simultaneous addition of a gauge function, giving rise to a set of potentials  $\phi$  and  $\vec{a}$  which leave the fields  $\vec{e}$  and  $\vec{b}$  unchanged, and therefore Maxwell's equations invariant. A specific choice of gauge function is then said to fix the gauge.

A common choice, and one that will be adopted throughout this work is the Coulomb gauge, in which  $\text{div} \vec{a} = 0$ . The potentials satisfy individual source dependent Maxwell's equations.  $\phi$  obeys

$$\epsilon_0 \nabla^2 \phi = -\rho, \quad (2.9)$$

which is immediately recognisable as Poisson's equation. Its solution represents the instantaneous Coulomb potential due to the charge density. Meanwhile  $\vec{a}$  satisfies the wave equation

$$\left( \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \vec{a} = -\frac{1}{\epsilon_0 c^2} \vec{j}^\perp, \quad (2.10)$$

where the transverse component of the current density  $\vec{j}^\perp(\vec{r})$  appears in Eq. (2.10), and is a direct consequence of the transverse gauge condition and Helmholtz's theorem [4]. It may be extracted with the help of the transverse delta function dyadic

$$\delta_{ij}^\perp(\vec{r}) = \frac{1}{(2\pi)^3} \int (\delta_{ij} - \hat{k}_i \hat{k}_j) e^{i\vec{k} \cdot \vec{r}} d^3 \vec{k} = (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{1}{4\pi r}, \quad (2.11)$$

with the longitudinal component given for completeness by

$$\delta_{ij}^\parallel(\vec{r}) = \frac{1}{(2\pi)^3} \int \hat{k}_i \hat{k}_j e^{i\vec{k} \cdot \vec{r}} d^3 \vec{k} = -\nabla_i \nabla_j \frac{1}{4\pi r}, \quad (2.12)$$

the sum of the two yielding [6]

$$\delta_{ij}^\perp(\vec{r}) + \delta_{ij}^\parallel(\vec{r}) = \delta_{ij} \delta(\vec{r}). \quad (2.13)$$

In the last three formulae the Latin subscripts denote Cartesian tensor components. When indices repeat, a sum over each component is implied. Clearly evident from Eqs. (2.9) and (2.10) is the separation of the static and dynamic parts of the sources of the field in the Coulomb gauge, with  $\vec{e}^\perp = -\partial \vec{a}^\perp / \partial t$ , and  $\vec{e}^\parallel = -\nabla \phi$ . Incidentally, the vector potential is transverse in *all* gauges.

An interesting case occurs when both  $\rho$  and  $\vec{j}$  vanish, corresponding to a free radiation field since there are no sources present. Solutions of Maxwell's equations then represent propagation of electromagnetic waves in vacuum. They are obtained by solving the wave equation

$$\left( \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \vec{e} = 0, \quad (2.14)$$

here written for the electric field, with a similar equation holding for  $\vec{a}$  and  $\vec{b}$ . Plane wave solutions of the form

$$\vec{e}(\vec{r}, t) = \varepsilon \vec{e}^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r} - i\omega t}, \quad (2.15)$$

follow straightforwardly, in which  $\varepsilon$  is the amplitude of the electric field, and  $e^{(\lambda)}(\vec{k})$  is its complex unit electric polarisation vector for radiation propagating with wave

vector  $\vec{k}$  and index of polarisation  $\lambda$ , with circular frequency  $\omega$ . Together  $\vec{k}$  and  $\lambda$  describe the mode of the radiation field. Identical harmonic functional form solutions apply to the magnetic induction field and vector potential, the latter obtained from solution of Eq. (2.10) after setting the right-hand side equal to zero. The magnitude of  $\vec{k}$  is  $k = |\vec{k}| = \omega/c$ . The unit electric and magnetic polarisation vectors, and direction of propagation, describe a right-handed triad, indicative of transverse wave propagation. Free electromagnetic radiation is in general elliptically polarised, but linear combinations of waves with appropriate choice of field strength and phase components readily produce linearly (plane) or circularly polarised light. To enumerate the allowed values of  $\vec{k}$  to a countable infinity, radiation is confined to a cubic box of volume  $V$ , with the vector potential satisfying the periodic boundary condition that it have identical value on opposite sides of the box. The components of  $\vec{k}$  are then restricted to  $k_i = 2\pi n_i/l$ , with  $n_i$ ,  $i = x, y, z$  taking on integer values, and  $l$  is the length of one side of the box.

In this section the laws underlying the classical mechanical behaviour and electromagnetic characteristics associated with charged particles have been summarized. The more interesting problem of interaction of microscopic forms of matter with the radiation field is examined next.

## 2.2 Lagrangian for a Charged Particle Coupled to Electromagnetic Radiation

Consider a particle  $\alpha$ , with charge  $e_\alpha$ , mass  $m_\alpha$  and generalized coordinate  $\vec{q}_\alpha$ , and velocity  $\dot{\vec{q}}_\alpha$ , interacting with electromagnetic radiation described by scalar and vector potentials  $\phi(\vec{r})$  and  $\vec{a}(\vec{r})$ . To facilitate construction of the QED Hamiltonian by means of the canonical quantization procedure, well known from particles only quantum mechanics [3], we begin by writing down the classical Lagrangian function for the particle, the electromagnetic field, and the interaction between the two as

$$L = L_{part} + L_{rad} + L_{int}. \quad (2.16)$$

Each of the three terms is given explicitly by:

$$L_{part} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \dot{\vec{q}}_{\alpha}^2 - V(\vec{q}), \quad (2.17)$$

where  $V(\vec{q})$  is the potential energy;

$$L_{rad} = \frac{1}{2} \epsilon_0 \int \{ \dot{\vec{a}}^2(\vec{r}) - c^2 (\text{curl} \vec{a}(\vec{r}))^2 \} d^3\vec{r}, \quad (2.18)$$

and

$$L_{int} = \int \vec{j}^\perp(\vec{r}) \cdot \vec{a}(\vec{r}) d^3\vec{r}. \quad (2.19)$$

The choice of Lagrangian is justified if it leads to the correct equations of motion for the system under consideration. Since  $L$  in Eq. (2.16) is additive, it is instructive to consider each of the sub-systems individually before dealing with the total Lagrangian in the following section.

Assume for the moment that there is no radiation field. The last two terms of Eq. (2.16) consequently vanish. Substituting  $L_{part}$  from Eq. (2.17) into the Euler-Lagrange Eq. (2.2) produces for the equation of motion,

$$m_\alpha \frac{d^2 \vec{q}_\alpha}{dt^2} = - \frac{\partial V}{\partial \vec{q}_\alpha}, \quad (2.20)$$

which is immediately recognisable as Newton's Second Law of Motion, as is to be expected for non-relativistic kinematics. Proceeding with the canonical prescription in order to transition from classical to quantum mechanics, the next step involves the evaluation of the momentum canonically conjugate to the coordinate variable,

$$\vec{p}_\alpha = \frac{\partial L}{\partial \dot{\vec{q}}_\alpha}, \quad (2.21)$$

which for  $L_{part}$  above yields  $\vec{p}_\alpha = m_\alpha \dot{\vec{q}}_\alpha$ , for which kinetic and canonical momenta are equal.

Hamilton's principal function is then constructed via

$$H = \sum_\alpha \vec{p}_\alpha \dot{\vec{q}}_\alpha - L \quad (2.22)$$

after eliminating the velocity in favour of the momentum. Hamilton's canonical equations follow on taking the total derivative of  $H$  in Eq. (2.22), giving

$$\dot{\vec{q}}_\alpha = \frac{\partial H}{\partial \vec{p}_\alpha}, \quad (2.23)$$

$$\dot{\vec{p}}_\alpha = - \frac{\partial H}{\partial \vec{q}_\alpha}, \quad (2.24)$$

and

$$\frac{\partial H}{\partial t} = - \frac{\partial L}{\partial t}, \quad (2.25)$$

if  $L$  is explicitly time-dependent. Continuing with this particles only scenario, inserting the velocity and  $L_{part}$  in Eq. (2.22) results in the particle Hamiltonian

$$H_{part} = \sum_{\alpha} \frac{1}{2m_{\alpha}} \vec{p}_{\alpha}^2 + V(\vec{q}), \quad (2.26)$$

which represents the total classical energy of a conservative system, and is a sum of kinetic and potential energy contributions.

Let us now assume that there are no sources of charge and current. Only  $L_{rad}$  of Eq. (2.16) therefore remains, corresponding to the free radiation field. Choosing the vector potential to be the analogue of the “coordinate” variable, and its time derivative to be the “velocity” variable, the canonical formalism valid for particles may be applied to the electromagnetic field. Because the field is continuous, neighbouring points in space are related via the spatial gradient as well as by the displacement between them. Accounting for this fact results in the Euler-Lagrange Eq. (2.2) being modified by an additional term, which for the  $i$ th component reads in total as

$$\frac{\partial}{\partial t} \left( \frac{\partial L^D}{\partial \dot{a}_i} \right) + \frac{\partial}{\partial x_j} \frac{\partial L^D}{\partial (\partial a_i / \partial x_j)} - \frac{\partial L^D}{\partial a_i} = 0. \quad (2.27)$$

$L^D$  is a Lagrangian density. Its integral over all space yields  $L$ . With  $L_{rad}^D$  from Eq. (2.18) given by  $\frac{1}{2} \epsilon_0 [\dot{\vec{a}}^2 - c^2 (\text{curl} \vec{a})^2]$ , application of Eq. (2.27) gives rise to the source free wave equation

$$\left( \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) a_i = 0, \quad (2.28)$$

validating the choice of radiation field Lagrangian Eq. (2.18).

Analogously to Eq. (2.21), the momentum canonically conjugate to the field coordinate is defined as

$$\vec{\Pi}(\vec{r}) = \frac{\partial L^D}{\partial \dot{\vec{a}}(\vec{r})}. \quad (2.29)$$

From  $L_{rad}^D$ ,  $\vec{\Pi}(\vec{r})$  is explicitly found in this case to be

$$\vec{\Pi}(\vec{r}) = \epsilon_0 \dot{\vec{a}}(\vec{r}) = -\epsilon_0 \vec{e}^{\perp}(\vec{r}). \quad (2.30)$$

Proceeding with the canonical formulation, the classical Hamiltonian for the free radiation field is then calculated from

$$H_{rad} = \int (\vec{\Pi}(\vec{r}) \cdot \dot{\vec{a}}(\vec{r}) - L_{rad}^D) d^3 \vec{r}, \quad (2.31)$$

with the integrand corresponding to the Hamiltonian density. Eliminating  $\vec{a}$  in terms of  $\vec{\Pi}$  from Eq. (2.30),  $H_{rad}$  when expressed in terms of canonical variables is written as

$$H_{rad} = \frac{1}{2} \int \{ [\vec{\Pi}^2(\vec{r})/\epsilon_0] + \epsilon_0 c^2 [\text{curl} \vec{a}(\vec{r})]^2 \} d^3 \vec{r}. \quad (2.32)$$

On making use of the definition of the vector potential, and the right-hand most form of Eq. (2.30),  $H_{rad}$  can be written more transparently as functions of the electric and magnetic induction fields, as in

$$H_{rad} = \frac{\epsilon_0}{2} \int \{ \vec{e}^{\perp 2}(\vec{r}) + c^2 \vec{b}^2(\vec{r}) \} d^3 \vec{r}. \quad (2.33)$$

Either of the last two integrands provides an expression for the electromagnetic energy density.

Interestingly, it was recognised by Born, Heisenberg and Jordan [7] that the quantum mechanical version of  $H_{rad}$  is equivalent to the Hamiltonian of a mechanically vibrating system, as demonstrated by Jeans' theorem in the classical regime [8]. By defining two real variables

$$q_{\vec{k}}^{(\lambda)} = (\epsilon_0 V)^{1/2} (a_{\vec{k}}^{(\lambda)} + \bar{a}_{\vec{k}}^{(\lambda)}) \quad (2.34)$$

$$p_{\vec{k}}^{(\lambda)} = -i\omega(\epsilon_0 V)^{1/2} (a_{\vec{k}}^{(\lambda)} - \bar{a}_{\vec{k}}^{(\lambda)}), \quad (2.35)$$

where  $a_{\vec{k}}^{(\lambda)}$  are complex Fourier mode components [4] of the vector potential, with the overbar denoting the complex conjugate, and  $V$  is the quantisation volume,  $H_{rad}$  may be re-expressed as a sum of simple harmonic oscillator Hamiltonians, one for each mode  $(\vec{k}, \lambda)$

$$H_{rad} = \sum_{\vec{k}, \lambda} \frac{1}{2} \{ p_{\vec{k}}^{(\lambda)2} + \omega^2 q_{\vec{k}}^{(\lambda)2} \} = \sum_{\vec{k}, \lambda} H_{\vec{k}, \lambda}. \quad (2.36)$$

The new variables (2.34) and (2.35) are canonically conjugate, and result in the correct Hamilton's equations of motion being obtained on using (2.23) and (2.24).

Having established that  $L_{part}$  and  $L_{rad}$  contained in the total Lagrangian Eq. (2.16) each correctly describe the dynamics in the absence of a radiation field, and when there are no sources present, respectively, in the next section we examine the coupled matter-electromagnetic field system, and see how the equations of motion are modified due to interaction. The system is then quantised and a QED Hamiltonian operator is finally obtained.



## 2.3 Minimal-Coupling QED Hamiltonian

We now verify that the total Lagrangian for the interacting system, Eq. (2.16), leads to the correct equations of motion, appropriately changed to account for the inclusion of  $L_{int}$ . Application of Eq. (2.2) gives rise to [9]

$$m_\alpha \frac{d^2 q_{i(\alpha)}}{dt^2} = -\frac{\partial V}{\partial q_{i(\alpha)}} + e_\alpha e_i^\perp(\vec{q}_\alpha) + e_\alpha \left( \frac{d\vec{q}_\alpha}{dt} \times \vec{b}(\vec{q}_\alpha) \right)_i, \quad (2.37)$$

instead of Eq. (2.20). Newton's equations of motion are now modified by the addition of Lorentz force law terms describing the coupling of the charged particle to the electromagnetic field. Application of Eq. (2.27) to the full Lagrangian (2.16) changes Eq. (2.28) to Eq. (2.10), the expected wave equation satisfied by the vector potential in the presence of sources.

The classical Hamiltonian function for the coupled system may be obtained by following the canonical scheme implemented in the previous section. The particle momentum is no longer equal to its kinetic momentum, but changes to

$$\vec{p}_\alpha = m_\alpha \frac{d\vec{q}_\alpha}{dt} + e_\alpha \vec{a}(\vec{q}_\alpha). \quad (2.38)$$

$\vec{\Pi}(\vec{r})$ , however, remains identical to Eq. (2.30).  $H$  is then calculated from

$$H = \sum_\alpha \vec{p}_\alpha \cdot \dot{\vec{q}}_\alpha + \int \vec{\Pi}(\vec{r}) \cdot \dot{\vec{a}}(\vec{r}) d^3\vec{r} - L, \quad (2.39)$$

which for a many-particle system is found to be [9, 10]

$$H = \sum_\alpha \frac{1}{2m_\alpha} \{ \vec{p}_\alpha - e_\alpha \vec{a}(\vec{q}_\alpha) \}^2 + V(\vec{q}) + \frac{1}{2} \int \left\{ \frac{\vec{\Pi}^2}{\epsilon_0} + \epsilon_0 c^2 (\text{curl} \vec{a})^2 \right\} d^3\vec{r}. \quad (2.40)$$

Equation (2.40) is known as the minimal-coupling Hamiltonian on account of the minimum action principle being applied to its construction. Coupling of radiation with matter simply amounts to replacing the particle momentum by  $\vec{p}_\alpha - e_\alpha \vec{a}(\vec{q}_\alpha)$ .

At this point in the development it is convenient to collect the charged particles  $\alpha$  and form atoms and molecules  $\xi$ . Furthermore, the nuclei are henceforth taken to be stationary, with the positions and momenta of the electrons only being considered. As a result, the Hamiltonian Eq. (2.40) may be partitioned as [9, 10]

$$H = \sum_{\xi} H_{part}(\xi) + H_{rad} + \sum_{\substack{\xi, \xi' \\ \xi < \xi'}} H_{int}(\xi, \xi'), \quad (2.41)$$

into a sum of particle, radiation field, and interaction contributions. Decomposing the electrostatic energy into a sum of single- and two-particle terms,

$$V = V(\xi) + V(\xi, \xi'), \quad (2.42)$$

enables the first term of Eq. (2.41) to be written as

$$H_{part}(\xi) = \sum_{\alpha} \frac{1}{2m_{\alpha}} \vec{p}_{\alpha}^2(\xi) + V(\xi), \quad (2.43)$$

and which differs slightly from Eq. (2.26) in that  $V(\xi)$  is now interpreted as the intra-molecular potential energy. Hence Eq. (2.43) corresponds to the familiar molecular Hamiltonian of non-relativistic quantum mechanics in the Born-Oppenheimer approximation [11]. The second term of Eq. (2.41) is given by the third term of Eq. (2.40) and is seen to be identical to  $H_{rad}$  calculated for the free radiation field Eq. (2.32). The remaining terms of Eq. (2.40), along with the second term of Eq. (2.42) constitute the interaction Hamiltonian,

$$H_{int}(\xi, \xi') = - \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}} \vec{p}_{\alpha}(\xi) \cdot \vec{a}(\vec{q}_{\alpha}(\xi)) + \sum_{\alpha} \frac{e_{\alpha}^2}{2m_{\alpha}} \vec{a}^2(\vec{q}_{\alpha}(\xi)) + V(\xi, \xi'), \quad (2.44)$$

where the third term of Eq. (2.44) is the instantaneous inter-particle Coulomb potential. Even though  $V(\xi, \xi')$  appears explicitly, a fully retarded result is obtained on using Eq. (2.44) on account of exact cancellation of static terms with those arising from the vector potential, which contains non-retarded contributions in the Coulomb gauge. The first two terms of the interaction Hamiltonian are linear and quadratic in the vector potential evaluated at the position of electron  $\alpha$  in atom or molecule  $\xi$ .

Quantisation of the classical minimal-coupling Hamiltonian (2.41) then follows by promoting the classical dynamical variables, for both particles and radiation field, namely the respective coordinates  $\vec{q}_{\alpha}(\xi)$  and  $\vec{a}(\vec{r})$ , and momenta  $\vec{p}_{\alpha}(\xi)$  and  $\vec{\Pi}(\vec{r})$ , to quantum mechanical operators subject to the canonical equal time commutation relations

$$[q_{i(\alpha)}(\xi), p_{j(\beta)}(\xi')] = i\hbar \delta_{ij} \delta_{\alpha\beta} \delta_{\xi\xi'}, \quad (2.45)$$

and

$$[a_i(\vec{r}), \Pi_j(\vec{r}')] = i\hbar \delta_{ij}^{\perp}(\vec{r} - \vec{r}'). \quad (2.46)$$

Recalling that the equations describing the electromagnetic field are formally equivalent to that of an oscillating mechanical system, quantisation of the radiation

field corresponds to quantisation of the simple harmonic oscillator Hamiltonian Eq. (2.36). A powerful and elegant method of obtaining eigenvalue and eigenfunction solutions to this problem is through the techniques of second quantisation via the introduction of lowering and raising operators [12]

$$a = \frac{1}{\sqrt{2}} \left( \sqrt{\frac{m\omega}{\hbar}} q + i \sqrt{\frac{1}{m\omega\hbar}} p \right), \quad (2.47)$$

and

$$a^\dagger = \frac{1}{\sqrt{2}} \left( \sqrt{\frac{m\omega}{\hbar}} q - i \sqrt{\frac{1}{m\omega\hbar}} p \right), \quad (2.48)$$

which are real and mutually adjoint, but are not symmetric and therefore non-Hermitian. Thus the radiation field Hamiltonian Eq. (2.36) can be expressed in terms of  $(\vec{k}, \lambda)$ – mode annihilation and creation operators  $a^{(\lambda)}(\vec{k})$  and  $a^{\dagger(\lambda)}(\vec{k})$  as

$$H_{rad} = \sum_{\vec{k}, \lambda} \{ a^{\dagger(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) + \frac{1}{2} \} \hbar \omega, \quad (2.49)$$

subject to the commutator

$$[a^{(\lambda)}(\vec{k}), a^{\dagger(\lambda')}(\vec{k}')] = \delta_{\lambda\lambda'} \delta(\vec{k} - \vec{k}'), \quad (2.50)$$

with all other boson operator combinations commuting.

Identification of the operator combination  $a^{\dagger(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k})$  as the number operator  $n(\vec{k}, \lambda)$ , allows the eigenvalue spectrum of the quantised electromagnetic field to be written down immediately as  $(n + \frac{1}{2})\hbar\omega$ ,  $n = 0, 1, 2, \dots$ . The excitation quanta therefore correspond to the number of photons in the radiation field, which is characteristic of the occupation number representation adopted. The state of the electromagnetic field is specified by the ket  $|n(\vec{k}, \lambda)\rangle$ . It is usual to suppress states with zero photons. The bosonic operators  $a^{(\lambda)}(\vec{k})$  and  $a^{\dagger(\lambda)}(\vec{k})$ , respectively decrease or increase the number of photons in the radiation field by unity according to the operator relations [3, 6]

$$\begin{aligned} a^{(\lambda)}(\vec{k}) |n(\vec{k}, \lambda)\rangle &= 0, & n &= 0, \\ &= n^{1/2} |(n-1)(\vec{k}, \lambda)\rangle, & n &= 1, 2, \dots \end{aligned}, \quad (2.51)$$

and

$$a^{\dagger(\lambda)}(\vec{k})|n(\vec{k}, \lambda)\rangle = (n+1)^{1/2}|(n+1)(\vec{k}, \lambda)\rangle, \quad n = 0, 1, 2, \dots, \quad (2.52)$$

along with the number operator

$$a^{\dagger(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})|n(\vec{k}, \lambda)\rangle = n|n(\vec{k}, \lambda)\rangle, \quad n = 0, 1, 2, \dots \quad (2.53)$$

It is interesting to note that the state of the radiation field in which there are no photons represents its ground state, corresponding to the electromagnetic vacuum, for which  $n = 0$  [13]. An ever present  $\frac{1}{2}\hbar\omega$  of zero-point energy is associated per mode of the field, resulting in an infinite ground state field energy. Nonetheless, measurable effects ensue from vacuum fluctuations, with the van der Waals dispersion force perhaps being one of the most important. Others include spontaneous emission (since  $a^{\dagger(\lambda)}(\vec{k})$  can act on the vacuum state to create a photon), and the Lamb shift [1].

A Fourier mode expansion [4] of the vector potential as a function of the creation and destruction operators in the Schrödinger picture takes the form

$$\vec{a}(\vec{r}) = \sum_{\vec{k}, \lambda} \left( \frac{\hbar}{2\varepsilon_0 c k V} \right)^{1/2} [\vec{e}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}} + \vec{e}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}}], \quad (2.54)$$

where  $\vec{e}^{(\lambda)}(\vec{k})$  is a complex unit electric polarisation vector for a  $(\vec{k}, \lambda)$ -mode photon, and  $V$  is the box quantisation volume. Similar expressions for  $\vec{e}^{\perp}(\vec{r})$ ,  $\vec{b}(\vec{r})$  and  $\vec{\Pi}(\vec{r})$  follow from their definitions in terms of  $\vec{a}(\vec{r})$  given earlier, namely  $\vec{e}^{\perp}(\vec{r}) = -\dot{\vec{a}}(\vec{r}) = -e_0^{-1}\vec{\Pi}(\vec{r})$ , and  $\vec{b}(\vec{r}) = \text{curl}\vec{a}(\vec{r})$ . They are

$$\vec{e}^{\perp}(\vec{r}) = i \sum_{\vec{k}, \lambda} \left( \frac{\hbar c k}{2\varepsilon_0 V} \right)^{1/2} [\vec{e}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}} - \vec{e}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}}], \quad (2.55)$$

$$\vec{b}(\vec{r}) = i \sum_{\vec{k}, \lambda} \left( \frac{\hbar k}{2\varepsilon_0 c V} \right)^{1/2} [\vec{b}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}} - \vec{b}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}}], \quad (2.56)$$

where the unit magnetic polarisation vector is  $\vec{b}^{(\lambda)}(\vec{k}) = \hat{k} \times \vec{e}^{(\lambda)}(\vec{k})$ , and

$$\vec{\Pi}(\vec{r}) = -i \sum_{\vec{k}, \lambda} \left( \frac{\hbar c k \varepsilon_0}{2V} \right)^{1/2} [\vec{e}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}} - \vec{e}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}}], \quad (2.57)$$

the first factor after each sum in the mode expansion ensures that each field is correctly normalised to reproduce the energy of the electromagnetic field.

## 2.4 Multipolar-Coupling QED Hamiltonian

While the minimal-coupling Hamiltonian Eq. (2.41) may be employed to compute light-matter and inter-particle interactions, the form of coupling Hamiltonian Eq. (2.44) isn't the most advantageous to work with from the point of view of treating chemical systems. Inspection of  $H_{int}(\xi, \xi')$  reveals the presence of the particle momentum operator in the first term, the vector potential operator and its square in the first and second terms, respectively, and the instantaneous two-particle coupling  $V(\xi, \xi')$  given by the last contribution of Eq. (2.44). A superior alternative QED Hamiltonian is provided by the multipolar counterpart. Here atoms and molecules couple directly to the causal Maxwell field operators through their molecular multipole moment distributions, and all instantaneous couplings have been eliminated. Use of either Hamiltonian leads to results that are properly retarded. In the minimal-coupling scheme this occurs through explicit cancellation of static contributions. The multipolar version may be obtained from the minimal-coupling form by applying a quantum canonical transformation on  $H_{min}$ , Eq. (2.40), using a generating function  $S$  that is independent of time. Although the new Hamiltonian differs in functional form relative to the old one, identical eigenspectra result with the use of either Hamiltonian since the transformation is unitary. It is of the form

$$e^{iS} H_{min} e^{-iS} = H_{mult}. \quad (2.58)$$

Hamiltonians related in this way are said to be equivalent [14]. An intrinsic feature of quantum canonical transformations is that they leave the commutator between canonically conjugate dynamical variables invariant, for instance

$$[q, p] = i\hbar, \quad (2.59)$$

and they leave the Heisenberg operator equations of motion unchanged, the latter being the quantum versions of Hamilton's canonical equations,

$$i\hbar\dot{q} = [q, H], \quad (2.60)$$

and

$$i\hbar\dot{p} = [p, H]. \quad (2.61)$$

It is easily verified that transformation (2.58) guarantees that these properties are satisfied [9]. Hence a quantum canonical transformation in essence amounts to transforming the original canonically conjugate dynamical variables of the system and expressing the original Hamiltonian in terms of the newly transformed

quantities. It is therefore the quantum mechanical analogue of a contact transformation in classical mechanics [2, 3].

The specific form of the generator  $S$  that enables transformation of minimal-coupling variables to those in the multipolar formalism is [15]

$$S = \frac{1}{\hbar} \int \vec{p}^\perp(\vec{r}) \cdot \vec{a}(\vec{r}) d^3\vec{r}. \quad (2.62)$$

In Eq. (2.62),  $\vec{p}^\perp(\vec{r})$  is the transverse component of the electric polarisation field for a molecular assembly,

$$\vec{p}(\vec{r}) = \sum_{\xi} \vec{p}(\xi; \vec{r}), \quad (2.63)$$

where a closed form expression for the electronic part of  $\vec{p}(\xi; \vec{r})$ , written in terms of a parametric integral, is [16]

$$\vec{p}(\xi; \vec{r}) = -e \sum_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \int_0^1 \delta(\vec{r} - \vec{R}_{\xi} - \lambda(\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})) d\lambda, \quad (2.64)$$

where  $\vec{R}_{\xi}$  is the position vector of the centre of species  $\xi$ . Because the generator is a function only of the particle and field coordinates,  $\vec{q}_{\alpha}(\xi)$  and  $\vec{a}(\vec{r})$  remain unchanged by the transformation, with only the canonically conjugate momenta being transformed.

Employing the Baker-Hausdorff identity for two non-commuting operators  $A$  and  $B$ ,

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!} [A, [A, B]] + \frac{1}{3!} [A, [A, [A, B]]] + \dots, \quad (2.65)$$

it can be shown [9] that the particle momentum transforms as

$$\begin{aligned} \vec{p}_{\alpha}^{mult}(\xi) &= e^{iS} \vec{p}_{\alpha}^{min}(\xi) e^{-iS} = \vec{p}_{\alpha}^{min}(\xi) + i[S, \vec{p}_{\alpha}^{min}(\xi)] + \dots \\ &= \vec{p}_{\alpha}^{min}(\xi) + e\vec{a}(\vec{q}_{\alpha}(\xi)) - \int \vec{n}_{\alpha}(\xi; \vec{r}) \times \vec{b}(\vec{r}) d^3\vec{r}, \end{aligned} \quad (2.66)$$

on inserting the generator (2.62). In Eq. (2.66), the vector field  $\vec{n}_{\alpha}(\xi; \vec{r})$  is defined as

$$\vec{n}_{\alpha}(\xi; \vec{r}) = -e(\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \int_0^1 \lambda \delta(\vec{r} - \vec{R}_{\xi} - \lambda(\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})) d\lambda, \quad (2.67)$$

with

$$\vec{n}(\vec{r}) = \sum_{\xi, \alpha} \vec{n}_\alpha(\xi; \vec{r}). \quad (2.68)$$

Carrying out the transformation on the field momentum, we find in similar fashion

$$\begin{aligned} \vec{\Pi}^{mult}(\vec{r}) &= e^{iS} \vec{\Pi}^{min}(\vec{r}) e^{-iS} = \vec{\Pi}^{min}(\vec{r}) + i[S, \vec{\Pi}^{min}(\vec{r})] + \dots \\ &= \Pi^{min}(\vec{r}) + \frac{i}{\hbar} \left[ \int \vec{p}^\perp(\vec{r}') \cdot \vec{d}(\vec{r}') d^3\vec{r}', \vec{\Pi}^{min}(\vec{r}) \right] + \dots \end{aligned} \quad (2.69)$$

On using the field commutation relation (2.46), it is seen that  $S$  commutes with the minimal-coupling field momentum so that all subsequent higher-order nested commutators not explicitly written in Eq. (2.69), but present in Eq. (2.65) vanish, leaving the canonically conjugate field momentum in multipolar framework as

$$\vec{\Pi}^{mult}(\vec{r}) = \vec{\Pi}^{min}(\vec{r}) - \vec{p}^\perp(\vec{r}). \quad (2.70)$$

Recalling from Eq. (2.30) that  $\vec{\Pi}^{min}(\vec{r}) = -\epsilon_0 \vec{e}^\perp(\vec{r})$ , it is seen that

$$\vec{\Pi}^{mult}(\vec{r}) = -\vec{d}^\perp(\vec{r}), \quad (2.71)$$

where  $\vec{d}^\perp(\vec{r})$  is the transverse component of the electric displacement field  $\vec{d}(\vec{r})$  defined by

$$\vec{d}(\vec{r}) = \epsilon_0 \vec{e}(\vec{r}) + \vec{p}(\vec{r}). \quad (2.72)$$

Hence in the multipolar formalism, the canonically conjugate field momentum is no longer proportional to the transverse electric field, but is instead equal to the negative of the displacement field. A mode expansion for this last field quantity is given by

$$\vec{d}^\perp(\vec{r}) = i \sum_{\vec{k}, \lambda} \left( \frac{\hbar c k \epsilon_0}{2V} \right)^{1/2} [\vec{e}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \vec{e}^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}}]. \quad (2.73)$$

The multipolar form of Hamiltonian follows on substituting for  $\vec{p}_\alpha^{mult}(\xi)$ , Eq. (2.66) and  $\vec{\Pi}^{mult}(\vec{r})$ , Eq. (2.70) into the minimal-coupling Hamiltonian Eq. (2.40),

$$\begin{aligned}
H^{mult} = & \sum_{\xi} \frac{1}{2m} \sum_{\alpha} \{ \vec{p}_{\alpha}(\xi) + \int \vec{n}_{\alpha}(\xi; \vec{r}) \times \vec{b}(\vec{r}) d^3 \vec{r} \}^2 + \sum_{\xi} V(\xi) \\
& + \frac{1}{2\epsilon_0} \int \{ [\vec{\Pi}(\vec{r}) + \vec{p}^{\perp}(\vec{r})]^2 + \epsilon_0^2 c^2 (\text{curl} \vec{a}(\vec{r}))^2 \} d^3 \vec{r} + \sum_{\substack{\xi, \xi' \\ \xi > \xi'}} V(\xi, \xi'), \quad (2.74)
\end{aligned}$$

on employing decomposition (2.42). As done for its minimal-coupling counterpart,  $H^{mult}$  may be partitioned into particle, radiation field, and interaction Hamiltonian terms. Thus

$$H^{mult} = H_{part}^{mult} + H_{rad}^{mult} + H_{int}^{mult} + \frac{1}{2\epsilon_0} \int \sum_{\xi} |\vec{p}^{\perp}(\xi; \vec{r})|^2 d^3 \vec{r}, \quad (2.75)$$

with

$$H_{part}^{mult} = \sum_{\xi} \{ \frac{1}{2m} \sum_{\alpha} \vec{p}_{\alpha}^2(\xi) + V(\xi) \}, \quad (2.76)$$

and

$$H_{rad}^{mult} = \frac{1}{2\epsilon_0} \int \{ \vec{d}^{\perp 2}(\vec{r}) + \epsilon_0^2 c^2 \vec{b}^2(\vec{r}) \} d^3 \vec{r}, \quad (2.77)$$

when written explicitly in terms of Maxwell fields, and

$$\begin{aligned}
H_{int}^{mult} = & -\epsilon_0^{-1} \int \vec{p}(\vec{r}) \cdot \vec{d}^{\perp}(\vec{r}) d^3 \vec{r} \\
& - \int \vec{m}(\vec{r}) \cdot \vec{b}(\vec{r}) d^3 \vec{r} + \frac{1}{2} \int O_{ij}(\vec{r}, \vec{r}') b_i(\vec{r}) b_j(\vec{r}') d^3 \vec{r} d^3 \vec{r}'. \quad (2.78)
\end{aligned}$$

$\vec{p}(\vec{r})$  appearing in the first term of  $H_{int}^{mult}$  is the electric polarisation field (2.63). Two new fields feature in the remaining contributions. One is the magnetisation field,

$$\vec{m}(\vec{r}) = \frac{1}{2m} \sum_{\xi, \alpha} [\vec{n}_{\alpha}(\xi; \vec{r}) \times \vec{p}_{\alpha}(\xi) - \vec{p}_{\alpha}(\xi) \times \vec{n}_{\alpha}(\xi; \vec{r})], \quad (2.79)$$

and the other is the diamagnetisation field

$$O_{ij}(\vec{r}, \vec{r}') = \sum_{\xi} \sum_{\xi'} \frac{1}{m} \epsilon_{ikl} \epsilon_{jml} n_k(\xi; \vec{r}) n_m(\xi'; \vec{r}'), \quad (2.80)$$

where the  $\alpha$ -dependence of the  $n_i$  tensors is implicit. A remarkable aspect of the multipolar Hamiltonian relative to its minimal-coupling precursor is the



disappearance of the static inter-particle coupling term  $V(\xi, \xi')$ . On separating the square of the transverse polarisation contribution from (2.74) into a sum of intra- and inter-molecular parts, it is found that the inter-molecular contribution exactly cancels  $V(\xi, \xi')$ . What remains is a one-centre transverse electric polarisation field squared contribution, the last term of Eq. (2.75). Because it is independent of the radiation field, it may be neglected when considering effects that produce a change in the state of the electromagnetic field. When evaluating corrections to the self-energy, however, this contribution must be retained. Another feature of Eq. (2.75) is the explicit presence of the transverse electric displacement field. This is a direct consequence of the transformed field momentum Eq. (2.70). Furthermore, atoms and molecules couple directly to the electric displacement and magnetic induction fields through electric polarisation, magnetisation and diamagnetisation distributions. Because the Maxwell fields are strictly causal, interactions between centres of charge and current are properly retarded, with electromagnetic signals propagating at the correct speed, namely that of light,  $c$ . There are no static coupling terms.

The transformation of the minimal-coupling Hamiltonian to  $H^{mult}$  via Eq. (2.58) and the generator (2.62) is known as the Power-Zienau-Woolley transformation [9, 10, 14–21]. An alternative method of arriving at  $H^{mult}$  is to first transform the minimal-coupling Lagrangian, Eq. (2.16). This may be accomplished by the addition to  $L$  of the time derivative of a function of the coordinates and the time only. The effect of such a modification is to generate an equivalent Lagrangian, in the sense that the Euler-Lagrange equations of motion (2.2) remain identical in form [2]. Again the coordinate variable remains invariant, but the new canonically conjugate momentum is changed to  $\vec{p} + \frac{\partial f(\vec{q}, t)}{\partial \vec{q}}$ , where  $f$  is the transformation function.

The general connection between  $f$  and the generator  $S$  that yields equivalent Hamiltonians is easily found. Applying the first line of Eq. (2.66), the new momentum obtained via canonical transformation is  $\vec{p} - \hbar \frac{\partial S}{\partial \vec{q}}$ , so that  $f = -\hbar S$ . Hence the multipolar Hamiltonian Eq. (2.75) will result when  $-\frac{d}{dt} \int \vec{p}^\perp(\vec{r}) \cdot \vec{a}(\vec{r}) d^3\vec{r}$  is added to  $L_{min}$ , Eq. (2.16) to give  $L_{mult}$  [14, 22, 23]. This addition has the desired effect of removing coupling via the transverse current. On account of

$$\vec{j}(\vec{r}) = \frac{d\vec{p}(\vec{r})}{dt} + \text{curl} \vec{m}(\vec{r}), \quad (2.81)$$

interaction now occurs through the polarisation and magnetisation fields instead. The newly transformed Lagrangian,  $L_{mult}$ , leads to the correct equations of motion. In the case of particles, this is the Newton-Lorentz force law Eq. (2.37). For the radiation field, the resulting equations are known as the atomic field equations. They are intermediate between the microscopic Maxwell-Lorentz Eqs. (2.3)–(2.6), and the macroscopic Maxwell equations. The source free Maxwell Eqs. (2.4) and (2.5) are trivially satisfied by the form of the electromagnetic potentials in the Coulomb gauge. Meanwhile Eq. (2.3) becomes

$$\text{div} \vec{d}(\vec{r}) = \rho^{\text{true}}(\vec{r}), \quad (2.82)$$

where  $\vec{d}(\vec{r})$  was defined by Eq. (2.72), showing that the true charges are solely responsible for the electric displacement field. The second source dependent Maxwell-Lorentz Eq. (2.6) becomes

$$\text{curl} \vec{h}(\vec{r}) = \frac{\partial \vec{d}^\perp(\vec{r})}{\partial t}, \quad (2.83)$$

on defining the auxiliary magnetic field

$$\vec{h}(\vec{r}) = \varepsilon_0 c^2 \vec{b}(\vec{r}) - \vec{m}(\vec{r}), \quad (2.84)$$

after taking the transverse component of relation (2.81), thereby ensuring the implicit presence of the current density. Hence the sources are represented by electric polarisation and magnetisation distributions, which are in turn the origins of the microscopic fields  $\vec{d}(\vec{r})$  and  $\vec{h}(\vec{r})$ .

By expanding  $\vec{p}(\vec{r})$  and  $\vec{m}(\vec{r})$  about  $\vec{R}_\xi$  in a Taylor series [5], and retaining the first few terms in the series, electric dipole and quadrupole polarisation distributions,

$$\vec{p}(\xi; \vec{r}) = \sum_\alpha e_\alpha (\vec{q}_\alpha(\xi) - \vec{R}_\xi) \left\{ 1 - \frac{1}{2!} (\vec{q}_\alpha(\xi) - \vec{R}_\xi) \cdot \nabla + \dots \right\} \delta(\vec{r} - \vec{R}_\xi), \quad (2.85)$$

and the magnetic dipole contribution to the magnetisation field,

$$\vec{m}(\xi; \vec{r}) = \sum_\alpha \frac{e_\alpha}{m_\alpha} \{ (\vec{q}_\alpha(\xi) - \vec{R}_\xi) \times \vec{p}_\alpha(\xi) \} \left\{ \frac{1}{2!} - \dots \right\} \delta(\vec{r} - \vec{R}_\xi), \quad (2.86)$$

ensue, and similarly for the diamagnetisation distribution,  $O_{ij}(\vec{r}, \vec{r}')$ . Integrating over all space yields for the interaction Hamiltonian Eq. (2.78), the multipole expanded form

$$\begin{aligned} H_{int}^{mult}(\xi) = & -\varepsilon_0^{-1} \vec{\mu}(\xi) \cdot \vec{d}^\perp(\vec{R}_\xi) - \varepsilon_0^{-1} Q_{ij}(\xi) \nabla_j d_i^\perp(\vec{R}_\xi) + \dots \\ & - \vec{m}(\xi) \cdot \vec{b}(\vec{R}_\xi) + \dots \\ & + \frac{e^2}{8m} \sum_\alpha \{ (\vec{q}_\alpha(\xi) - \vec{R}_\xi) \times \vec{b}(\vec{R}_\xi) \}^2 + \dots \end{aligned} \quad (2.87)$$

where the electric dipole moment operator,

$$\vec{\mu}(\xi) = -\frac{e}{1!} \sum_\alpha (\vec{q}_\alpha(\xi) - \vec{R}_\xi), \quad (2.88)$$

the electric quadrupole moment is

$$Q_{ij}(\xi) = -\frac{e}{2!} \sum_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})_i (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})_j, \quad (2.89)$$

the magnetic dipole moment is

$$\vec{m}(\xi) = \frac{1}{2!} \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}} \{ (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \times \vec{p}_{\alpha}(\xi) \}, \quad (2.90)$$

and the last term written explicitly in Eq. (2.87) is the leading order diamagnetic contribution.

If the dimensions of  $\xi$  are very small relative to the wavelength of light, it is sufficient to keep only the first coupling term of Eq. (2.87), in what is known as the electric dipole approximation. This is further justified on account of  $\vec{m}(\xi)$  and  $\vec{Q}(\xi)$  typically being of the order of the fine structure constant smaller than  $\vec{\mu}(\xi)$ , these higher-order multipolar terms providing small corrections to the electric dipole interaction term. For improved accuracy, and when treating optically active species, however, it is necessary to include contributions from higher multipole moments.

## 2.5 Perturbative Solution to the QED Hamiltonian

If the coupling between electromagnetic radiation and matter is taken to be weak compared to the strength of intra-atomic or molecular Coulomb fields, as is frequently the case if the magnitude of the electric field strength of the radiation is of the order of  $10^6 \text{ Vcm}^{-1}$  or less, eigenvalue and eigenfunction solutions to the QED Hamiltonian operator may be obtained perturbatively. The total Hamiltonian is separated into an unperturbed part,  $H_0$ , comprising the sum of  $H_{part}$  and  $H_{rad}$ , and the perturbation operator given by  $H_{int}$ , namely

$$H = H_0 + H_{int}, \quad (2.91)$$

with

$$H_0 = H_{part} + H_{rad}. \quad (2.92)$$

As was demonstrated in Sect. 2.2 of this chapter, when there is no radiation field, the total system is made up of charged particles only, while when these sources vanish, there is only the free field. Hence  $H_0$  represents a solved problem, and which is separable when the sub-systems do not interact. Known solutions to the atomic and molecular Hamiltonian are represented by  $H_{part}(\xi)|E_m^{\xi}\rangle = E_m^{\xi}|E_m^{\xi}\rangle$ , where  $|E_m^{\xi}\rangle$  is the energy eigenket associated with energy eigenvalue  $E_m^{\xi}$  for species

$\xi$  in electronic state represented by quantum number  $m$ , with additional labels being inserted to describe extra degrees of freedom. An occupation number state is used to specify the radiation field according to  $H_{rad}|n(\vec{k}, \lambda)\rangle = (n + \frac{1}{2})\hbar\omega|n(\vec{k}, \lambda)\rangle$ , where the energy of the electromagnetic field is  $E_{rad} = (n + \frac{1}{2})\hbar\omega$ , when there are  $n$  photons of mode  $(\vec{k}, \lambda)$ . Other radiation field states, such as a coherent state representation [9], may be used in place of a number state specification. Hence the basis functions employed in the perturbation theory solution to Eq. (2.91) are product particle-radiation field states

$$|part\rangle|rad\rangle = |part; rad\rangle = |E_m^\xi; n(\vec{k}, \lambda)\rangle. \quad (2.93)$$

The total energy of state (2.93) is given by  $E_m^\xi + n\hbar\omega$ .

The question often asked in any quantum mechanical problem, is given that the system at some initial time  $t_i$  is in state  $|i\rangle$ , what is the probability that it is in state  $|f\rangle$  at some later time  $t_f$ , due to the influence of the perturbation, which may or may not be time-dependent, but acts during the time interval? With exact analytical solutions only possible for a few limited choices of  $H_{int}$ , a perturbation theory solution is developed for the probability amplitude  $M_{fi}$  in series of powers of  $H_{int}$  for the transition  $|f\rangle \leftarrow |i\rangle$ . The observable quantity commonly derived from the matrix element is the transition rate,  $\Gamma$ , associated with Fermi's golden rule [9],

$$\Gamma = \frac{2\pi}{\hbar} |M_{fi}|^2 \rho_f, \quad (2.94)$$

where  $\rho_f$  is the density of final states. Equation (2.94) holds in the weak-coupling regime. When the initial and final states are identical, corresponding to a diagonal matrix element, the resulting observable may be interpreted as an energy shift, which is especially useful in the chapters to follow when dispersion potentials are evaluated. In powers of the perturbation operator, we find for the perturbed energy

$$E_m = E_m^{(0)} + \langle m^{(0)} | H_{int} | m^{(0)} \rangle + \sum_{n \neq m} \frac{\langle m^{(0)} | H_{int} | n^{(0)} \rangle \langle n^{(0)} | H_{int} | m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} + \dots, \quad (2.95)$$

in terms of the unperturbed states and energies  $|m^{(0)}\rangle$  and  $E_m^{(0)}$ , respectively, a sum of zeroth-, first-, second-, and higher-order terms in  $H_{int}$ .

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