

CHAPTER 1

MOLECULAR QUANTUM ELECTRODYNAMICS: BASIC THEORY

One finds then that the Hamiltonian for the interaction of the field with an atom is of the same form as that for the interaction of an assembly of light-quanta with the atom. There is thus a complete formal reconciliation between the wave and light-quantum points of view.

—P. A. M. Dirac, *Proc. R. Soc. Lond. A* **114**, 710 (1927).

1.1 BACKGROUND

Quantum electrodynamics (QED) (Schwinger, 1958) is the physical theory that describes the interaction of electromagnetic radiation with matter. Its characteristic feature is that the radiation field, as well as the material system, is subject to the postulates of quantum mechanics. Therefore, the theoretical framework consists of a single, closed dynamical system comprising both matter and electromagnetic radiation in mutual interaction within which energy is conserved. This is unlike the situation in the so-called semiclassical theory, the historical precursor to QED. In the former construct, only matter obeys quantum mechanical principles, while the radiation field is considered as a prescribed, external perturbation on the

system and does not form an integral part of it. Even though use of the semiclassical formalism remains widespread, due largely to its physical and computational simplicity relative to QED, its inherent deficiencies lead to critical shortcomings and ultimately limit its scope of availability. This is especially the case in the treatment of electromagnetic fields interacting with atoms and molecules, where continuing progress in the generation of coherent light sources has necessitated a fully quantum mechanical approach to calculating and explaining a variety of optical phenomena (Mukamel, 1995; Andrews and Allcock, 2002). In this regard, QED is the most successful physical theory to date (Feynman, 1985). This statement is justified on two counts. First, development of the QED formalism has provided a rigorous foundation for the understanding of electron–photon interactions at the most fundamental level currently known. Phenomena cover a vast range of length scales, manifested by particles varying in size from the gigameter down to the attometer. Second, and perhaps more convincing, is the ability of the theory to yield numerical values of measurable properties and the unprecedented agreement with experiment in those cases where comparison is possible.

A key step that led to the formulation of QED was the recognition that the mechanical vibrations of a system with infinitely many degrees of freedom could be represented by quantizing a collection of noninteracting harmonic oscillators (Born et al., 1926). This insight prompted Dirac (1927) to quantize the electromagnetic field and to calculate quantum mechanical probabilities for the absorption, stimulated emission, and spontaneous emission of light by atoms. Subsequent advances carried out by many workers, in particular, the significant contributions of Feynman, Schwinger, Tomonaga, and Dyson, resulted in a formulation of QED that satisfied all of the requirements stipulated by the special theory of relativity, which was ultimately explicated in both the particle and field theoretic points of view (Schweber, 1994). This last aspect, for instance, finally enabled the duality of the wave and particle descriptions of radiation and matter to be rationalized on the basis of a single theoretical scheme. Interacting quantum mechanical fermionic matter and bosonic electromagnetic fields are therefore entirely equivalent to a many-body representation of a system of material particles—electrons—interacting with quantized particles of light—the photons.

Early application of both the nonrelativistic and fully covariant versions of the theory was made to outstanding problems. These included calculations of spontaneous decay rates from atoms in electronically excited states, the Lamb shift, and the anomalous magnetic moment of the electron, to select but three historically significant examples. With continuing advances

occurring in computational power and experimental procedure during the intervening years, convergence between theory and experiment has been ever closer. More accurate calculations and improvements in measurement capability have yielded for the electronic g -factor, for instance, values in units of Bohr magnetons of $g/2$ (experiment) = 1.00115965218073(28) (Hanneke et al., 2008) and $g/2$ (theory) = 1.00115965218279 (Aoyama et al., 2007). In the case of the Lamb shift in atomic hydrogen, experimental and calculated values for the splitting between the $2S_{1/2}$ and $2P_{1/2}$ levels are 1,057,839(12) kHz (Hagley and Pipkin, 1994) and 1,057,838(6) kHz (Pachucki, 1994), respectively.

While these and other achievements are indeed remarkably impressive, there remain difficulties in the underlying foundations of the theory. Chief among them is the renormalization procedure, without whose aid no finite quantities may be calculated but which even today lacks rigorous mathematical justification. This problem continues to beset other field theories of modern physics, of which QED is but one example. Another limitation, which also applies in general to other field theories, is the approximate nature of solutions generated when systems interact. A common method of solution is a perturbative expansion in series of powers of some appropriate coupling constant, with no *a priori* guarantee of convergence of successively higher order terms, or whether summation of the infinite series is indeed possible. In QED, for example, the eigenstates of one or more charged particles in isolation are taken to be known, and the microscopic Maxwell's equations in free space can be solved and appropriately quantized. By forming a product state, the wavefunctions of this separable system are then used as base states for a perturbation theory solution in series of powers of the electronic charge or the fine structure constant.

Although QED correctly treats the coupling of radiation and matter at high energies, where fermionic pair particle creation and destruction events occur concomitantly with changes in photon number, the emphasis in the presentation to follow will be on conservation of the number of charged particles, which may exchange energy directly or indirectly with the radiation field. Conversely, as there is no conservation of photon number, any integer quantity of real or virtual photons may be created and annihilated during the course of a particular process. Hence, the formalism to be developed and applied will be suitable for systems composed of charged particles such as bound electrons in atoms and molecules possessing energies much less than mc^2 , m being the mass of the aggregate and c the speed of light. Since the mass is assumed to be a constant, the system of interest is slow moving, with low velocity v , and automatically satisfies the condition $v \ll c$. When this limiting procedure is applied to covariant

QED, the result is a nonrelativistic version of the theory, which is more commonly known as molecular QED (Power, 1964; Healy, 1982; Craig and Thirunamachandran, 1998a). Its construction from first principles and its application to a variety of long-range intermolecular interactions form the subject of this book.

In addition to providing valuable insight and expressions for forces between particles, the most celebrated being the formula for the retarded van der Waals dispersion potential between a pair of neutral molecules in the ground state, the theory of molecular QED has been employed with considerable success to radiation–molecule interactions. Examples include single- and multiphoton absorption, emission and scattering of light, optical activity and chiroptical spectroscopy, and nonlinear and quantum optical phenomena. Specific processes studied involving the interaction of radiation with one center include calculation of the circular dichroism rate, the angle of rotation of plane polarized light as it traverses a chiral medium, Rayleigh and Raman scattering of linear and circularly polarized radiation and their hyperanalogues, second, third, and higher harmonic generation, four-, five-, and six-wave mixing, and laser-induced optical activity.

Since intermolecular interactions are mediated by electromagnetic forces, coupling of radiation with matter, as well as between two or more particles, may be treated correctly and consistently within the framework provided by the nonrelativistic quantum theory of electron–photon interaction or molecular QED. This is most commonly delineated for the interaction of a charged particle with electromagnetic radiation; it begins with the classical Lagrangian function and ends with the construction of a quantum mechanical Hamiltonian operator that is arrived at via the familiar canonical quantization procedure. Details are presented in this chapter.

More fundamental, though less well known—despite much progress being made in the past 25 years or so—is the field theoretic formulation of molecular QED (Salam, 2008), involving the interaction of second quantized matter and radiation fields, which is the subject of Chapter 2. For a variety of applications, this approach offers a number of advantages over the conventional method in which only the radiation field is second quantized. For instance, properties directly related to electron and photon fields, such as the Maxwell fields in the vicinity of a source of charge, its energy density, and rates of flow of electromagnetic energy, may be evaluated. Moreover, the electromagnetic fields are subsequently employed to calculate energy shifts between molecules using a version of response theory.

The interactions occurring between atomic and molecular systems, especially those operating at large separation distances, form the focus of the remainder of the work. In Chapter 3, the standard presentation of

intermolecular forces originating from classical electrostatics is given. The pair potential is first divided into short- and long-range regions, with the exchange–repulsion energy being the major contribution to the interaction energy in the former distance regime. At large separations, the charge distribution between pairs of molecules is expanded in an electric multipole series and quantum mechanical perturbation theory is used to extract the electrostatic, induction, and dispersion terms within the formalism of semiclassical radiation theory in which no account is taken of the photonic character of electromagnetic radiation. Applications of the quantum electrodynamical theory to intermolecular interactions are then given in the chapters to follow. In Chapter 4, the theory of resonance energy transfer is given, a fundamental process taking place in microscopic systems but prototypical in that its interpretation as due to the exchange of a single virtual photon between the pair serves as a basis for the study of other molecular interactions using the formalism of molecular QED. Both perturbation and response theory calculations are presented, followed by their application to the evaluation of the transfer rate between two chiral species. Chapter 5 is devoted to van der Waals dispersion forces. Three different physical viewpoints and calculational techniques are detailed for the computation of the energy shift between two neutral polarizable molecules in the ground state. In addition to perturbation and response theories, the induced multipole moment approach is introduced and shown to simplify calculations considerably. Results are also obtained for electronically excited molecules undergoing dispersive coupling, and the functional form of the discriminatory potential between two optically active molecules is derived. Chapter 6 covers nonadditive and many-body forces. Attention is focused on the effects of retardation on energy transfer and dispersion interactions taking place among three or more particles. In Chapter 7, the effect of an external electromagnetic field in modifying the molecular pair interaction energy is treated. Adoption of the approach whereby molecules couple with each other and to the incident laser via the moments induced by the radiation field is shown to be a more efficient calculational method than the diagrammatic perturbation theory computation. Changes in energy shift induced by an applied field and dependent on the handedness of individual bodies are also studied.

1.2 QUANTUM DESCRIPTION OF MATTER

The continued failure of the application of the laws of classical mechanics to microscopic particles eventually led to the formulation of a new

dynamics—quantum mechanics (Dirac, 1958). At its foundation, however, remain a number of key concepts and ideas from classical theory (Goldstein, 1960). One of these fundamental constructs is the Lagrangian function, and another is the physical variational principle and the versatility associated with it. Taken together, they yield the Euler–Lagrange equations of motion and provide an alternative formulation of classical mechanics to Newton’s laws of motion. The former may be used to solve any problem within the classical domain and ultimately to provide a rigorous means of quantizing the specific system of interest. As long as a judicious choice of coordinates is made, often the most difficult task at hand, the ensuing equations to be solved are frequently simpler than those obtained by direct application of Newton’s laws, and yet contain all of the essential physics. This freedom in the selection of the specific coordinate representation lends itself to the formulation of the classical Lagrangian L for a system of particles in terms of generalized coordinates and velocities q and \dot{q} ; the Lagrangian is a function of these two variables as well as of the time t . If the Lagrangian does not depend explicitly on the time, then it is defined to be the difference of the kinetic energy T and the potential energy V ; the energy of the system is therefore conserved. For a system in which the potential energy is a function of the position only, the Lagrangian has identical definition, namely, $L = T - V$. The equations of motion follow after invoking Hamilton’s principle, namely, that of all of the allowed paths the system may pursue between initial and final times t_i and t_f , the actual one taken in configuration space is that for which the variation of the time integral of the Lagrangian, also called the variation of the action S , is an extremum. By application of standard calculus of variations, the Euler–Lagrange equations of motion for a system of particles ξ , with N degrees of freedom, are found to be

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_\xi} \right) - \frac{\partial L}{\partial q_\xi} = 0, \quad \xi = 1, 2, \dots, N. \quad (1.2.1)$$

From the form of the Lagrangian, it is evident that motion in classical mechanics is reversible. Replacing t by $-t$ leaves the Lagrangian as well as the equations of motion unaltered.

To facilitate the transition to quantum mechanics, in which the positions and momenta of the system of particles are canonical, it is convenient to define the Hamiltonian H as

$$H = \sum_{\xi=1}^N p_\xi \dot{q}_\xi - L. \quad (1.2.2)$$

This quantity is a function of the generalized coordinates, their canonically conjugate momenta, and time. The momenta are found from

$$p_\xi = \frac{\partial L}{\partial \dot{q}_\xi}, \quad \xi = 1, 2, \dots, N. \quad (1.2.3)$$

When the Hamiltonian is time independent, it is equal to the sum of the kinetic and potential energy, $H = T + V$. Evaluating the total differential of (1.2.2) and noting from equations (1.2.1) and (1.2.3) that

$$\dot{p}_\xi = \frac{\partial L}{\partial q_\xi} \quad (1.2.4)$$

yields Hamilton's canonical equations

$$\dot{q}_\xi = \frac{\partial H}{\partial p_\xi}; \quad \dot{p}_\xi = -\frac{\partial H}{\partial q_\xi}, \quad \xi = 1, 2, \dots, N, \quad (1.2.5)$$

and

$$\frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}, \quad (1.2.6)$$

which are now the equations of motion. A consequence of the resulting dynamics is that $2N$ first-order equations (1.2.5) have to be solved, rather than N second-order equations (1.2.1). After writing the classical Hamiltonian function in terms of the canonically conjugate dynamical variables, the quantum mechanical form of the Hamiltonian operator is obtained straightforwardly by promoting the classical variables to quantum operators, the latter obeying the canonical commutation relations for particles ξ and ξ' ,

$$[\vec{q}_\xi, \vec{q}_{\xi'}] = 0; \quad [\vec{p}_\xi, \vec{p}_{\xi'}] = 0; \quad [\vec{q}_\xi, \vec{p}_{\xi'}] = i\hbar\delta_{\xi\xi'}. \quad (1.2.7)$$

By way of illustration of the development above, consider a system of particles ξ with charges e_ξ , masses m_ξ , and position and velocity vectors \vec{q}_ξ and $\dot{\vec{q}}_\xi$, whose classical Lagrangian function is (Landau and Lifshitz, 1972)

$$L(\vec{q}, \dot{\vec{q}}) = \frac{1}{2} \sum_{\xi} m_{\xi} \dot{\vec{q}}_{\xi}^2 - \frac{1}{4\pi\epsilon_0} \sum_{\xi < \xi'} \frac{e_{\xi} e_{\xi'}}{|\vec{q}_{\xi} - \vec{q}_{\xi'}|}. \quad (1.2.8)$$

This leads to the quantum mechanical Hamiltonian operator

$$H(\vec{q}, \vec{p}) = \sum_{\xi} \frac{\vec{p}_{\xi}^2}{2m_{\xi}} + \frac{1}{4\pi\epsilon_0} \sum_{\xi < \xi'} \frac{e_{\xi}e_{\xi'}}{|\vec{q}_{\xi} - \vec{q}_{\xi'}|}. \quad (1.2.9)$$

It is easily verified that the Lagrangian (1.2.8) gives rise to the correct equations of motion: applying (1.2.1) produces Newton's second law equation for particle ξ ,

$$m_{\xi} \ddot{\vec{q}}_{\xi} = \frac{1}{4\pi\epsilon_0} \sum_{\xi < \xi'} \frac{e_{\xi}e_{\xi'}}{|\vec{q}_{\xi} - \vec{q}_{\xi'}|^2}, \quad (1.2.10)$$

whose right-hand side is recognizable as the generalized Coulomb force, obtained from the potential energy term in the Lagrangian via $\vec{F} = -\partial V(\vec{q})/\partial \vec{q}$.

1.3 ELECTRODYNAMICS AND MAXWELL EQUATIONS

The unification of electricity and magnetism with classical optics occurred with the formulation of Maxwell's equations (Jackson, 1963)—the basic laws underlying the behavior of electromagnetic radiation. As a consequence, light was understood to be an electromagnetic wave in which radiation of all frequencies could, in principle, be generated. Maxwell's quartet of equations is expressed as

$$\vec{\nabla} \cdot \vec{D} = \rho, \quad (1.3.1)$$

$$\vec{\nabla} \cdot \vec{B} = 0, \quad (1.3.2)$$

$$\vec{\nabla} \times \vec{E} + \frac{\partial \vec{B}}{\partial t} = 0, \quad (1.3.3)$$

$$\vec{\nabla} \times \vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{J}. \quad (1.3.4)$$

These fundamental equations completely determine the electromagnetic field, and the electrodynamic nature of such radiation is clearly evident from them. The fields \vec{E} and \vec{B} shall be termed the electric and magnetic fields, respectively, even though the latter is more properly called the magnetic flux density or the magnetic induction. The auxiliary fields \vec{D}

and \vec{H} are designated the electric displacement and magnetic field, respectively. No confusion shall result from the use of the descriptor “magnetic field,” as the appropriate symbol shall be used for the quantity concerned, either \vec{B} or \vec{H} . The \vec{E} and \vec{B} fields are fundamental in that they propagate in regions of space that contain no sources of charge. Further, if the charge density ρ and the current density \vec{J} account for all charged entities, then \vec{E} and \vec{B} describe the radiation field in its totality. On the other hand, including the contributions to ρ and \vec{J} of the elementary charges and their currents, which are manifested in the form of polarization fields and currents, necessitates the introduction of the two auxiliary fields \vec{D} and \vec{H} . The bound charged particles are viewed as forming a medium that contains the fields. These in turn describe the response of the material system to the applied fields via the electric polarization and magnetization fields. The connection between the derived and fundamental fields is arrived at through constitutive relations and the introduction of the electric permittivity ϵ and the magnetic permeability μ to describe the properties of the medium.

Although the interaction of radiation and matter is to be applied to bound systems moving at a very small fraction of the velocity of light, the equations of electrodynamics are themselves invariant in form under Lorentz transformations and are compatible with Einstein’s relativity theories. When Maxwell’s equations are combined with Newton’s second law of motion and the Lorentz force equation, a complete description of the nonrelativistic classical dynamics of charged particles interacting with electromagnetic fields results.

For the subsequent development of the quantum theory of electron–photon interaction, it is advantageous to work with Maxwell’s equations in microscopic form rather than employ relations (1.3.1)–(1.3.4) that are applicable when the distribution of charge is taken to be continuous. In place of the macroscopic Maxwell equations, their microscopic equivalents can be expressed solely in terms of the microscopic forms of the electric and magnetic field vectors \vec{e} and \vec{b} and the sources of charge and are given by

$$\vec{\nabla} \cdot \vec{e} = \rho/\epsilon_0, \quad (1.3.5)$$

$$\vec{\nabla} \cdot \vec{b} = 0, \quad (1.3.6)$$

$$\vec{\nabla} \times \vec{e} + \frac{\partial \vec{b}}{\partial t} = 0, \quad (1.3.7)$$

$$\vec{\nabla} \times \vec{b} = \frac{1}{c^2} \frac{\partial \vec{e}}{\partial t} + \frac{1}{\epsilon_0 c^2} \vec{j}. \quad (1.3.8)$$

To facilitate the microscopic treatment of matter, a discrete particle description is adopted for a collection of charged particles α possessing electrical charge e_α , situated at \vec{q}_α and moving with velocity $\dot{\vec{q}}_\alpha$, for which the charge and current density are defined to be

$$\rho(\vec{r}) = \sum_\alpha e_\alpha \delta(\vec{r} - \vec{q}_\alpha) \quad (1.3.9)$$

and

$$\vec{j}(\vec{r}) = \sum_\alpha e_\alpha \dot{\vec{q}}_\alpha \delta(\vec{r} - \vec{q}_\alpha), \quad (1.3.10)$$

where $\delta(\vec{r})$ is the Dirac delta function, which is strongly localized at the origin of the charge. By carrying out an average of the microscopic field over the molecular volume, the macroscopic Maxwell equations can be obtained from the microscopic Maxwell–Lorentz equations (1.3.5)–(1.3.8). In Section 1.2, it was remarked that forward and reverse motions are identical in classical mechanics. The same is true for the electromagnetic field in relativity theory, with the additional requirement that the sign of the magnetic field is reversed as well as $t \rightarrow -t$. It is easy to see that the equations of motion of a charged particle in a field are unchanged on transforming $t \rightarrow -t$, $\vec{e} \rightarrow \vec{e}$, and $\vec{b} \rightarrow -\vec{b}$ in the Lorentz force expression

$$\frac{d\vec{p}_\alpha}{dt} = -e_\alpha(\vec{e} + \vec{v}_\alpha \times \vec{b}), \quad (1.3.11)$$

where $\vec{v}_\alpha = d\vec{q}_\alpha/dt$ is the velocity and $\vec{p}_\alpha = m_\alpha \vec{v}_\alpha$ is the momentum of particle α .

The coupled first-order partial differential equations of Maxwell can be solved for the fields \vec{e} and \vec{b} for a variety of simple cases in electromagnetic theory. However, for many other situations and for the eventual quantization of the radiation field via the canonical quantization scheme, it is convenient to introduce two electromagnetic potentials and to rewrite Maxwell's equations in terms of them. One is the scalar potential ϕ and the other is the vector potential \vec{a} . The definition of the latter readily follows from the second Maxwell equation (1.3.6),

$$\vec{b} = \vec{\nabla} \times \vec{a}, \quad (1.3.12)$$

on noting that the divergence of the curl of a vector field vanishes. Inserting (1.3.12) into the third Maxwell equation (1.3.7) yields

$$\vec{\nabla} \times \left(\vec{e} + \frac{\partial \vec{a}}{\partial t} \right) = 0, \quad (1.3.13)$$

so that the factor within parentheses can be defined in terms of the gradient of a scalar function, in this case the scalar potential, since the curl of the gradient of a scalar field is zero,

$$-\vec{\nabla} \phi = \vec{e} + \frac{\partial \vec{a}}{\partial t}. \quad (1.3.14)$$

Substituting relation (1.3.14) into the first inhomogeneous microscopic Maxwell equation (1.3.5) produces

$$\vec{\nabla}^2 \phi + \frac{\partial}{\partial t} (\vec{\nabla} \cdot \vec{a}) = -\frac{\rho}{\epsilon_0}, \quad (1.3.15)$$

while using definitions (1.3.12) and (1.3.14) in the last Maxwell equation (1.3.8) gives

$$\vec{\nabla}^2 \vec{a} - \frac{1}{c^2} \frac{\partial^2 \vec{a}}{\partial t^2} - \vec{\nabla} \left(\vec{\nabla} \cdot \vec{a} + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \right) = -\frac{1}{\epsilon_0 c^2} \vec{j} \quad (1.3.16)$$

on using the vector identity

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{a}) = -\vec{\nabla}^2 \vec{a} + \vec{\nabla} (\vec{\nabla} \cdot \vec{a}). \quad (1.3.17)$$

Maxwell's equations have now been reduced to two coupled equations instead of four, with the potentials related directly to the sources. The equations (1.3.15) and (1.3.16) can be further simplified into two separate inhomogeneous wave equations, one dependent on ϕ only and the other on \vec{a} only. This may be achieved by taking advantage of the gauge freedom associated with the potentials. From relation (1.3.12), it can be seen that \vec{a} is undetermined to the extent that the gradient of a scalar function of the position and time, f , can be added to it,

$$\vec{a} \rightarrow \vec{a}' = \vec{a} + \vec{\nabla} f, \quad (1.3.18)$$

a transformation that leaves \vec{b} invariant. Substituting (1.3.18) into (1.3.14) enables the form of the transformation that must simultaneously be made to the scalar potential such that \vec{e} is unchanged to be derived:

$$-\vec{e} = \frac{\partial \vec{a}}{\partial t} + \vec{\nabla} \phi = \frac{\partial}{\partial t} (\vec{a} + \vec{\nabla} f) + \vec{\nabla} \phi', \quad (1.3.19)$$

from which

$$\vec{\nabla} \left(\phi' - \phi + \frac{\partial f}{\partial t} \right) = 0 \quad (1.3.20)$$

or

$$\phi \rightarrow \phi' = \phi - \frac{\partial f}{\partial t}. \quad (1.3.21)$$

The scalar potential is therefore determined to within the time derivative of the same function f . The two relations (1.3.18) and (1.3.21) constitute the gauge transformation. From them, a set of potentials (\vec{a}, ϕ) can always be chosen such that the Lorentz condition (1.3.22) is satisfied:

$$\vec{\nabla} \cdot \vec{a} + \frac{1}{c^2} \frac{\partial \phi}{\partial t} = 0, \quad (1.3.22)$$

which when inserted into (1.3.15) and (1.3.16) results in the wave equations

$$\left(\vec{\nabla}^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \phi = -\frac{\rho}{\epsilon_0} \quad (1.3.23)$$

and

$$\left(\vec{\nabla}^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \vec{a} = -\frac{1}{\epsilon_0 c^2} \vec{j}. \quad (1.3.24)$$

The most convenient choice of gauge, from the point of view of nonrelativistic theory, is the one in which the vector potential is solenoidal, that is, $\vec{\nabla} \cdot \vec{a} = 0$, also known as the Coulomb, radiation, or transverse gauge. In this gauge, ϕ is seen from equations (1.3.22) and (1.3.23) to obey Poisson's equation

$$\vec{\nabla}^2 \phi = -\frac{\rho}{\epsilon_0}, \quad (1.3.25)$$

with solution

$$\phi(\vec{r}, t) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d^3\vec{r}', \quad (1.3.26)$$

which represents the instantaneous Coulomb potential due to the charge density and from which this gauge takes its primary name. Fixing the gauge in equation (1.3.16) yields the inhomogeneous wave equation

satisfied by the vector potential,

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}\right) \vec{a} - \frac{1}{c^2} \nabla \left(\frac{\partial \phi}{\partial t}\right) = -\frac{1}{\epsilon_0 c^2} \vec{j}. \quad (1.3.27)$$

A further advance is made through the explicit decomposition of the vector fields \vec{e} and \vec{b} into their parallel (\parallel) and perpendicular (\perp) components; this is known as Helmholtz's theorem, which holds for any vector field and gives rise to irrotational and solenoidal vectors, respectively. From (1.3.6), \vec{b} is purely transverse and (1.3.5) and (1.3.7) become

$$\nabla \cdot \vec{e}^{\parallel} = \frac{\rho}{\epsilon_0} \quad (1.3.28)$$

and

$$\nabla \times \vec{e}^{\perp} = -\frac{\partial \vec{b}}{\partial t}, \quad (1.3.29)$$

while the fourth microscopic Maxwell equation (1.3.8) separates into

$$0 = \frac{1}{c^2} \frac{\partial \vec{e}^{\parallel}}{\partial t} + \frac{1}{\epsilon_0 c^2} \vec{j}^{\parallel} \quad (1.3.30)$$

and

$$\nabla \times \vec{b} = \frac{1}{c^2} \frac{\partial \vec{e}^{\perp}}{\partial t} + \frac{1}{\epsilon_0 c^2} \vec{j}^{\perp}. \quad (1.3.31)$$

The equation of continuity,

$$\nabla \cdot \vec{j}^{\parallel} + \frac{\partial \rho}{\partial t} = 0, \quad (1.3.32)$$

follows immediately on taking the divergence of (1.3.30) and using (1.3.28). Similarly, equation (1.3.14) divides as

$$\vec{e}^{\parallel} = -\nabla \phi \quad (1.3.33)$$

and

$$\vec{e}^{\perp} = -\frac{\partial \vec{a}}{\partial t} \quad (1.3.34)$$

in the Coulomb gauge, enabling the inhomogeneous wave equation for the vector potential (1.3.27) to be expressed exclusively in terms of

transverse variables,

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}\right) \vec{a} = -\frac{1}{\epsilon_0 c^2} \vec{j}^\perp, \quad (1.3.35)$$

with ϕ continuing to satisfy Poisson's equation (1.3.25). The solution of the equation (1.3.35) for the vector potential is given by

$$\vec{a}(\vec{r}, t) = \frac{1}{4\pi\epsilon_0 c^2} \int \frac{\vec{j}^\perp(\vec{r}', t - |\vec{r} - \vec{r}'|/c)}{|\vec{r} - \vec{r}'|} d^3\vec{r}', \quad (1.3.36)$$

which appears to be retarded, but is in fact not so. This is because its source is the transverse rather than the total current, the former being nonlocal, resulting in \vec{a}^\perp having identical characteristics also. Causality is recovered in the Coulomb gauge by including both transverse and longitudinal components, thereby ensuring that all static contributions cancel one another. No such difficulty arises in the Lorentz gauge (1.3.22), the solutions to the wave equations (1.3.23) and (1.3.24) being properly retarded, recognizing that the total current appears as the source in the equation for \vec{a} ,

$$\phi(\vec{r}, t) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}', t - |\vec{r} - \vec{r}'|/c)}{|\vec{r} - \vec{r}'|} d^3\vec{r}', \quad (1.3.37)$$

$$\vec{a}(\vec{r}, t) = \frac{1}{4\pi\epsilon_0 c^2} \int \frac{\vec{j}(\vec{r}', t - |\vec{r} - \vec{r}'|/c)}{|\vec{r} - \vec{r}'|} d^3\vec{r}'. \quad (1.3.38)$$

It is worth noting that \vec{a}^\perp is gauge invariant, since from the transformation (1.3.18) only the longitudinal component of \vec{a} can change. Consequently, from (1.3.34), it is seen that $\vec{e}^\perp = -\dot{\vec{a}}^\perp$ in all gauges, and the effect of a gauge transformation is to change the contributions from \vec{a} and ϕ to \vec{e}^\parallel .

1.4 QUANTIZATION OF THE FREE ELECTROMAGNETIC FIELD

In Section 1.2, it was shown how the quantum mechanics of a system of particles is rigorously built up from a classical mechanics in canonical form. In this section, it is shown how the same principles may be applied and suitably adapted to the radiation field propagating *in vacuo*. Ultimately,

this will lead to the quantum mechanical Hamiltonian for the electromagnetic field and its corresponding eigenvalues and eigenfunctions, the latter in a form convenient for its later adoption as a basis set in the perturbation theory solution to the interacting matter–radiation problem.

When there are no sources present, both the charge and current density are zero so that the microscopic Maxwell equations (1.3.5)–(1.3.8) applicable to the electromagnetic field in free space become

$$\vec{\nabla} \cdot \vec{e} = 0, \quad (1.4.1)$$

$$\vec{\nabla} \cdot \vec{b} = 0, \quad (1.4.2)$$

$$\vec{\nabla} \times \vec{e} + \frac{\partial \vec{b}}{\partial t} = 0, \quad (1.4.3)$$

$$\vec{\nabla} \times \vec{b} - \frac{1}{c^2} \frac{\partial \vec{e}}{\partial t} = 0. \quad (1.4.4)$$

Solutions are easily found for the fields \vec{e} and \vec{b} , which describe electromagnetic waves in a vacuum, as well as for \vec{a} . Continuing the development in the Coulomb gauge, clearly from equation (1.4.1), \vec{e} is purely transverse, which from (1.3.14) means that ϕ can be taken to vanish so that $\vec{e} = -\dot{\vec{a}}$. Substituting this relation and (1.3.12) into (1.4.4) and using identity (1.3.17) leads to d’Alembert’s equation for the vector potential,

$$\left(\vec{\nabla}^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \vec{a} = 0. \quad (1.4.5)$$

\vec{e} and \vec{b} satisfy identical wave equations. By taking the curl of equation (1.4.3) and substituting for $\vec{\nabla} \times \vec{b}$ from (1.4.4) yields the wave equation for \vec{e} , and carrying out a similar procedure on (1.4.4) first, results in the equation for \vec{b} . One form of solution to the wave equation for each of the three fields is in terms of plane waves,

$$\vec{a} = \vec{a}_0 e^{i\vec{k} \cdot \vec{r} - i\omega t}, \quad (1.4.6)$$

$$\vec{e} = e_0 \vec{e}_0 e^{i\vec{k} \cdot \vec{r} - i\omega t}, \quad (1.4.7)$$

and

$$\vec{b} = b_0 \vec{b}_0 e^{i\vec{k} \cdot \vec{r} - i\omega t}, \quad (1.4.8)$$

where in the last two solutions the pre-exponential factors, respectively, denote the scalar amplitude and the polarization vector of the respective quantity, with $\vec{e}_0 = ick\vec{a}_0$ on using $\vec{e} = -\dot{\vec{a}}$. The direction of propagation of the electromagnetic wave is described by the wavevector \vec{k} , whose magnitude is obtained after insertion of the appropriate solution into the wave equation from which it is found. Thus, $|\vec{k}| = k = \omega/c$, where ω is the circular frequency. The relation between the amplitudes of the two electromagnetic fields is found on inserting (1.4.7) and (1.4.8) into (1.4.3) and (1.4.4), producing

$$\hat{k} \times \vec{e}_0 = c\vec{b}_0 \quad (1.4.9)$$

and

$$\hat{k} \times \vec{b}_0 = -\frac{1}{c}\vec{e}_0, \quad (1.4.10)$$

respectively, where the circumflex designates a unit vector. From the last two relations, it may be inferred that the three vectors \vec{e}_0 , \vec{b}_0 , and \hat{k} are mutually perpendicular and form a right-handed set, at the same time illustrating the transverse nature of electromagnetic waves. Transversality also follows on substituting the harmonic solutions (1.4.7) and (1.4.8) into the first two source-free Maxwell equations (1.4.1) and (1.4.2), respectively.

Because the respective polarization vectors in the plane wave solutions for \vec{e} (1.4.7) and \vec{b} (1.4.8) always point in the same direction, the waves are described as being linearly polarized. A wave with a more general state of polarization may be formed by combining two such independent waves. An example is the case of two different electric fields, each possessing a phase δ_1 and δ_2 , whose superposition produces an elliptically polarized wave

$$\vec{e}(\vec{r}, t) = (e_1\vec{e}_1 e^{i\delta_1} + e_2\vec{e}_2 e^{i\delta_2})e^{i\vec{k}\cdot\vec{r}-i\omega t}. \quad (1.4.11)$$

If both waves have identical amplitudes $e_1 = e_2 = e$, but a phase difference of $\pm\pi/2$, a circularly polarized wave results. For orthogonal unit vectors \hat{e}_1 and \hat{e}_2 , the left- and right-handed circular polarizations are defined to be

$$\hat{e}^{(L/R)} = \frac{1}{\sqrt{2}}(\hat{e}_1 \pm i\hat{e}_2). \quad (1.4.12)$$

If, however, the phase difference between the two waves in (1.4.11) is $\delta_1 - \delta_2 = 0, \pm\pi$, then linear polarization results, where the tangent of the

angle of the polarization vector with respect to \vec{e}_1 is given by the ratio of the amplitudes e_2 to e_1 , that is, $\tan \theta = (e_2/e_1)$, and with a modulus $e = \sqrt{e_1^2 + e_2^2}$.

In free space, the wavevector \vec{k} associated with the plane waves is unrestricted in value. To enumerate and normalize the allowed states in the quantum theory, the field is described in terms of modes as first carried out by Rayleigh (1900) and later by Jeans (1905). With \vec{a} , \vec{e} , and \vec{b} satisfying vector Helmholtz equations of the type (1.4.5), a complete set of states is readily obtained by expansion in Cartesian coordinates over a parallelepiped of volume $V = L_x L_y L_z$, where L_x , L_y , and L_z are the dimensions along the three axes of the box, x , y , and z . This corresponds to a multiple Fourier series, which for the vector potential, when subject to the periodic boundary condition that \vec{a} has identical values on opposite sides of the box, gives for the number of allowed modes

$$(n_x, n_y, n_z) = \frac{1}{(2\pi)^3} (k_x, k_y, k_z) L_x L_y L_z, \quad (1.4.13)$$

where n_x , n_y , and n_z are integers and k_i , $i = x, y, z$, are the wavevector components, with the two modes of the field characterized by the three values of n . Monochromatic solutions to the wave equation for the vector potential (1.4.5) are easily found via separation of variables $\vec{a}^{(\lambda)}(\vec{k}, \vec{r}, t) = \vec{a}^{(\lambda)}(\vec{k}, \vec{r})a(t)$, with the spatial part obeying the Helmholtz equation

$$\nabla^2 \vec{a}^{(\lambda)}(\vec{k}, \vec{r}) + k^2 \vec{a}^{(\lambda)}(\vec{k}, \vec{r}) = 0 \quad (1.4.14)$$

and the temporal part satisfying

$$\frac{\partial^2 a(t)}{\partial t^2} + \omega^2 a(t) = 0, \quad (1.4.15)$$

with $\omega = ck$ the circular frequency. As a Fourier series expansion in the plane waves subject to (1.4.13), the vector potential is

$$\vec{a}(\vec{r}, t) = \sum_{\vec{k}, \lambda} [\vec{e}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r} - i\omega t} + \vec{e}^{(\lambda)}(\vec{k}) \bar{a}^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r} + i\omega t}], \quad (1.4.16)$$

applicable to a wave propagating along \hat{k} at speed c . In expansion (1.4.16), $\vec{e}^{(\lambda)}(\vec{k})$ is the unit electric polarization vector of mode (\vec{k}, λ) , λ being the index of polarization, and $a^{(\lambda)}(\vec{k})$ is the Fourier amplitude, with the overbar

denoting the complex conjugate. From the Coulomb gauge condition, the transverse property of the modes is readily apparent, namely, $\hat{k} \cdot \vec{a}^{(\lambda)}(\vec{k}) = 0$. With \vec{e} and \vec{b} also transverse, their unit vectors are resolved parallel and perpendicular to the vector potential for each mode \vec{k} , so that $\vec{e}^{(\lambda_1)}(\vec{k}) = \vec{e}^{(\lambda)}(\vec{k})$, $\vec{e}^{(\lambda_2)}(\vec{k}) = \vec{b}^{(\lambda)}(\vec{k})$, and \hat{k} form a set of mutually orthogonal unit vectors. The mode expansions for the electric fields are easily obtained from (1.4.16) via $\vec{e}(\vec{r}, t) = -\partial\vec{a}(\vec{r}, t)/\partial t$ and $\vec{b}(\vec{r}, t) = \vec{\nabla} \times \vec{a}(\vec{r}, t)$. Once field quantization is carried out, their explicit normalized forms will be given.

Having outlined the essential characteristics of the free classical radiation field, and its description in terms of modes when confined to a box of volume V , as a precursor to quantization, electrodynamics is presented in terms of the Lagrangian formulation. To account for the infinite number of degrees of freedom possessed by the radiation field, the Euler–Lagrange equations (1.2.1) for a system of particles require modification. To accurately describe the smooth and continuous variation of the field, a Lagrangian density \mathcal{L} is introduced, which is a functional of the field and the variables that define the latter. Integrating \mathcal{L} over all space yields the Lagrangian function, L . Analogous to functions, which enable a variable to be converted to a number, a functional provides a means for going from a function to a number, in this case assigning a number to the field. It may be recalled that in the analytical dynamics of particles, the Lagrangian was a function of the generalized positions and velocities. For the electromagnetic field, however, instead of \vec{q} , the generalized coordinate is chosen to be the vector potential, while the velocity analogous to $\dot{\vec{q}}$ is taken to be $\dot{\vec{a}}$. In addition, \mathcal{L} is a function of the gradient of \vec{a} , thereby ensuring that spatial variations are properly included. Thus,

$$L = \int \mathcal{L}(\vec{a}, \vec{\nabla}\vec{a}, \dot{\vec{a}}, t) d^3\vec{r}. \quad (1.4.17)$$

Applying the variational calculus along with Hamilton's principle as in the case of particles earlier, but with variation now performed over the new variables, the Euler–Lagrange equations of motion for the electromagnetic field are modified to

$$\frac{\partial}{\partial t} \left(\frac{\partial \mathcal{L}}{\partial \dot{a}_i} \right) + \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}}{\partial (\partial a_i / \partial x_j)} - \frac{\partial \mathcal{L}}{\partial a_i} = 0, \quad (1.4.18)$$

in which the second term is new relative to equation (1.2.1) and expresses the rate of change with respect to position of the variation of the Lagrangian density with the spatial derivative of the vector potential.

On taking, as is common, the square of the electric field to be proportional to the kinetic energy of the field and the square of the magnetic field as contributing to the electromagnetic potential energy, the Lagrangian density for the free field in analogy with point particles is written as the difference in kinetic and potential energy,

$$\mathcal{L} = \frac{\epsilon_0}{2} \left\{ \dot{\vec{a}}^2 - c^2 (\vec{\nabla} \times \vec{a})^2 \right\}. \quad (1.4.19)$$

Using (1.4.19) in (1.4.18) leads to Maxwell's equations, the appropriate equations of motion for the radiation field. Specifically, the wave equation for \vec{a} (1.4.5) results,

$$\left(\vec{\nabla}^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) a_i = 0, \quad (1.4.20)$$

as originally obtained from Maxwell's equations.

Like the Lagrangian for the field (1.4.17), the Hamiltonian H is a functional and is defined in terms of a density functional \mathcal{H} ,

$$H = \int \mathcal{H}(\vec{a}, \vec{\Pi}, \vec{\nabla} \vec{a}, t) d^3 \vec{r}, \quad (1.4.21)$$

with \mathcal{H} itself found from

$$\mathcal{H} = \vec{\Pi} \cdot \dot{\vec{a}} - \mathcal{L}. \quad (1.4.22)$$

$\vec{\Pi}(\vec{r})$ is the field momentum canonically conjugate to the vector potential, defined as

$$\vec{\Pi}(\vec{r}) = \frac{\partial \mathcal{L}}{\partial \dot{\vec{a}}}, \quad (1.4.23)$$

which from (1.4.19) is seen to be

$$\vec{\Pi}(\vec{r}) = \epsilon_0 \dot{\vec{a}}, \quad (1.4.24)$$

being proportional to the electric field \vec{e} . When expressed in terms of canonically conjugate variables, the Hamiltonian density (1.4.22) is written as

$$\mathcal{H} = \frac{1}{2\epsilon_0} \left\{ \vec{\Pi}^2 + \epsilon_0^2 c^2 (\vec{\nabla} \times \vec{a})^2 \right\}, \quad (1.4.25)$$

which is equivalent to the electromagnetic energy density $(\epsilon_0/2)(\vec{e}^2 + c^2 \vec{b}^2)$. From the preceding development, in particular, the

description of electromagnetic radiation in terms of modes of the field, it is now a simple matter to show that the radiation field enclosed in a fixed volume is equivalent to a mechanical oscillator. This theorem was first proved by Jeans (1905). On substituting the mode expansions for \vec{a} and $\vec{\Pi}$ —the latter obtained from (1.4.24)—into the Hamiltonian density (1.4.25), or alternatively using the derived mode expansions for \vec{e} and \vec{b} in the energy density, the radiation field Hamiltonian (1.4.21) can be written as

$$H = 2\varepsilon_0 c^2 V \sum_{\vec{k}, \lambda} k^2 a^{(\lambda)}(\vec{k}) \bar{a}^{(\lambda)}(\vec{k}), \quad (1.4.26)$$

after the field modes have been normalized. Two new, real canonically conjugate variables are now defined according to

$$q_{\vec{k}, \lambda} = (\varepsilon_0 V)^{1/2} \left(a_{\vec{k}}^{(\lambda)} + \bar{a}_{\vec{k}}^{(\lambda)} \right) \quad (1.4.27)$$

and

$$p_{\vec{k}, \lambda} = -ick(\varepsilon_0 V)^{1/2} \left(a_{\vec{k}}^{(\lambda)} - \bar{a}_{\vec{k}}^{(\lambda)} \right), \quad (1.4.28)$$

which yields for the Hamiltonian (1.4.26) the expression

$$H = \sum_{\vec{k}, \lambda} H_{\vec{k}, \lambda} = \sum_{\vec{k}, \lambda} \frac{1}{2} (p_{\vec{k}, \lambda}^2 + \omega^2 q_{\vec{k}, \lambda}^2), \quad (1.4.29)$$

which is seen to be a mode sum over classical harmonic oscillator Hamiltonians in mass-weighted coordinates. Hamilton's canonical equations (1.2.5) are easily seen to be satisfied by the choice of conjugate variables. Recalling (1.4.6),

$$\frac{dq_{\vec{k}, \lambda}}{dt} = p_{\vec{k}, \lambda}; \quad \frac{dp_{\vec{k}, \lambda}}{dt} = -\omega^2 q_{\vec{k}, \lambda}, \quad (1.4.30)$$

and from (1.4.29)

$$\frac{\partial H}{\partial p_{\vec{k}, \lambda}} = p_{\vec{k}, \lambda} = \dot{q}_{\vec{k}, \lambda}; \quad \frac{\partial H}{\partial q_{\vec{k}, \lambda}} = \omega^2 q_{\vec{k}, \lambda} = -\dot{p}_{\vec{k}, \lambda}, \quad (1.4.31)$$

which provides desired confirmation of the result.

From (1.4.29), it may be concluded that quantization of the free field may be accomplished by quantizing a collection of noninteracting harmonic

oscillators. The solution of the latter problem is familiar from quantum mechanics. A brief summary is given of the method of solution and of the resulting energy eigenvalues and eigenfunctions in a form that makes it readily applicable to quantization of electromagnetic radiation (Dirac, 1958). For an individual oscillator α of mass m_α and angular frequency ω_α representing a single mode of the radiation field, the Hamiltonian for the electromagnetic field is given by

$$H = \sum_{\alpha} \frac{1}{2m_{\alpha}} (p_{\alpha}^2 + m_{\alpha}^2 \omega_{\alpha}^2 q_{\alpha}^2), \quad (1.4.32)$$

where the dynamical variables q_{α} and p_{α} are the coordinate and canonically conjugate momentum.

Consider a one-dimensional harmonic oscillator, whose classical Hamiltonian function is

$$H = \frac{1}{2m} (p^2 + m^2 \omega^2 q^2), \quad (1.4.33)$$

there now being no need for the subscript α . The corresponding quantum mechanical Hamiltonian is taken to be of the same form as (1.4.33), with q and p represented by their respective operator equivalents subject to the fundamental commutator

$$[q, p] = i\hbar. \quad (1.4.34)$$

By introducing two mutually adjoint operators a and a^{\dagger} in terms of p and q ,

$$a = \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} q + i\sqrt{\frac{1}{m\omega\hbar}} p \right) \quad (1.4.35)$$

and

$$a^{\dagger} = \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} q - i\sqrt{\frac{1}{m\omega\hbar}} p \right), \quad (1.4.36)$$

the quantum mechanical Hamiltonian can be expressed as

$$H = \frac{\hbar\omega}{2} (aa^{\dagger} + a^{\dagger}a). \quad (1.4.37)$$

Although both a and a^{\dagger} are real, they are not symmetric and hence not Hermitian unlike q and p . Using the fundamental commutator (1.4.34), it is

easily verified that

$$[a, a^\dagger] = 1. \quad (1.4.38)$$

Hence, the Hamiltonian can be written in two other ways equivalent to (1.4.37), namely,

$$H = \left(a^\dagger a + \frac{1}{2} \right) \hbar\omega = \left(aa^\dagger - \frac{1}{2} \right) \hbar\omega. \quad (1.4.39)$$

Its characteristic solutions are then given by the eigenvalues and eigenfunctions of the operator $a^\dagger a$. This operator is called the number operator n . Its eigenvalues are the positive integers and zero, representing the numbers of quantized particles in the allowed eigenstates $|n\rangle$. In the case of the electromagnetic field, these particles are called photons. They satisfy Bose–Einstein statistics, with the wavefunction for n identical such particles being totally symmetric. Thus,

$$a^\dagger a |n\rangle = n |n\rangle, \quad n = 0, 1, 2, \dots, \quad (1.4.40)$$

the ground state ket $|0\rangle$, for example, having an eigenvalue of zero. From (1.4.39), it is easily seen that the eigenvalues of the harmonic oscillator are

$$\left(n + \frac{1}{2} \right) \hbar\omega, \quad n = 0, 1, 2, \dots, \quad (1.4.41)$$

with the lowest energy corresponding to $(\hbar\omega/2)$, the zero-point energy of the field (Milonni, 1994). A ladder of states separated by a quantum of energy $\hbar\omega$ is generated in accord with Planck's quantum hypothesis. The individual operators a and a^\dagger are annihilation and creation operators, acting on the occupation number state and, respectively, decreasing and increasing the number of particles by unity. This aspect of being able to tackle changes in particle number together with the correct statistical laws that the particles obey is called second quantization. It provides the link between quantum field theory and the many-body formulation (Mandl, 1959). For a normalized state $|n\rangle$, the operator equations are

$$a |n\rangle = \begin{cases} 0, & n = 0, \\ n^{1/2} |n-1\rangle, & n = 1, 2, 3, \dots \end{cases} \quad (1.4.42)$$

and

$$a^\dagger |n\rangle = (n+1)^{1/2} |n+1\rangle, \quad n = 0, 1, 2, \dots \quad (1.4.43)$$

The wavefunction formed from the projection of the states in the Hilbert space of the system is now taken to be an operator instead of a classical number and is interpreted as a quantized field. This generalized many-particle occupation number space is called a Fock space and applies to both fermions and bosons (Fock, 1932).

The eigenvalues and eigenfunctions found for a single harmonic oscillator are easily adapted to the solution of the many-particle uncoupled harmonic oscillator Hamiltonian (1.4.32), which has been shown to be equivalent to a sum over Hamiltonians for each mode of the radiation field. In terms of the destruction and creation operators (1.4.35) and (1.4.36) for a (\vec{k}, λ) -mode photon, which are subject to the commutation relations

$$\begin{aligned} [a^{(\lambda)}(\vec{k}), a^{(\lambda')}(\vec{k}')] &= 0, \\ [a^{\dagger(\lambda)}(\vec{k}), a^{\dagger(\lambda')}(\vec{k}')] &= 0, \\ [a^{(\lambda)}(\vec{k}), a^{\dagger(\lambda')}(\vec{k}')] &= \delta_{\lambda\lambda'} \delta_{\vec{k}\vec{k}'}, \end{aligned} \quad (1.4.44)$$

the analogues of (1.4.37) and (1.4.39) are

$$\begin{aligned} H &= \sum_{\vec{k}, \lambda} \frac{1}{2} \left[a^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) + a^{\dagger(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) \right] \hbar c k \\ &= \sum_{\vec{k}, \lambda} \left[a^{\dagger(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) + \frac{1}{2} \right] \hbar c k \\ &= \sum_{\vec{k}, \lambda} \left[a^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) - \frac{1}{2} \right] \hbar c k, \end{aligned} \quad (1.4.45)$$

whose eigenenergy is the sum over all oscillators α of the energy of a single oscillator,

$$\begin{aligned} H |n_1(\vec{k}_1, \lambda_1), n_2(\vec{k}_2, \lambda_2), \dots\rangle &= \sum_{\alpha} \left(n_{\alpha}(\vec{k}_{\alpha}, \lambda_{\alpha}) + \frac{1}{2} \right) \hbar \omega_{\alpha} |n_1(\vec{k}_1, \lambda_1), \\ & n_2(\vec{k}_2, \lambda_2), \dots\rangle, \end{aligned} \quad (1.4.46)$$

where n_{α} denotes the occupation number of oscillator α . From (1.4.42), it is seen that when $n = 0$, it is not possible to absorb a particle from the ground

state of the system. For the electromagnetic field, the state in which all single particle states are empty, that is, $n_\alpha = 0$ for all α , corresponds to the electromagnetic vacuum. By successive application of the creation operators on the vacuum state, all other basis states of the field may be generated, as in

$$|n_1(\vec{k}_1, \lambda_1), n_2(\vec{k}_2, \lambda_2), \dots\rangle = \prod_{\alpha} \frac{[a^{\dagger(\lambda_\alpha)}(\vec{k}_\alpha)]^{n_\alpha}}{(n_\alpha!)^{1/2}} |0(\vec{k}_1, \lambda_1), 0(\vec{k}_2, \lambda_2), \dots\rangle, \quad (1.4.47)$$

and are known as number states, and they form an orthonormal basis set. It is customary to specify only nonzero occupation numbers of the field. The expression (1.4.47) is the analogue of the wavefunction in the one-particle theory. Hence for a (\vec{k}, λ) -mode photon,

$$a^{\dagger(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})|n(\vec{k}, \lambda)\rangle = n|n(\vec{k}, \lambda)\rangle, \quad n = 0, 1, 2, \dots, \quad (1.4.48)$$

$$a^{(\lambda)}(\vec{k})|n(\vec{k}, \lambda)\rangle = n^{1/2}|(n-1)(\vec{k}, \lambda)\rangle, \quad n = 1, 2, \dots, \quad (1.4.49)$$

$$a^{\dagger(\lambda)}(\vec{k})|n(\vec{k}, \lambda)\rangle = (n+1)^{1/2}|(n+1)(\vec{k}, \lambda)\rangle, \quad n = 0, 1, 2, \dots \quad (1.4.50)$$

The quantum mechanical counterpart to the classical mode expansion for the vector potential (1.4.16) at $t=0$ is of the form

$$\vec{a}(\vec{r}) = \sum_{\vec{k}, \lambda} \left(\frac{\hbar}{2\varepsilon_0 c k V} \right)^{1/2} \left[\vec{e}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} + \vec{e}^{\prime(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \right], \quad (1.4.51)$$

where in the quantum theory the Fourier amplitudes a and a^\dagger are understood to be annihilation and creation operators obeying the rules of commutation (1.4.44). The normalizing factor appearing in (1.4.51) is obtained on evaluating the expectation value of the energy of the radiation field for a number state $|n(\vec{k}, \lambda)\rangle$, which is known to be $(n+1/2)\hbar\omega$. The mode expansions for the quantum electric, magnetic, and canonically conjugate momentum field $\vec{\Pi}(\vec{r})$ follow from (1.4.51) and their defining equations

given earlier. They are

$$\vec{e}(\vec{r}) = i \sum_{\vec{k}, \lambda} \left(\frac{\hbar ck}{2\epsilon_0 V} \right)^{1/2} \left[\vec{e}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \vec{e}^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \right], \quad (1.4.52)$$

$$\vec{b}(\vec{r}) = i \sum_{\vec{k}, \lambda} \left(\frac{\hbar k}{2\epsilon_0 c V} \right)^{1/2} \left[\vec{b}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \vec{b}^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \right], \quad (1.4.53)$$

$$\vec{\Pi}(\vec{r}) = -i \sum_{\vec{k}, \lambda} \left(\frac{\hbar ck \epsilon_0}{2V} \right)^{1/2} \left[\vec{e}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \vec{e}^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \right]. \quad (1.4.54)$$

In the expressions for the mode expansions, the quantization volume appears explicitly. Quantum mechanical observables, however, are of course independent of this quantity. For systems normalized in finite but large volumes, the summation over the allowed wavevectors \vec{k} , which are restricted by (1.4.13), may be replaced by an integral through the correspondence

$$\frac{1}{V} \sum_{\vec{k}} \xrightarrow{V \rightarrow \infty} \frac{1}{(2\pi)^3} \int d^3\vec{k}, \quad (1.4.55)$$

where $d^3\vec{k}$ is the volume element in momentum space.

Often when calculating transfer rates, scattering cross sections, and energy shifts involving photons of a particular polarization—be they real or virtual photons, a sum over the two polarizations is required. Recalling that $\vec{e}^{(1)}(\vec{k})$, $\vec{e}^{(2)}(\vec{k})$, which can in general be complex, and \hat{k} form a set of mutually perpendicular unit vectors, it follows that

$$\sum_{\lambda=1,2} e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k}) = \delta_{ij} - \hat{k}_i \hat{k}_j. \quad (1.4.56)$$

Using the definition for the unit magnetic polarization vector $\vec{b}^{(\lambda)}(\vec{k}) = \hat{k} \times \vec{e}^{(\lambda)}(\vec{k})$ allows two additional sum rules to be obtained for electric–magnetic and magnetic–magnetic combinations. They are

$$\sum_{\lambda=1,2} e_i^{(\lambda)}(\vec{k}) \bar{b}_j^{(\lambda)}(\vec{k}) = \epsilon_{ijk} \hat{k}_k, \quad (1.4.57)$$

where ε_{ijk} is the Levi-Civita third rank antisymmetric tensor, and

$$\sum_{\lambda=1,2} b_i^{(\lambda)}(\vec{k}) \bar{b}_j^{(\lambda)}(\vec{k}) = \delta_{ij} - \hat{k}_i \hat{k}_j. \quad (1.4.58)$$

The imposition of quantum mechanical principles to the vibrational modes of a classical electromagnetic wave led to the automatic emergence of the quantized particle of light—the photon—from the formalism. In the process, the underlying duality of the wave and particle pictures of light has been revealed. This complementary description can also be found in reverse. Beginning instead with the photon, application of quantum mechanics to assemblies of such particles yields quantization of a set of classical mode oscillators. This second viewpoint is applicable to bosons in general, as well as to fermions, and forms the basis of quantum field theory. The presentation of the latter in a form applicable to interacting matter and electromagnetic wavefields is the subject of Chapter 2.

1.5 INTERACTING PARTICLE–RADIATION FIELD SYSTEM

Thus far, the variational calculus and Hamilton's principle of least action have been applied first to a system of isolated charged particles and then to the free radiation field. In each case, the equations of motion were obtained from the classical Lagrangian function expressed in terms of generalized coordinates and velocities. For material particles undergoing nonrelativistic kinematics, the equations of motion lead directly to Newton's dynamical laws, while for electromagnetic radiation, Maxwell's equations resulted. The classical Hamiltonian function was then constructed for each non-interacting system by defining the momentum canonically conjugate to the generalized coordinate variable and eliminating the generalized velocity in favor of this new quantity. The respective Hamiltonian was then converted to its quantum mechanical form by elevating the dynamical particle and field variables to operators, and the ensuing Schrödinger equation was solved for radiation and matter eigenvalues and eigenfunctions. An analogous procedure is now followed for a system of charged particles and radiation field in mutual interaction (Heitler, 1954; Power, 1964; Healy, 1982; Craig and Thirunamachandran, 1998a). It will be seen that this problem is no longer separable. Particle and field are inextricably linked—the dynamics of one affecting the other, and vice versa. Overall, however, energy is conserved as that given up by matter is gained by the field and that lost by radiation is acquired by the system of charged particles. Ultimately, this leads to perturbation theory solutions of the coupled matter–field system. As before, there is considerable freedom in the specific choice of classical Lagrangian function. Its only limitation is that it must lead to the

correct equations of motion. Since the noninteracting matter–field system constitutes a completely separable case, it is sensible to partition the total Lagrangian into a sum of molecule, field, and interaction Lagrangians,

$$L = L_{\text{mol}} + L_{\text{rad}} + L_{\text{int}}, \quad (1.5.1)$$

where

$$L_{\text{mol}} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \dot{\vec{q}}_{\alpha}^2 - V(\vec{q}), \quad (1.5.2)$$

$$L_{\text{rad}} = \int \mathcal{L}_{\text{rad}} d^3\vec{r} = \frac{1}{2} \epsilon_0 \int \{ \dot{\vec{a}}^2 - c^2 (\vec{\nabla} \times \vec{a})^2 \} d^3\vec{r}, \quad (1.5.3)$$

$$L_{\text{int}} = \int \mathcal{L}_{\text{int}}(\vec{r}) d^3\vec{r} = \int \vec{j}^{\perp}(\vec{r}) \cdot \vec{a}(\vec{r}) d^3\vec{r}. \quad (1.5.4)$$

Unsurprisingly, the molecular and radiation field Lagrangians (1.5.2) and (1.5.3) are identical to the Lagrangians (1.2.8) and (1.4.19), respectively, when the quantum mechanics of a collection of charged particles, and the electromagnetic field in the absence of sources, was studied. The form of the interaction Lagrangian (1.5.4) is a direct result of working in the Coulomb gauge. The scalar potential, describing the electrostatic Coulomb potential, is replaced by the electrostatic potential energy with the transverse vector potential describing the radiation field. In (1.5.4), $\vec{j}^{\perp}(\vec{r})$ is the transverse part of the current density, obtained by projecting the total current density onto the transverse delta function dyadic $\delta_{ij}^{\perp}(\vec{r})$ (Belinfante, 1946) so that

$$\vec{j}_i^{\perp}(\vec{r}) = \sum_{\alpha} e_{\alpha} \dot{q}_{j(\alpha)} \delta_{ij}^{\perp}(\vec{r} - \vec{q}_{\alpha}). \quad (1.5.5)$$

It is straightforward to demonstrate that the Lagrangian (1.5.1) is of the appropriate form. Using (1.5.1) in the Euler–Lagrange equations for the field (1.4.18), the vector potential is seen to obey the inhomogeneous wave equation,

$$\left(\vec{\nabla}^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \vec{a}(\vec{r}) = -\frac{1}{\epsilon_0 c^2} \vec{j}^{\perp}(\vec{r}), \quad (1.5.6)$$

instead of its source-free counterpart (1.4.20). Note that (1.5.6) is identical to equation (1.3.35), the latter following directly from the Maxwell–Lorentz equations in the Coulomb gauge. Substituting the total Lagrangian (1.5.1) into the Euler–Lagrange equations for an assembly of

particles (1.2.1) yields for the i th component

$$m_\alpha \ddot{q}_{i(\alpha)} = -\frac{\partial V}{\partial q_{i(\alpha)}} + e_\alpha e_i^\perp(\vec{q}_\alpha) + e_\alpha [\dot{\vec{q}}_\alpha \times \vec{b}(\vec{q}_\alpha)]_i, \quad (1.5.7)$$

where relations (1.3.12) and (1.3.34) have been used, and which is immediately recognizable as Newton's equation of motion modified by the addition of the Lorentz force law terms representing the interaction of charged particles with the transverse radiation field.

The total Hamiltonian may be evaluated from the total Lagrangian in the usual way according to

$$H = \sum_\alpha \vec{p}_\alpha \cdot \dot{\vec{q}}_\alpha + \int \vec{\Pi} \cdot \dot{\vec{a}} \, d^3\vec{r} - L, \quad (1.5.8)$$

after calculating the momenta canonically conjugate to the generalized position and vector potential. The former is now given by

$$\vec{p}_\alpha = \frac{\partial L}{\partial \dot{\vec{q}}_\alpha} = m_\alpha \dot{\vec{q}}_\alpha + e_\alpha \vec{a}(\vec{q}_\alpha), \quad (1.5.9)$$

while the latter is identical to that obtained using the free field,

$$\vec{\Pi}(\vec{r}) = \frac{\partial \mathcal{L}}{\partial \dot{\vec{a}}} = \epsilon_0 \dot{\vec{a}}(\vec{r}) = -\epsilon_0 \vec{e}^\perp(\vec{r}). \quad (1.5.10)$$

Substituting for $\dot{\vec{q}}_\alpha$ and $\dot{\vec{a}}$ into (1.5.8) produces what is universally known as the minimal-coupling Hamiltonian (Craig and Thirunamachandran, 1998a),

$$H^{\min} = \sum_\alpha \frac{1}{2m_\alpha} \{\vec{p}_\alpha - e_\alpha \vec{a}(\vec{q}_\alpha)\}^2 + V(\vec{q}) + \frac{1}{2\epsilon_0} \int \{\vec{\Pi}^2(\vec{r}) + \epsilon_0^2 c^2 (\vec{\nabla} \times \vec{a}(\vec{r}))^2\} d^3\vec{r}. \quad (1.5.11)$$

At this stage, it is advantageous to collect the charged particles α together to form atoms and molecules ξ . Further, it is approximated that the nuclei are located at fixed positions in space relative to electrons, which are allowed to move. Hence, the dynamical variables of the charged particle system are the electronic coordinates and momenta. The clamped nuclei approximation is justified on the grounds that the nucleons are significantly more massive than electrons. This is a simplification that is frequently made in chemical physics and is adopted in what follows. For many situations, however, such as the treatment of molecular vibrations and the dynamics of chemical reactions, nuclear motions cannot be ignored. For such applications, it is convenient to describe the interaction of radiation with quantum mechanical electrons, but with the nuclei moving classically in a

specific version of a semiclassical formulation of the theory. This has been achieved by coupling the Maxwell and Schrödinger equations in a canonical prescription (Masiello et al., 2005). The time evolution is followed by integrating the first-order Hamilton's equations subject to well-defined initial conditions for the dynamical variables. The solutions are formally exact in the limit of infinite basis sets, though in practice computations are carried out with a set of truncated functions. The other, more difficult option, is a fully quantum mechanical treatment of electronic and nuclear degrees of freedom coupled to radiation.

By dividing the total electrostatic potential energy into a sum of one-particle and two-center terms,

$$V = \sum_{\xi} V(\xi) + \sum_{\xi < \xi'} V(\xi, \xi'), \quad (1.5.12)$$

the Hamiltonian (1.5.11) can be written as

$$H^{\min} = H_{\text{mol}}^{\min} + H_{\text{rad}}^{\min} + H_{\text{int}}^{\min}, \quad (1.5.13)$$

where the molecular Hamiltonian is

$$H_{\text{mol}}^{\min} = \sum_{\xi} \left\{ \frac{1}{2m} \sum_{\alpha} \vec{p}_{\alpha}^2(\xi) + V(\xi) \right\}, \quad (1.5.14)$$

in which \vec{p}_{α} is the momentum of electron α with position vector \vec{q}_{α} and $V(\xi)$ is the intramolecular potential energy of molecule ξ . The radiation field Hamiltonian is

$$H_{\text{rad}}^{\min} = \frac{1}{2\epsilon_0} \int \left\{ \vec{\Pi}^2 + \epsilon_0^2 c^2 (\vec{\nabla} \times \vec{a})^2 \right\} d^3\vec{r} = \frac{\epsilon_0}{2} \int (\vec{e}^{\perp 2} + c^2 \vec{b}^2) d^3\vec{r}, \quad (1.5.15)$$

expressed in terms of the vector potential and its canonically conjugate momentum, or in terms of electric and magnetic fields. The third term of (1.5.13) accounts for the interaction between radiation and matter and is explicitly given by

$$H_{\text{int}}^{\min} = \frac{e}{m} \sum_{\xi} \sum_{\alpha} \vec{p}_{\alpha}(\xi) \cdot \vec{a}(\vec{q}_{\alpha}(\xi)) + \frac{e^2}{2m} \sum_{\xi} \sum_{\alpha} \vec{a}^2(\vec{q}_{\alpha}(\xi)) + V_{\text{inter}}, \quad (1.5.16)$$

while V_{inter} is given by the second term of (1.5.12) and describes the intermolecular potential energy between molecules ξ and ξ' . The

superscript min is inserted because the total and individual Hamiltonians are constructed from dynamical variables specific to this particular formulation.

The quantum mechanical analogue of the classical Hamiltonian (1.5.13) is obtained on promoting the particle and field coordinates and canonically conjugate momenta to quantum operators subject to the following commutation relations valid at equal time:

$$[q_{i(\alpha)}(\xi), p_{j(\beta)}(\xi')] = i\hbar\delta_{ij}\delta_{\alpha\beta}\delta_{\xi\xi'} \quad (1.5.17)$$

and

$$[a_i(\vec{r}), \Pi_j(\vec{r}')] = i\hbar\delta_{ij}^{\perp}(\vec{r}-\vec{r}'). \quad (1.5.18)$$

The commutator between field operators (1.5.18) was expressed alternatively by (1.4.44) in terms of the annihilation and destruction operators for a mode of the radiation field in free space.

While the minimal-coupling Hamiltonian (1.5.13) rigorously describes the interaction of a charged particle with the electromagnetic field, it proves to be awkward when it is applied to radiation–molecule and molecule–molecule processes. This is due to the appearance of the particle momentum, the vector potential of the radiation field, and the intermolecular coupling term in the interaction component of the Hamiltonian (1.5.16). The first of these variables is not the most appropriate for a chemical species, the second is more often expressed in terms of the fundamental electric and magnetic fields, while the third term must always be included when treating two or more particles. In the following two sections, an alternative Lagrangian and Hamiltonian are obtained that have proved to be more suitable for application to atomic and molecular systems interacting with the radiation field.

1.6 MULTIPOLAR LAGRANGIAN

The Lagrangian for the interacting charged particle–electromagnetic field system (1.5.1) is a function of particle coordinates and velocities \vec{q}_α and $\dot{\vec{q}}_\alpha$ as well as a functional of the analogous field dynamical variables $\vec{a}(\vec{r})$ and $\dot{\vec{a}}(\vec{r})$. It was shown to lead to the correct Euler–Lagrange equations of motion. Lagrangians that differ in the total time derivative of a function or functional of the coordinates and the time, $f(\vec{q}, \dot{\vec{a}}, t)$, are said to be

equivalent. Thus,

$$L^{\text{new}} = L^{\text{old}} - \frac{d}{dt}f(\vec{q}, \vec{a}, t). \quad (1.6.1)$$

Because the variations in the path correct to first order between the initial and final times vanish,

$$\delta q(t_i) = \delta q(t_f) = 0, \quad (1.6.2a)$$

$$\delta a_j(t_i) = \delta a_j(t_f) = 0, \quad (1.6.2b)$$

the variations of the action integral involving old and new Lagrangians are then identical,

$$\delta S^{\text{new}} = \delta \int_{t_i}^{t_f} L^{\text{new}} dt = \delta \int_{t_i}^{t_f} L^{\text{old}} dt = \delta S^{\text{old}}, \quad (1.6.3)$$

where the action S is the time integral of the Lagrangian. Hence, identical Euler–Lagrange equations of motion follow from L^{new} as derived from L^{old} .

A Lagrangian equivalent to that of (1.5.1), one that leads to a Hamiltonian that is better suited to deal with atomic and molecular systems, is obtained by adding a function of the form

$$\int \vec{p}^\perp(\vec{r}) \cdot \vec{a}(\vec{r}) d^3\vec{r}, \quad (1.6.4)$$

as was first suggested by Göppert-Mayer (1931). If $\vec{p}^\perp(\vec{r})$ in (1.6.4) is taken to be the transverse component of the electric polarization field, the resulting new Lagrangian is of the multipolar form, whose explicit structure will be given below. Before going on to this, the decomposition of charge and current densities in terms of electric and magnetic polarization fields is carried out and their multipole expanded forms are given.

In a medium, the electric and magnetic polarizations result from charge and current densities. The former is separated into contributions from free and bound charges, while the current density is composed of terms arising from electric polarization and magnetization currents due to the relative motions of bound charges, and the contributions from convective and Röntgen currents. For a neutral system, the convective current vanishes, while for stationary nuclei there is no Röntgen term.

The charge density (1.3.9) may be partitioned as

$$\rho(\vec{r}) = \sum_{\alpha} e_{\alpha} \delta(\vec{r} - \vec{q}_{\alpha}) = \sum_{\alpha} e_{\alpha} \delta(\vec{r} - \vec{R}) - \vec{\nabla} \cdot \vec{p}(\vec{r}) = \rho^{\text{true}} - \vec{\nabla} \cdot \vec{p}(\vec{r}), \quad (1.6.5)$$

in which $\rho^{\text{true}} = \sum_{\alpha} e_{\alpha} \delta(\vec{r} - \vec{R})$ is the net charge density of the distribution. This division of the source necessitates the introduction of the vector \vec{R}_{ξ} , an expansion point about which multipole moments are defined and which may be taken as the center of mass, an inversion center, or the origin of a local chromophore center. The electric polarization field $\vec{p}(\vec{r})$ can be written in closed form as the parametric integral (Woolley, 1971)

$$\begin{aligned} \vec{p}(\xi, \vec{r}) = & \sum_{\alpha} e_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \int_0^1 \delta(\vec{r} - \vec{R}_{\xi} - \lambda(\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})) d\lambda \\ & + \sum_a e_a Z_a(\xi) (\vec{Q}_a(\xi) - \vec{R}_{\xi}) \int_0^1 \delta(\vec{r} - \vec{R}_{\xi} - \lambda(\vec{Q}_a(\xi) - \vec{R}_{\xi})) d\lambda, \end{aligned} \quad (1.6.6)$$

a sum of electronic and nuclear contributions, with $Z_a(\xi)$ and $\vec{Q}_a(\xi)$ the atomic number and position of nucleus a of molecule ξ , and

$$\vec{p}(\vec{r}) = \sum_{\xi} \vec{p}(\xi, \vec{r}). \quad (1.6.7)$$

Concentrating on the electronic term and expanding the delta function produces

$$\begin{aligned} \vec{p}(\xi, \vec{r}) = & \sum_{\alpha} e_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \int_0^1 \left[1 - \left\{ \lambda(\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \cdot \vec{\nabla} \right\} \right. \\ & \left. + \frac{1}{2!} \left\{ \lambda(\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \cdot \vec{\nabla} \right\}^2 - \dots \right] \delta(\vec{r} - \vec{R}_{\xi}) d\lambda, \end{aligned} \quad (1.6.8)$$

which after carrying out the λ -integral results in the familiar electric multipole series expansion of the polarization distribution; the dipole term is given by

$$\vec{p}^{(1)}(\xi, \vec{r}) = \sum_{\alpha} e_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \delta(\vec{r} - \vec{R}_{\xi}) \quad (1.6.9)$$

and the quadrupole polarization by

$$\vec{p}^{(2)}(\xi, \vec{r}) = - \sum_{\alpha} \frac{1}{2!} e_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \cdot \vec{\nabla} \delta(\vec{r} - \vec{R}_{\xi}). \quad (1.6.10)$$

The superscript indicates the order of the moment, with the familiar electric dipole defined as

$$\mu_i(\xi) = \sum_{\alpha} e_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})_i \quad (1.6.11)$$

and the electric quadrupole moment tensor as

$$Q_{ij}(\xi) = \frac{1}{2!} \sum_{\alpha} e_{\alpha} (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})_i (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi})_j. \quad (1.6.12)$$

With the polarization field defined by (1.6.8), the multipolar Lagrangian is obtained from the minimal-coupling Lagrangian (1.5.1) on using (1.6.4) in (1.6.1); that is,

$$\begin{aligned} L^{\text{mult}} &= L^{\text{min}} - \frac{d}{dt} \int \vec{p}^{\perp}(\vec{r}) \cdot \vec{a}(\vec{r}) d^3\vec{r} \\ &= \sum_{\xi} \left\{ \frac{m}{2} \sum_{\alpha} \dot{\vec{q}}_{\alpha}^2(\xi) - V(\xi) \right\} + \frac{\epsilon_0}{2} \int \left\{ \dot{\vec{a}}^2(\vec{r}) - c^2 (\vec{\nabla} \times \vec{a}(\vec{r}))^2 \right\} d^3\vec{r} \\ &\quad + \int \left(\vec{j}^{\perp}(\vec{r}) - \frac{d\vec{p}^{\perp}(\vec{r})}{dt} \right) \cdot \vec{a}(\vec{r}) d^3\vec{r} - \int \vec{p}^{\perp}(\vec{r}) \cdot \dot{\vec{a}}(\vec{r}) d^3\vec{r} - \sum_{\xi < \xi'} V_{\text{inter}}(\xi, \xi'), \end{aligned} \quad (1.6.13)$$

where the partitioning of the total electrostatic potential energy into intra- and intermolecular terms according to (1.5.12) has been used explicitly.

From the definition of the transverse current density and the electric dipole polarization distribution (1.6.9), it is seen that in the electric dipole approximation,

$$\vec{j}^{\perp}(\vec{r}) = \frac{d\vec{p}^{\perp}(\vec{r})}{dt}, \quad (1.6.14)$$

and the particle momentum canonically conjugate to the position,

$$\vec{p}_{\alpha} = \frac{\partial L^{\text{mult}}}{\partial \dot{\vec{q}}_{\alpha}} = m \dot{\vec{q}}_{\alpha}, \quad (1.6.15)$$

is equal to the kinetic momentum.

To proceed further, the third term of L^{mult} is examined in detail. Employing the identity (Power and Thirunamachandran, 1971)

$$\begin{aligned} \dot{\vec{q}} \delta(\vec{r} - \vec{q}) &= \frac{d}{dt} (\vec{q} - \vec{R}) \int_0^1 \delta(\vec{r} - \vec{R} - \lambda(\vec{q} - \vec{R})) d\lambda \\ &\quad + \vec{\nabla} \times \left[(\vec{q} - \vec{R}) \times \dot{\vec{q}} \int_0^1 \lambda \delta(\vec{r} - \vec{R} - \lambda(\vec{q} - \vec{R})) d\lambda \right] \end{aligned} \quad (1.6.16)$$

enables the difference between the transverse current and polarization densities to be written as

$$\vec{j}^\perp(\vec{r}) - \frac{d\vec{p}^\perp(\vec{r})}{dt} = \vec{\nabla} \times \vec{m}(\vec{r}), \quad (1.6.17)$$

showing that the current density for a system of neutral molecules moving with zero velocity is composed of electric and magnetic polarization contributions. On the right-hand side of (1.6.17) is the curl of the magnetization field, $\vec{m}(\vec{r})$,

$$\vec{m}(\xi, \vec{r}) = \sum_\alpha e_\alpha \{(\vec{q}_\alpha(\xi) - \vec{R}_\xi) \times \dot{\vec{q}}_\alpha(\xi)\} \int_0^1 \lambda \delta(\vec{r} - \vec{R}_\xi - \lambda(\vec{q}_\alpha(\xi) - \vec{R}_\xi)) d\lambda, \quad (1.6.18)$$

with the contribution from nuclei given by

$$+ \sum_a e_a Z_a(\xi) \{(\vec{Q}_a(\xi) - \vec{R}_\xi) \times \dot{\vec{Q}}_a(\xi)\} \int_0^1 \lambda \delta(\vec{r} - \vec{R}_\xi - \lambda(\vec{Q}_a(\xi) - \vec{R}_\xi)) d\lambda, \quad (1.6.19)$$

so that

$$\vec{m}(\vec{r}) = \sum_\xi \vec{m}(\xi, \vec{r}). \quad (1.6.20)$$

On again expanding the δ -function in a Taylor series and performing the λ -integral, the i th component of the electronic contribution to the magnetization (1.6.18) is given by

$$\begin{aligned} m_i(\xi, \vec{r}) &= \sum_\alpha e_\alpha \{(\vec{q}_\alpha(\xi) - \vec{R}_\xi) \times \dot{\vec{q}}_\alpha(\xi)\}_i \int_0^1 \lambda \left[1 - \{ \lambda(\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j \vec{\nabla}_j \} \right. \\ &\quad \left. + \frac{1}{2!} \{ \lambda(\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_k \vec{\nabla}_j \vec{\nabla}_k \}^2 - \dots \right] \delta(\vec{r} - \vec{R}_\xi) d\lambda \\ &= \sum_\alpha e_\alpha \{(\vec{q}_\alpha(\xi) - \vec{R}_\xi) \times \dot{\vec{q}}_\alpha(\xi)\}_i \\ &\quad \times \left\{ \begin{array}{l} \frac{1}{2!} - \frac{2}{3!} (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j \vec{\nabla}_j \\ + \frac{3}{4!} (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_k \vec{\nabla}_j \vec{\nabla}_k - \dots \end{array} \right\} \delta(\vec{r} - \vec{R}_\xi) \\ &= \left\{ m_i^{(1)} - m_{ij}^{(2)} \vec{\nabla}_j + m_{ijk}^{(3)} \vec{\nabla}_j \vec{\nabla}_k - \dots \right\} \delta(\vec{r} - \vec{R}_\xi), \quad (1.6.21) \end{aligned}$$

where the first term, including $\delta(\vec{r}-\vec{R}_\xi)$, is the magnetic dipole magnetization, the second is the magnetic quadrupole magnetization, and so on, with the magnetic multipole moments defined as

$$m_i^{(1)}(\xi) = \sum_\alpha \frac{1}{2!} e_\alpha \{ (\vec{q}_\alpha(\xi) - \vec{R}_\xi) \times \dot{\vec{q}}_\alpha(\xi) \}_i, \quad (1.6.22)$$

$$m_{ij}^{(2)}(\xi) = \sum_\alpha \frac{2}{3!} e_\alpha \{ (\vec{q}_\alpha(\xi) - \vec{R}_\xi) \times \dot{\vec{q}}_\alpha(\xi) \}_i (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j. \quad (1.6.23)$$

Of course, the right-hand side of (1.6.17) and the form of (1.6.18) are obtained by explicitly evaluating the left-hand side of the former, the two terms being given by

$$\begin{aligned} j_i(\vec{r}) = & \sum_\alpha e_\alpha \dot{q}_{i(\alpha)}(\xi) \left[1 - (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j \vec{\nabla}_j \right. \\ & \left. + \frac{1}{2!} (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_k \vec{\nabla}_j \vec{\nabla}_k - \dots \right] \delta(\vec{r} - \vec{R}_\xi) \end{aligned} \quad (1.6.24)$$

and

$$\begin{aligned} \frac{dp_i(\vec{r})}{dt} = & \sum_\alpha e_\alpha \dot{q}_{i(\alpha)}(\xi) \left[1 - \frac{1}{2!} (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j \vec{\nabla}_j \right. \\ & \left. + \frac{1}{3!} (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_j (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_k \vec{\nabla}_j \vec{\nabla}_k - \dots \right] \delta(\vec{r} - \vec{R}_\xi) \\ & - \sum_\alpha e_\alpha (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_i \dot{q}_{j(\alpha)}(\xi) \vec{\nabla}_j \left[\frac{1}{2!} - \frac{2}{3!} (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_k \vec{\nabla}_k + \dots \right] \delta(\vec{r} - \vec{R}_\xi). \end{aligned} \quad (1.6.25)$$

Returning to the multipolar Lagrangian (1.6.13), inserting (1.6.17) produces for L^{mult}

$$L^{\text{mult}} = L_{\text{mol}} + L_{\text{rad}} + \int [\vec{\nabla} \times \vec{m}(\vec{r})] \cdot \vec{a}(\vec{r}) d^3\vec{r} - \int \vec{p}^\perp(\vec{r}) \cdot \dot{\vec{a}}(\vec{r}) d^3\vec{r} - \sum_{\xi < \xi'} V_{\text{inter}}(\xi, \xi'), \quad (1.6.26)$$

where

$$L_{\text{mol}} = \sum_\xi \left\{ \frac{1}{2} m \sum_\alpha \dot{\vec{q}}_\alpha^2(\xi) - V(\xi) \right\} \quad (1.6.27)$$

and

$$L_{\text{rad}} = \frac{\varepsilon_0}{2} \int \left\{ \dot{\vec{a}}^2(\vec{r}) - c^2 (\vec{\nabla} \times \vec{a}(\vec{r}))^2 \right\} d^3\vec{r}. \quad (1.6.28)$$

The last three terms of (1.6.26) now constitute the new interaction terms with coupling now occurring through the polarization and magnetization fields instead of through the transverse current density as in (1.5.4) (Power and Thirunamachandran, 1978).

Even though the formal equations of motion are identical for equivalent Lagrangians, their actual expressions will differ due to the introduction of new variables. The result of the addition of the time derivative of (1.6.4) to the minimal-coupling Lagrangian to form L^{mult} led to the appearance of polarization and magnetization fields. The equations of motion for the radiation field, expressed in terms of $\vec{p}(\vec{r})$ and $\vec{m}(\vec{r})$, are known as the atomic field equations. They are obtained from the Euler–Lagrange equations of motion for the field and (1.6.26) as follows. Defining the appropriate Lagrangian density $\mathcal{L}^{\text{mult}}$ from (1.6.26), the three terms of the equations of motion

$$\frac{\partial}{\partial t} \left(\frac{\partial \mathcal{L}^{\text{mult}}}{\partial \dot{a}_i} \right) + \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}^{\text{mult}}}{\partial (\partial a_i / \partial x_j)} - \frac{\partial \mathcal{L}^{\text{mult}}}{\partial a_i} = 0 \quad (1.6.29)$$

are

$$\frac{\partial \mathcal{L}^{\text{mult}}}{\partial \dot{a}_i} = \varepsilon_0 \dot{a}_i(\vec{r}) - p_i^\perp(\vec{r}) = -d_i^\perp(\vec{r}), \quad (1.6.30)$$

where $d_i^\perp(\vec{r})$ is the transverse component of the electric displacement field,

$$\vec{d}(\vec{r}) = \varepsilon_0 \vec{e}(\vec{r}) + \vec{p}(\vec{r}), \quad (1.6.31)$$

$$\frac{\partial \mathcal{L}^{\text{mult}}}{\partial (\partial a_i / \partial x_j)} = -c^2 \varepsilon_0 \left(\frac{\partial a_i}{\partial x_j} - \frac{\partial a_j}{\partial x_i} \right), \quad (1.6.32)$$

and

$$\frac{\partial \mathcal{L}^{\text{mult}}}{\partial a_i} = [\vec{\nabla} \times \vec{m}(\vec{r})]_i. \quad (1.6.33)$$

Taking the time derivative of (1.6.30) and adding to (1.6.32) and (1.6.33) produces for (1.6.29)

$$\vec{\nabla} \times \vec{b}(\vec{r}) = \frac{1}{\varepsilon_0 c^2} \left\{ \frac{\partial \vec{d}^\perp(\vec{r})}{\partial t} + [\vec{\nabla} \times \vec{m}(\vec{r})] \right\}, \quad (1.6.34)$$

which on substituting (1.6.17) for $\vec{j}^\perp(\vec{r})$ and using (1.6.31) yields the source-dependent Maxwell–Lorentz equation

$$\vec{\nabla} \times \vec{b}(\vec{r}) = \frac{1}{c^2} \frac{\partial \vec{e}^\perp(\vec{r})}{\partial t} + \frac{1}{\epsilon_0 c^2} \vec{j}^\perp(\vec{r}). \quad (1.6.35)$$

By defining the magnetic analogue $\vec{h}(\vec{r})$ of the displacement field,

$$\vec{h}(\vec{r}) = \epsilon_0 c^2 \vec{b}(\vec{r}) - \vec{m}(\vec{r}), \quad (1.6.36)$$

(1.6.34) can be written in terms of both auxiliary fields as

$$\vec{\nabla} \times \vec{h}(\vec{r}) = \frac{\partial \vec{d}^\perp(\vec{r})}{\partial t}, \quad (1.6.37)$$

which expresses the Maxwell–Lorentz equation (1.6.35) in terms of $\vec{d}(\vec{r})$ and $\vec{h}(\vec{r})$.

As expected, Newton’s force law with Lorentz term—the equation of motion for the particle (1.5.7)—results when L^{mult} (1.6.26) is used in the Euler–Lagrange equation

$$\frac{d}{dt} \frac{\partial L^{\text{mult}}}{\partial \dot{\vec{q}}_\alpha(\xi)} - \frac{\partial L^{\text{mult}}}{\partial \vec{q}_\alpha(\xi)} = 0. \quad (1.6.38)$$

1.7 MULTIPOLAR HAMILTONIAN

Having obtained in the previous section the equations of motion satisfied by the multipolar Lagrangian for the interaction of a system of charged particles and electromagnetic radiation, it remains to apply the canonical quantization scheme to L^{mult} given by (1.6.26) to derive the multipolar form of the Hamiltonian operator. Before the latter can be constructed, the momenta canonically conjugate to the particle coordinate and the vector potential of the field are first evaluated using (1.6.26). The first of these is given by

$$\begin{aligned} \vec{p}_\alpha(\xi) &= \frac{\partial L^{\text{mult}}}{\partial \dot{\vec{q}}_\alpha(\xi)} = m \dot{\vec{q}}_\alpha(\xi) + \frac{\partial}{\partial \dot{\vec{q}}_\alpha(\xi)} \int \{ \vec{\nabla} \times \vec{m}_\alpha(\vec{r}) \} \cdot \vec{a}(\vec{r}) d^3 \vec{r} \\ &= m \dot{\vec{q}}_\alpha(\xi) + e (\vec{q}_\alpha(\xi) - \vec{R}_\xi) \int \int_0^1 \lambda \delta(\vec{r} - \vec{R}_\xi - \lambda(\vec{q}_\alpha(\xi) - \vec{R}_\xi)) d\lambda \times \vec{b}(\vec{r}) d^3 \vec{r} \end{aligned} \quad (1.7.1)$$

after inserting the expression for the magnetization field applicable to a single charged particle (1.6.18). Defining a further vector field,

$$\vec{n}_\alpha(\xi; \vec{r}) = -e(\vec{q}_\alpha(\xi) - \vec{R}_\xi) \int_0^1 \lambda \delta(\vec{r} - \vec{R}_\xi - \lambda(\vec{q}_\alpha(\xi) - \vec{R}_\xi)) d\lambda, \quad (1.7.2)$$

which is seen to be λ times the electronic part of the polarization field $\vec{p}(\xi, \vec{r})$ (1.6.6), with

$$\vec{n}(\vec{r}) = \sum_{\xi, \alpha} \vec{n}_\alpha(\xi, \vec{r}), \quad (1.7.3)$$

the conjugate momentum (1.7.1) can be written more succinctly as

$$\vec{p}_\alpha(\xi) = m\dot{\vec{q}}_\alpha(\xi) - \int \vec{n}_\alpha(\xi; \vec{r}) \times \vec{b}(\vec{r}) d^3\vec{r}. \quad (1.7.4)$$

Note that the kinetic and canonical momenta are no longer identical, but differ in the second term on the right-hand side of the last relation. The momentum conjugate to the field has been evaluated previously and is given by

$$\Pi_i(\vec{r}) = \frac{\partial \mathcal{L}^{\text{mult}}}{\partial \dot{a}_i(\vec{r})} = \varepsilon_0 \dot{a}_i(\vec{r}) - p_i^\perp(\vec{r}) = -d_i^\perp(\vec{r}), \quad (1.7.5)$$

being the negative of the transverse displacement field; this is unlike the situation in minimal coupling, where $\vec{\Pi}(\vec{r})$ was found to be proportional to the negative transverse electric field (1.5.10). The multipolar Hamiltonian is obtained from (1.5.8) on inserting L^{mult} and summing over particles α and aggregates ξ ,

$$H^{\text{mult}} = \sum_{\xi, \alpha} \vec{p}_\alpha(\xi) \cdot \dot{\vec{q}}_\alpha(\xi) + \int \vec{\Pi}(\vec{r}) \cdot \dot{\vec{a}}(\vec{r}) d^3\vec{r} - L^{\text{mult}}, \quad (1.7.6)$$

and replacing $\dot{\vec{q}}$ and $\dot{\vec{a}}$ by using (1.7.4) and (1.7.5). This results in

$$\begin{aligned} H^{\text{mult}} = & \frac{1}{2m} \sum_{\xi, \alpha} \vec{p}_\alpha^2(\xi) + \sum_{\xi} V(\xi) + \frac{\varepsilon_0}{2} \int \left\{ \left(\frac{\vec{\Pi}(\vec{r})}{\varepsilon_0} \right)^2 + c^2 \vec{b}^2(\vec{r}) \right\} d^3\vec{r} \\ & + \varepsilon_0^{-1} \int \vec{p}^\perp(\vec{r}) \cdot \vec{\Pi}(\vec{r}) d^3\vec{r} - \int \vec{m}(\vec{r}) \cdot \vec{b}(\vec{r}) d^3\vec{r} \\ & + \frac{1}{2m} \sum_{\xi, \alpha} \left\{ \int \vec{n}_\alpha(\xi, \vec{r}) \times \vec{b}(\vec{r}) d^3\vec{r} \right\}^2 \\ & + \frac{1}{2\varepsilon_0} \int |\vec{p}^\perp(\vec{r})|^2 d^3\vec{r} + \sum_{\xi < \xi'} V_{\text{inter}}(\xi, \xi'), \end{aligned} \quad (1.7.7)$$

where the magnetization field $\vec{m}(\vec{r})$ is given in symmetrized form by

$$\vec{m}(\vec{r}) = \frac{1}{2m} \sum_{\xi, \alpha} \{ \vec{n}_\alpha(\xi, \vec{r}) \times \vec{p}_\alpha(\xi) - \vec{p}_\alpha(\xi) \times \vec{n}_\alpha(\xi, \vec{r}) \}, \quad (1.7.8)$$

and which differs from (1.6.18) because the kinetic and canonical momenta are now no longer equal to each other.

The penultimate term of (1.7.7), proportional to the square of the transverse polarization, is composed of intra- and intermolecular terms,

$$\varepsilon_0^{-1} \int \sum_{\xi} |\vec{p}^\perp(\xi, \vec{r})|^2 d^3\vec{r} + \varepsilon_0^{-1} \int \sum_{\xi \neq \xi'} \vec{p}^\perp(\xi, \vec{r}) \cdot \vec{p}^\perp(\xi', \vec{r}) d^3\vec{r}. \quad (1.7.9)$$

Noting that $\vec{p}(\vec{r}) = \vec{p}^\perp(\vec{r}) + \vec{p}^\parallel(\vec{r})$, the total intermolecular polarization product vanishes for nonoverlapping charge distributions due to the rapid fall off with r of the polarization field outside the source molecule. Hence,

$$\varepsilon_0^{-1} \int \sum_{\xi \neq \xi'} \vec{p}^\perp(\xi, \vec{r}) \cdot \vec{p}^\perp(\xi', \vec{r}) d^3\vec{r} = -\varepsilon_0^{-1} \int \sum_{\xi \neq \xi'} \vec{p}^\parallel(\xi, \vec{r}) \cdot \vec{p}^\parallel(\xi', \vec{r}) d^3\vec{r}. \quad (1.7.10)$$

The right-hand side of (1.7.10) can be shown to be equal to $-\sum_{\xi < \xi'} V_{\text{inter}}(\xi, \xi')$. An explicit demonstration within the context of electron wavefields is given in Section 2.3. Therefore, in the multipolar Hamiltonian, the intermolecular Coulomb interaction energy is canceled by the intermolecular part of the transverse polarization, leaving an intramolecular self-energy term $(1/2\varepsilon_0) \int \sum_{\xi} |\vec{p}^\perp(\xi, \vec{r})|^2 d^3\vec{r}$. The multipolar Hamiltonian (1.7.7) can now be written as

$$H^{\text{mult}} = H_{\text{mol}}^{\text{mult}} + H_{\text{rad}}^{\text{mult}} + H_{\text{int}}^{\text{mult}} + \frac{1}{2\varepsilon_0} \int \sum_{\xi} |\vec{p}^\perp(\xi, \vec{r})|^2 d^3\vec{r}, \quad (1.7.11)$$

where

$$H_{\text{mol}}^{\text{mult}} = \sum_{\xi} \left\{ \frac{1}{2m} \sum_{\alpha} \vec{p}_\alpha^2(\xi) + V(\xi) \right\}, \quad (1.7.12)$$

$$\begin{aligned} H_{\text{rad}}^{\text{mult}} &= \frac{1}{2} \int \left\{ \frac{\vec{\Pi}^2(\vec{r})}{\varepsilon_0} + \varepsilon_0 c^2 (\vec{\nabla} \times \vec{a}(\vec{r}))^2 \right\} d^3\vec{r} \\ &= \frac{1}{2\varepsilon_0} \int \{ \vec{d}^{\perp 2}(\vec{r}) + \varepsilon_0^2 c^2 \vec{b}^2(\vec{r}) \} d^3\vec{r}, \end{aligned} \quad (1.7.13)$$

and

$$\begin{aligned}
 H_{\text{int}}^{\text{mult}} &= \varepsilon_0^{-1} \int \vec{p}^\perp(\vec{r}) \cdot \vec{\Pi}(\vec{r}) d^3\vec{r} - \int \vec{m}(\vec{r}) \cdot (\vec{\nabla} \times \vec{a}(\vec{r})) d^3\vec{r} + \frac{1}{2m} \left\{ \int \vec{n}(\vec{r}) \right. \\
 &\quad \left. \times (\vec{\nabla} \times \vec{a}(\vec{r})) d^3\vec{r} \right\}^2 = -\varepsilon_0^{-1} \int \vec{p}(\vec{r}) \cdot \vec{d}^\perp(\vec{r}) d^3\vec{r} - \int \vec{m}(\vec{r}) \cdot \vec{b}(\vec{r}) d^3\vec{r} \\
 &\quad + \frac{1}{2} \int O_{ij}(\vec{r}, \vec{r}') b_i(\vec{r}) b_j(\vec{r}') d^3\vec{r} d^3\vec{r}'. \tag{1.7.14}
 \end{aligned}$$

The last term in (1.7.11) is the aforementioned one-center contribution from the transverse electric polarization field; it is independent of the radiation field and does not contribute to processes that involve a change in the state of the electromagnetic field, although it must be included when calculating self-energy corrections. The last term of (1.7.14) represents the diamagnetic interaction, with the field $O_{ij}(\vec{r}, \vec{r}')$ given by

$$\begin{aligned}
 O_{ij}(\vec{r}, \vec{r}') &= \sum_{\xi, \xi'} \frac{1}{m} \varepsilon_{ikl} \varepsilon_{jml} n_k(\xi, \vec{r}) n_m(\xi', \vec{r}') \\
 &= \frac{e^2}{m} \varepsilon_{ikl} \varepsilon_{jml} \sum_{\xi, \xi'} \sum_{\alpha, \beta} (\vec{q}_\alpha(\xi) - \vec{R}_\xi)_k (\vec{q}_\beta(\xi') - \vec{R}_{\xi'})_m \\
 &\quad \times \int_0^1 \int_0^1 \lambda \lambda' \delta(\vec{r} - \vec{R}_\xi - \lambda(\vec{q}_\alpha(\xi) - \vec{R}_\xi)) \delta(\vec{r}' - \vec{R}_{\xi'} - \lambda'(\vec{q}_\beta(\xi') - \vec{R}_{\xi'})) d\lambda d\lambda'. \tag{1.7.15}
 \end{aligned}$$

Noteworthy features of the multipolar Hamiltonian include the fact that the Maxwell fields $\vec{d}^\perp(\vec{r})$ and $\vec{b}(\vec{r})$ appear explicitly in the radiation field and interaction Hamiltonians. The dependence of $H_{\text{int}}^{\text{mult}}$ on the electromagnetic fields only, rather than on the electromagnetic potentials clearly has the advantage of making equation (1.7.14) independent of gauge. Molecules couple directly to the radiation fields through the electric polarization, magnetization, and diamagnetization fields. Absent from H^{mult} is the intermolecular electrostatic interaction term. Interaction between molecules is now mediated by the field via the exchange of transverse photons that propagate with speed c .

The interaction Hamiltonian may be conveniently expanded in terms of multipole moments using the relations (1.6.8), (1.6.21), and (1.7.15) for the fields $\vec{p}(\xi, \vec{r})$, $\vec{m}(\xi, \vec{r})$, and $O_{ij}(\vec{r}, \vec{r}')$, respectively, so as to simplify its use in subsequent applications that depend only on specific multipole moments. After carrying out the volume integral, the first few terms of (1.7.14) are

therefore

$$\begin{aligned}
 H_{\text{int}}^{\text{mult}} = & \sum_{\xi} \{ -\varepsilon_0^{-1} \vec{\mu}(\xi) \cdot \vec{d}^{\perp}(\vec{R}_{\xi}) - \varepsilon_0^{-1} Q_{ij}(\xi) \nabla_j d_i^{\perp}(\vec{R}_{\xi}) - \vec{m}(\xi) \cdot \vec{b}(\vec{R}_{\xi}) \} \\
 & + \frac{e^2}{8m} \sum_{\xi, \alpha} \{ (\vec{q}_{\alpha}(\xi) - \vec{R}_{\xi}) \times \vec{b}(\vec{R}_{\xi}) \}^2 + \dots,
 \end{aligned} \tag{1.7.16}$$

comprising electric dipole $\vec{\mu}(\xi)$, electric quadrupole $Q_{ij}(\xi)$, magnetic dipole $\vec{m}(\xi)$, and lowest order diamagnetic coupling of species ξ , with this last term of (1.7.16) being proportional to the square of the magnetic field.

From the definition of the electric displacement field (1.7.5) and the mode expansion (1.4.54) for the canonically conjugate momentum $\vec{\Pi}(\vec{r})$, the mode expansion for the transverse electric displacement field operator is

$$\vec{d}^{\perp}(\vec{r}) = i \sum_{\vec{k}, \lambda} \left(\frac{\hbar c k \varepsilon_0}{2V} \right)^{1/2} \left[\vec{e}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \vec{e}^{-(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \right]. \tag{1.7.17}$$

It is of interest to point out that from the definition of the transverse current density (1.5.5) and the electric dipole polarization distribution (1.6.9)

$$\vec{j}^{\perp}(\vec{r}) = \frac{d\vec{p}^{\perp}(\vec{r})}{dt} \tag{1.7.18}$$

in the electric dipole approximation and that the particle momentum canonically conjugate to the position operator,

$$\vec{p}_{\alpha} = \frac{\partial L^{\text{mult}}}{\partial \dot{\vec{q}}_{\alpha}} = m \dot{\vec{q}}_{\alpha}, \tag{1.7.19}$$

is equal to the kinetic momentum. Relation (1.7.5) still holds for the momentum canonically conjugate to the vector potential, but now also in the long-wavelength approximation. The effect of (1.7.18) is to replace coupling to $\vec{j}^{\perp}(\vec{r})$ by the transverse polarization in the multipolar Lagrangian (1.6.13) so that

$$L_{\text{int}}^{\text{mult}} = - \int \vec{p}^{\perp}(\vec{r}) \cdot \dot{\vec{a}}(\vec{r}) d^3\vec{r} - \sum_{\xi < \xi'} V_{\text{inter}}(\xi, \xi'). \tag{1.7.20}$$

As before, H^{mult} equation (1.7.11) results when (1.7.20) is used instead of the last three terms of (1.6.13), but with $H_{\text{int}}^{\text{mult}}$ now given by the first term of equation (1.7.16) only, which is the electric dipole form of the interaction operator.

Converting the dynamical variables to quantum mechanical operators, which obey the commutation rules

$$[q_{i(\alpha)}(\xi), p_{j(\beta)}(\xi')] = i\hbar\delta_{ij}\delta_{\alpha\beta}\delta_{\xi\xi'} \quad (1.7.21)$$

and

$$[a_i(\vec{r}), \Pi_j(\vec{r}')] = i\hbar\delta_{ij}^{\perp}(\vec{r}-\vec{r}'), \quad (1.7.22)$$

produces the quantum analogue of the multipolar Hamiltonian (1.7.11). This Hamiltonian is frequently used as the starting point in the calculation of processes involving the interaction of radiation with matter as well as for the study of long-range intermolecular forces. A completely second quantized form of H^{mult} proves to be advantageous for many of the applications to be detailed in subsequent chapters. The presentation of this field theoretic viewpoint is left for Chapter 2. Finally, it is interesting to note that the commutation relations (1.7.21) and (1.7.22) are identical to those occurring for minimal-coupling variables. The preservation of commutation rules is a direct consequence of carrying out a transformation that yielded an equivalent Lagrangian.

1.8 CANONICAL TRANSFORMATION

In the Hamiltonian formulation of classical mechanics, the equations of motion satisfied by the generalized coordinates q_i and momenta p_i , $i = 1, \dots, 3N$, for a system of N particles are Hamilton's canonical equations (1.2.5). Alternatively, these relations may be expressed in terms of the Poisson bracket, which for two differentiable functions f and g that are functions of p and q ,

$$\{f, g\} = \left\{ \frac{\partial f}{\partial q} \frac{\partial g}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial g}{\partial q} \right\}, \quad (1.8.1)$$

so that

$$\dot{q} = \{q, H\} \quad (1.8.2)$$

and

$$\dot{p} = \{p, H\}. \quad (1.8.3)$$

From the definition (1.8.1), it is seen that the Poisson bracket for the canonical pair q and p is unity,

$$\{q, p\} = 1. \quad (1.8.4)$$

If f is explicitly a function of time, namely, $f = f(q, p, t)$, then the time evolution of f is given by

$$\dot{f} = \{f, H\} + \frac{\partial f}{\partial t}. \quad (1.8.5)$$

In Section 1.6, it was shown how equivalent Lagrangians could be generated by the addition of the total time derivative of a function of the coordinates, which amounted to a canonical transformation of the dynamical variables, with construction of the corresponding Hamiltonian function requiring the evaluation of the canonically conjugate momenta. In general, the momenta obtained from two equivalent Lagrangians differ. Under a canonical transformation, however, the Poisson bracket (1.8.1) and Hamilton's canonical equations of motion (1.8.2) and (1.8.3) are preserved.

When f is a quantum mechanical operator, the counterpart to (1.8.5) is the Heisenberg equation of motion

$$\dot{f} = \frac{1}{i\hbar} [f, H] + \frac{\partial f}{\partial t}, \quad (1.8.6)$$

in which the commutator bracket now appears instead of the Poisson bracket. Analogously, the quantum versions of Hamilton's canonical equations take the form

$$i\hbar\dot{q} = [q, H] \quad (1.8.7)$$

and

$$i\hbar\dot{p} = [p, H], \quad (1.8.8)$$

with the fundamental commutator between position and momentum given by

$$[q, p] = i\hbar. \quad (1.8.9)$$

Application of a quantum canonical transformation leaves the commutation relation (1.8.9) and the operator equations of motion (1.8.7) and (1.8.8) unchanged. One type of transformation that possesses these

properties is given by

$$q' = e^{iS} q e^{-iS} \quad (1.8.10)$$

and

$$p' = e^{iS} p e^{-iS}, \quad (1.8.11)$$

where S is an Hermitian operator and is called the generating function of the transformation. The transformed Hamiltonian is then found from the starting one by expressing it in terms of the transformed variables. In effect, this amounts to transforming the original Hamiltonian by the application of the canonical transformation; that is,

$$H' = e^{iS} H e^{-iS}. \quad (1.8.12)$$

Hence, the multipolar Hamiltonian can be obtained from the minimal-coupling Hamiltonian via the application of a canonical transformation of the form (1.8.12) with a suitable choice of the generator S (Power and Zienau, 1959). It now remains to find the connection between the function f , whose time derivative when taken and added to a Lagrangian produces equivalent Lagrangians, and the function S , which when utilized according to (1.8.12) gives rise to equivalent Hamiltonians.

Beginning with the Lagrangian L , an equivalent Lagrangian L' is given by

$$L'(q, \dot{q}, t) = L(q, \dot{q}, t) + \frac{d}{dt} f(q, t) = L(q, \dot{q}, t) + \frac{\partial}{\partial q} f(q, t) \dot{q} + \frac{\partial}{\partial t} f(q, t), \quad (1.8.13)$$

where f does not depend on the velocities. The Hamiltonian obtained from L' is

$$H' = p' \dot{q} - L', \quad (1.8.14)$$

with

$$p' = \frac{\partial L'}{\partial \dot{q}} = \frac{\partial L}{\partial \dot{q}} + \frac{\partial f(q, t)}{\partial q}, \quad (1.8.15)$$

since $q' = q$.

Employing the identity (Craig and Thirunamachandran, 1998a)

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!} [A, [A, B]] + \frac{1}{3!} [A, [A, [A, B]]] + \dots, \quad (1.8.16)$$

in which A and B are two noncommuting operators, the transformed momentum (1.8.11) becomes

$$\begin{aligned} p' &= p + i[S, p] + \frac{i^2}{2!}[S, [S, p]] + \dots \\ &= p - \hbar \frac{\partial S}{\partial q}, \end{aligned} \quad (1.8.17)$$

where S is taken to be a function of q only, and making use of the commutation relation

$$[S(q), p] = i\hbar \frac{\partial S}{\partial q}, \quad (1.8.18)$$

which results in only the first two terms of (1.8.17) surviving and all successive commutator expressions vanishing. From (1.8.15) and (1.8.17), the relation between the function f and the generator S is easily seen to be

$$f = -\hbar S. \quad (1.8.19)$$

Recalling (1.6.4), the generator that transforms H^{\min} to give the same H^{mult} as that calculated from L^{mult} when starting with L^{\min} is therefore

$$S = \frac{1}{\hbar} \int \vec{p}^\perp(\vec{r}) \cdot \vec{a}(\vec{r}) d^3\vec{r}. \quad (1.8.20)$$

Because S is a function only of the generalized coordinates, only the canonically conjugate particle and field momenta are affected by the canonical transformation. Thus, the former is calculated from

$$\vec{p}_{(x)}^{\text{mult}}(\xi) = e^{iS} \vec{p}_{(x)}^{\min}(\xi) e^{-iS} = \vec{p}_{(x)}^{\min}(\xi) + i[S, \vec{p}_{(x)}^{\min}(\xi)] + \dots, \quad (1.8.21)$$

on using the identity (1.8.16). Inserting the expression for the electronic part of the electric polarization field (1.6.6), it can be shown that

$$\vec{p}_{(x)}^{\text{mult}}(\xi) = \vec{p}_{(x)}^{\min}(\xi) + e\vec{a}(\vec{q}_\alpha(\xi)) - \int \vec{n}_\alpha(\xi, \vec{r}) \times \vec{b}(\vec{r}) d^3\vec{r}. \quad (1.8.22)$$

Similarly, the transformed field momentum is

$$\begin{aligned} \vec{\Pi}^{\text{mult}}(\vec{r}) &= e^{iS} \vec{\Pi}^{\min}(\vec{r}) e^{-iS} = \vec{\Pi}^{\min}(\vec{r}) + i[S, \vec{\Pi}^{\min}(\vec{r})] + \dots \\ &= \vec{\Pi}^{\min}(\vec{r}) + \frac{i}{\hbar} \left[\int \vec{p}^\perp(\vec{r}') \cdot \vec{a}(\vec{r}') d^3\vec{r}', \vec{\Pi}^{\min}(\vec{r}) \right] + \dots \end{aligned} \quad (1.8.23)$$

The commutator bracket is evaluated using the relation (1.7.22), giving

$$\vec{\Pi}^{\text{mult}}(\vec{r}) = \vec{\Pi}^{\text{min}}(\vec{r}) - \vec{p}^{\perp}(\vec{r}), \quad (1.8.24)$$

with all subsequent terms in the expansion (1.8.23) vanishing due to the fact that S commutes with the first commutator.

Substituting for $\vec{p}_{\alpha}^{\text{mult}}(\xi)$ and $\vec{\Pi}^{\text{mult}}(\vec{r})$ from (1.8.22) and (1.8.24) into the minimal-coupling Hamiltonian (1.5.11) results in

$$\begin{aligned} H^{\text{mult}} = & \sum_{\xi} \left[\frac{1}{2m} \sum_{\alpha} \left\{ \vec{p}_{\alpha}(\xi) + \int \vec{n}_{\alpha}(\xi, \vec{r}) \times \vec{b}(\vec{r}) d^3\vec{r} \right\}^2 + V(\xi) \right] \\ & + \frac{1}{2\epsilon_0} \int \{ [\vec{\Pi}(\vec{r}) + \vec{p}^{\perp}(\vec{r})]^2 + \epsilon_0^2 c^2 (\vec{\nabla} \times \vec{a}(\vec{r}))^2 \} d^3\vec{r} + \sum_{\xi < \xi'} V_{\text{inter}}(\xi, \xi'), \end{aligned} \quad (1.8.25)$$

which is identical to the multipolar Hamiltonian (1.7.7) constructed from the multipolar Lagrangian.

It is straightforward to demonstrate that the time derivatives of the generalized coordinates are unchanged by the canonical transformation and are in fact equal to each other in the two formalisms. For this purpose, it is convenient to use the Heisenberg equation of motion (1.8.7). Thus,

$$\dot{\vec{q}}_{\alpha}^{\text{min}}(\xi) = \frac{1}{i\hbar} [\vec{q}_{\alpha}(\xi), H^{\text{min}}] = \frac{1}{m} \{ \vec{p}_{\alpha}^{\text{min}}(\xi) + e\vec{a}(\vec{q}_{\alpha}(\xi)) \} \quad (1.8.26)$$

and

$$\dot{\vec{q}}_{\alpha}^{\text{mult}}(\xi) = \frac{1}{i\hbar} [\vec{q}_{\alpha}(\xi), H^{\text{mult}}] = \frac{1}{m} \left\{ \vec{p}_{\alpha}^{\text{mult}}(\xi) + \int \vec{n}(\xi, \vec{r}) \times \vec{b}(\vec{r}) d^3\vec{r} \right\}. \quad (1.8.27)$$

Clearly,

$$\dot{\vec{q}}_{\alpha}^{\text{min}}(\xi) = \dot{\vec{q}}_{\alpha}^{\text{mult}}(\xi) \quad (1.8.28)$$

on using (1.8.22). In a similar fashion,

$$\dot{\vec{a}}^{\text{min}}(\vec{r}) = \frac{1}{i\hbar} [\vec{a}(\vec{r}), H^{\text{min}}] = \epsilon_0^{-1} \vec{\Pi}^{\text{min}}(\vec{r}) \quad (1.8.29)$$

and

$$\dot{\vec{a}}^{\text{mult}}(\vec{r}) = \frac{1}{i\hbar} [\vec{a}(\vec{r}), H^{\text{mult}}] = \epsilon_0^{-1} \left\{ \vec{\Pi}^{\text{mult}}(\vec{r}) + \vec{p}^{\perp}(\vec{r}) \right\}, \quad (1.8.30)$$

which with the aid of (1.8.24) prove that

$$\dot{\vec{a}}^{\text{min}}(\vec{r}) = \dot{\vec{a}}^{\text{mult}}(\vec{r}). \quad (1.8.31)$$

Finally, it should be mentioned that the transformation discussed in this section is more precisely known as a Lagrangian-induced quantum completely canonical transformation (Power, 1978). This corresponds to a quantum canonical transformation with time-independent generator S . The transformation is therefore unitary, and the eigenspectra resulting from the use of either H^{min} or H^{mult} are identical.

1.9 PERTURBATION THEORY SOLUTION

In Section 1.7, it was shown how the multipolar Hamiltonian in Coulomb gauge for a system of charged particles in interaction with electromagnetic radiation could be written as a sum of molecular, radiation field, and interaction Hamiltonians, as well as including a term involving the square of the intramolecular transverse polarization field (1.7.11). It now remains to discuss how such a system of quantum mechanical equations is solved in general.

In the absence of any interaction between radiation and matter, the total Hamiltonian is simply a sum of molecular and radiation field Hamiltonians, $H_{\text{mol}} + H_{\text{rad}}$. Such a Hamiltonian is separable, with eigenenergy being the sum of the molecule and radiation field energies and eigenfunctions being the product states of molecule and radiation field wavefunctions. The quantization of the free electromagnetic field was carried out in Section 1.4, where an occupation number representation was used to specify the state of the radiation field, with n quanta of frequency ω having energy $n\hbar\omega$. Earlier in Section 1.2 it was shown how the application of the variational calculus to the classical Lagrangian function for a system of charged particles and the subsequent application of the canonical quantization prescription led to the familiar quantum mechanical molecular Hamiltonian H_{mol} , whose solution using a vast array of quantum chemical techniques is formally taken to be known, yielding eigenfunctions $|E_m\rangle$ for a molecular state of the system characterized by quantum number m with eigenenergy E_m . The form of the total Hamiltonian for the coupled matter–field system, be it in the minimal-coupling or multipolar frameworks (1.5.13) and (1.7.11), respectively, naturally lends itself to a perturbation theory solution.

The total quantum electrodynamical Hamiltonian is divided according to

$$H = H_0 + H_{\text{int}}, \quad (1.9.1)$$

where

$$H_0 = H_{\text{mol}} + H_{\text{rad}} \quad (1.9.2)$$

constitutes the unperturbed Hamiltonian, with

$$H_{\text{mol}} = \sum_{\xi} \left\{ \frac{1}{2m} \sum_{\alpha} \vec{p}_{\alpha}^2(\xi) + V(\xi) \right\} \quad (1.9.3)$$

and

$$H_{\text{rad}} = \frac{1}{2\epsilon_0} \int \{ \vec{\Pi}^2(\vec{r}) + \epsilon_0^2 c^2 (\vec{\nabla} \times \vec{a}(\vec{r}))^2 \} d^3\vec{r}. \quad (1.9.4)$$

The eigenstates of H_0 are written as product states of molecular and radiation field eigenfunctions $|E_m^{\xi}; n(\vec{k}, \lambda)\rangle = |E_m^{\xi}\rangle |n(\vec{k}, \lambda)\rangle$ corresponding to molecule ξ in electronic state $|m\rangle$ and the electromagnetic field characterized by n photons of mode (\vec{k}, λ) . These orthonormal functions form a basis set that is employed in the perturbation theory solution. The justification for such a treatment is that H_0 represents the solution to a known problem, in the case of (1.9.2) the noninteracting system of molecule(s) and the radiation field. Further, the coupling of radiation and matter, given by the second term of (1.9.1), is viewed as a small perturbation on the total system. This is based on the fact that the particle–field interaction terms are considerably smaller in magnitude than the strengths of Coulombic fields present within an atomic or molecular system. Except for very intense fields, of the order of 10^{12} V m^{-1} , the perturbation approximation holds true for both the minimal- and multipolar-coupling schemes. The interaction Hamiltonians for these two formalisms are, respectively, given by

$$H_{\text{int}}^{\text{min}} = \frac{e}{m} \sum_{\xi} \sum_{\alpha} \vec{p}_{\alpha}(\xi) \cdot \vec{a}(\vec{q}_{\alpha}(\xi)) + \frac{e^2}{2m} \sum_{\xi} \sum_{\alpha} \vec{a}^2(\vec{q}_{\alpha}(\xi)) + V_{\text{inter}} \quad (1.9.5)$$

and

$$H_{\text{int}}^{\text{mult}} = -\epsilon_0^{-1} \int \vec{p}(\vec{r}) \cdot \vec{d}^{\perp}(\vec{r}) d^3\vec{r} - \int \vec{m}(\vec{r}) \cdot \vec{b}(\vec{r}) d^3\vec{r} + \frac{1}{2} \int O_{ij}(\vec{r}, \vec{r}') b_i(\vec{r}) b_j(\vec{r}') d^3\vec{r} d^3\vec{r}'. \quad (1.9.6)$$

The expansion of the three terms of (1.9.6) in lowest order multipole moments was given by equation (1.7.16).

The two most common perturbative approaches for the solution of equations of the type (1.9.1) differ in their dependence on time. In time-independent perturbation theory, the equation to be solved is the time-independent Schrödinger equation,

$$(H_0 + \lambda H_{\text{int}})|i\rangle = E_i|i\rangle, \quad (1.9.7)$$

for the energy of the perturbed system E_i , which is taken to be nondegenerate, and its corresponding perturbed state function $|i\rangle$ in a power series expansion in the perturbation operator H_{int} . This is most frequently done using the method of Rayleigh and Schrödinger (Levine, 2000) for Hamiltonians that do not depend on time and is most useful for calculating shifts in energy levels of the perturbed system along with its perturbed wavefunction. The parameter λ , which lies between 0 and 1, ensures the perturbation operator, in the present case the interaction Hamiltonian, is applied smoothly. Ultimately, λ is eliminated by setting it equal to unity, corresponding to the situation in which the perturbation is acting fully. When $\lambda = 0$, equation (1.9.7) reduces to the unperturbed problem, represented by the Hamiltonian H_0 , which satisfies the eigenvalue equation

$$H_0|i^{(0)}\rangle = E_i^{(0)}|i^{(0)}\rangle, \quad (1.9.8)$$

whose eigenfunction $|i^{(0)}\rangle$ and eigenenergy $E_i^{(0)}$ are taken to be known. The perturbed state and energy are expanded in series of powers of λ ,

$$|i\rangle = |i^{(0)}\rangle + \lambda|i^{(1)}\rangle + \lambda^2|i^{(2)}\rangle + \dots \quad (1.9.9)$$

and

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda E_i^{(2)} + \dots; \quad (1.9.10)$$

$|i^{(1)}\rangle, |i^{(2)}\rangle, \dots$ and $E^{(1)}, E^{(2)}, \dots$ are successive perturbative corrections to the state function and energy, respectively, of the perturbed problem. Well-known formulas result for the perturbed state $|i\rangle$ and energy E_i . In terms of the unperturbed state $|i^{(0)}\rangle$ and energy $E_i^{(0)}$, they are

$$|i\rangle = |i^{(0)}\rangle + \sum_{j^{(0)} \neq i^{(0)}} \frac{\langle j^{(0)}|H_{\text{int}}|i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} |j^{(0)}\rangle + \dots \quad (1.9.11)$$

and

$$E_i = E_i^{(0)} + \langle i^{(0)} | H_{\text{int}} | i^{(0)} \rangle + \sum_{j^{(0)} \neq i^{(0)}} \frac{\langle i^{(0)} | H_{\text{int}} | j^{(0)} \rangle \langle j^{(0)} | H_{\text{int}} | i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} + \dots \quad (1.9.12)$$

In the term corresponding to the first-order correction to the wavefunction and to the second-order correction to the energy, the sum is executed over all unperturbed states except $|i^{(0)}\rangle$.

When the interaction Hamiltonian or the total Hamiltonian is time dependent, the dynamics involves the time evolution of the stationary states of the unperturbed system, which can now make transitions from one state to another under the influence of the perturbation. The dynamics is governed by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle, \quad (1.9.13)$$

in which the states $|\Psi(t)\rangle$ are explicitly time dependent. This is characteristic of the Schrödinger picture of quantum mechanics. It is convenient to view the time variation of the state function $|\Psi(t)\rangle$ as due to the action of a transformation operator $U(t)$ on a fixed state of the system at some initial time t_0 ,

$$|\Psi(t)\rangle = U(t) |\Psi(t_0)\rangle. \quad (1.9.14)$$

$U(t)$ is more commonly called the time evolution operator, and it is unitary so that the normalization properties associated with $|\Psi(t)\rangle$ are retained for all t . Substituting (1.9.14) into (1.9.13) shows that $U(t)$ satisfies the equation of motion

$$i\hbar \frac{\partial}{\partial t} U(t) = H U(t), \quad (1.9.15)$$

whose formal solution is simply

$$U(t) = e^{-iH(t-t_0)/\hbar}, \quad (1.9.16)$$

when subject to the initial condition $U(t_0) = 1$, enabling $|\Psi(t)\rangle$ to be evaluated at any time via (1.9.14).

In the standard treatment of time-dependent perturbation theory, all system states are written in terms of the eigenfunctions $|i\rangle$ of the

unperturbed Hamiltonian H_0 with energy E_i , $H_0|i\rangle = E_i|i\rangle$, along with their time-dependent factors, as in

$$|\Psi(t)\rangle = \sum_i a_i(t)e^{-iE_i t/\hbar}|i\rangle, \quad (1.9.17)$$

and the problem amounts to determining the time-dependent coefficients $a_i(t)$ from which state-to-state transition probabilities may be calculated. This is known as Dirac's variation of constants method. Equivalent results for the time evolution may be obtained in terms of the operator $U(t)$ introduced above (Ziman, 1969). Further calculational advantages ensue, however, if the time factor is removed from each basis state and absorbed into the operator itself, so that using (1.9.7)

$$|\Psi(t)\rangle = e^{-iH_0(t-t_0)/\hbar}U_I(t, t_0)|\Psi(t_0)\rangle. \quad (1.9.18)$$

The perturbation operator becomes

$$H_{\text{int}}^I(t) = e^{iH_0(t-t_0)/\hbar}H_{\text{int}}e^{-iH_0(t-t_0)/\hbar}. \quad (1.9.19)$$

Both the states and the operators are time dependent, and the focus is on the effect of the perturbation on the system. This representation lies in between the Schrödinger picture and the Heisenberg formalism. Recall that in the latter viewpoint, the dynamical variables are all time dependent and the states are time independent. The new picture symbolized by equations (1.9.18) and (1.9.19) is called the interaction representation or the Dirac representation, as indicated by the additional label I . Hence, $U_I(t, t_0)$ is the interaction picture time-evolution operator. It satisfies the operator equation of motion

$$i\hbar \frac{\partial}{\partial t}U_I(t, t_0) = H_{\text{int}}^I(t)U_I(t, t_0) \quad (1.9.20)$$

on using (1.9.18) and (1.9.19) in the time-dependent Schrödinger equation (1.9.13).

Continuing in the interaction representation, but now dropping the symbol I , the state function at time t is given by

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle. \quad (1.9.21)$$

If H_{int} is time independent, then analogously to (1.9.16), the formal solution to (1.9.20) is

$$U(t, t_0) = e^{-iH_{\text{int}}(t-t_0)/\hbar}. \quad (1.9.22)$$

On the other hand, if $H_{\text{int}} = H_{\text{int}}(t)$, but is taken to be a c -number, the differential equation (1.9.20) can be integrated to give for the time-evolution operator the solution

$$U(t, t_0) = \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t H_{\text{int}}(t') dt' \right\}. \quad (1.9.23)$$

This form of $U(t, t_0)$, however, cannot be used in the quantum theory, since H_{int} is an operator and does not, in general, commute with itself at two different times t_1 and t_2 . A formal series solution for $U(t, t_0)$ may be constructed for application in quantum mechanical problems when H_{int} is an operator. This is accomplished by integrating (1.9.20) with respect to time, subject to the initial condition

$$U(t_0, t_0) = 1, \quad (1.9.24)$$

to give

$$U(t, t_0) = 1 + \frac{1}{i\hbar} \int_{t_0}^t dt_1 H_{\text{int}}(t_1) U(t_1, t_0). \quad (1.9.25)$$

The right-hand side of (1.9.25) is reinserted as an expression for $U(t_1, t_0)$ under the integral sign and successively iterated in this way, eventually leading to a power series for $U(t, t_0)$ in terms of H_{int} . Thus,

$$U(t, t_0) = 1 + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar} \right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n H_{\text{int}}(t_1) \dots H_{\text{int}}(t_n). \quad (1.9.26)$$

The time ordering of the operators is explicit and the series result (1.9.26) is exact. In applying perturbation theory, the central problem is to compute successive terms, and if at all possible, the series sum.

It is now a simple matter to use (1.9.26) to calculate the probability amplitude of finding the system in the final state $|f\rangle$ at time t as a result of a perturbation H_{int} , which began to act at a time t_0 when the system was in the initial state $|i\rangle$. The matrix elements of the time evolution operator are

$$\langle f | U(t, t_0) | i \rangle = \delta_{if} - \sum_{\xi} M_{f\xi}(\xi) \frac{[e^{i(E_f - E_i)(t - t_0)/\hbar} - 1]}{E_f - E_i}, \quad (1.9.27)$$

where the matrix element for the process is denoted by $M_{f\xi}$. Clearly, there is no probability of finding the system in state $|f\rangle$ in zeroth order of H_{int}

because the initial and final states are orthogonal to one another. In powers of the perturbation operator, the matrix element is expanded as

$$\begin{aligned}
 M_{fi} = & \langle f | H_{\text{int}} | i \rangle + \sum_I \frac{\langle f | H_{\text{int}} | I \rangle \langle I | H_{\text{int}} | i \rangle}{(E_i - E_I)} + \sum_{I, II} \frac{\langle f | H_{\text{int}} | II \rangle \langle II | H_{\text{int}} | I \rangle \langle I | H_{\text{int}} | i \rangle}{(E_i - E_I)(E_i - E_{II})} \\
 & + \sum_{I, II, III} \frac{\langle f | H_{\text{int}} | III \rangle \langle III | H_{\text{int}} | II \rangle \langle II | H_{\text{int}} | I \rangle \langle I | H_{\text{int}} | i \rangle}{(E_i - E_I)(E_i - E_{II})(E_i - E_{III})} + \dots,
 \end{aligned} \tag{1.9.28}$$

where as before summation is carried out over all intermediate states that connect initial to final excluding the system states $|i\rangle$ and $|f\rangle$.

Ignoring the Kronecker delta term of (1.9.27), the time-dependent probability of finding the system in the final state is

$$P_{f \leftarrow i}(t) = |\langle f | U(t, t_0) | i \rangle|^2 = \sum_{\xi} 4 |M_{fi}(\xi)|^2 \frac{\sin^2 \omega_{fi}(t-t_0)/2}{\hbar^2 \omega_{fi}^2}, \tag{1.9.29}$$

where energy is conserved subject to

$$\hbar \omega_{fi} = (E_f - E_i). \tag{1.9.30}$$

In atomic and molecular systems, transitions can occur between discrete bound states that form part of an energy manifold. If the final state belongs to a continuum of levels centered at some frequency ω with range $\Delta\omega$, the total probability $P_{\text{tot}}(t)$ is a sum of all individual probabilities,

$$P_{\text{tot}}(t) = \sum_f P_{f \leftarrow i}(t), \tag{1.9.31}$$

with $P_{f \leftarrow i}(t)$ given by (1.9.29). This picture of a transition from a discrete state to a continuum of levels holds if each transition is taken to be independent of every other one. This is true for small $t - t_0$. Thus,

$$P_{\text{tot}}(t) = \sum_{\xi} \frac{2\pi}{\hbar} |M_{fi}(\xi)|^2 (t-t_0) \rho_f, \tag{1.9.32}$$

where ρ_f is the density of final states, namely, the number of levels per unit energy, dn_f/dE_f . Taking the time derivative of (1.9.32) leads to the familiar Fermi golden rule transition rate expression

$$\Gamma = \frac{d}{dt} P_{\text{tot}}(t) = \sum_{\xi} \frac{2\pi}{\hbar} |M_{fi}(\xi)|^2 \rho_f. \tag{1.9.33}$$

The evaluation of level shifts and spectroscopic rates using the perturbative expansions (1.9.12) and (1.9.28) is greatly facilitated by the introduction of diagrammatic techniques, the most well known being the time-ordered graphs of Feynman (Feynman, 1948, 1949a, 1949b; Mattuck, 1976). These diagrams have the additional advantage of yielding further valuable insight into the underlying physical process by providing a visual representation of individual electron–photon interactions in time-ordered sequences of emission and absorption events. For a process involving the interaction of n photons, the leading contribution to the quantum amplitude is given by the n th-order term in H_{int} when the coupling between radiation and matter is linear in the electric and magnetic fields, as is the case for the electric and magnetic multipolar series. At a specific order in perturbation theory, the summation over all intermediate states that link the same initial and final states $|i\rangle$ and $|f\rangle$ amounts to the drawing of all possible topologically distinct time orderings of photon creation and destruction operations. Therefore, an individual time-ordered diagram is isomorphic to one term in the time-dependent perturbation theory sum of the probability amplitude for a given n th-order process.

Feynman diagrams have proved to be extremely versatile in depicting, and beneficial in computing, electron–photon interactions occurring in elementary particle physics, many-body perturbation theory, atomic, molecular, and optical physics, and theoretical chemistry, though originally developed to be applied in quantum electrodynamics. Soon after their initial deployment, Dyson (1949) immediately recognized the power of the newly proposed visual representation, remarking that “In Feynman’s theory the graph corresponding to a particular matrix element is regarded, not merely as an aid to calculation, but as a picture of the physical process which gives rise to that matrix element.” As such, an adapted version of Feynman’s originally proposed diagrammatic technique aids in the calculation of matrix elements within nonrelativistic theory. Numerous radiation–molecule and molecule–molecule interactions have been calculated and understood at a fundamental level, through the employment of time-dependent perturbation theory together with time-ordered diagrams.

There are, however, a number of drawbacks associated with this particular pictorial representation. Chief among them is that for higher order processes, for example, those involving emission/absorption of a significant number of real and/or virtual photons at either single and/or multiple molecular centers, the number of possible time orderings describing evolution from the same initial to final state for a specific process can very quickly grow in number. Obviously, this limits the actual drawing of all

contributory diagrams required in the perturbation theory summation over all possible intermediate states to ensure that the resulting amplitude or energy shift correctly accounts for all terms. Illustration of a process by one graph on its own or by a finite subset of the total number of time orderings therefore provides an incomplete picture and is devoid of physical meaning. A further deficiency is that common features associated with distinct processes are not brought to the fore in the time-ordering approach. To overcome some of these shortcomings, a new visual representation of laser–matter and intermolecular interactions—a state sequence diagram—has recently been formulated. A summary of the principles underlying their formal construction is given in the next section.

1.10 STATE SEQUENCE DIAGRAMS

An alternative visual representation to time-ordered diagrams has been developed in which one picture, termed a state sequence diagram, is employed to illustrate and aid in the calculation of a specific laser–molecule or intermolecular process (Jenkins et al., 2002). Drawing of these latter type of diagrams is made possible by transforming the representation of photon–matter couplings in hyperspace, whose dimension is determined by the particular process under investigation, to a coordinate network existing in one plane; application of linkage rules allows valid connections to be forged between initial, intermediate, and final states in a systematic manner without explicit reference to individual photon emission and/or absorption events. The treatment given is general enough to enable both unique and indistinguishable electron–photon interactions to be examined in one formalism, thereby accommodating the effects of possible photon degeneracy.

The first step in the construction of a state sequence diagram involves initial identification of the total number of electron–photon interactions, n , occurring in some process. This quantifies the hyperspace dimension of the interacting system. Next, an index is assigned to each photon interaction. This labeling conceals any physical significance associated with photon creation and annihilation, with the procedure to be followed in the drawing of network planes and state sequence diagrams essentially involving index manipulation. Next, an orthonormal basis set that spans the n -space is introduced by representing each index by a vector \vec{i}_i ,

$$I = \{c_1\vec{i}_1, c_2\vec{i}_2, \dots, c_n\vec{i}_n\}, \quad (1.10.1)$$

where the coefficient c_i of the i th vector denotes the photon multiplicity. Clearly,

$$\sum_{i=1}^j c_i = n, \quad (1.10.2)$$

where the sum is executed over the number of distinct indices, j . Also evident is that when each of the photonic events is unique, $n=j$ and all of the vector coefficients are unity. When more than one photon of a particular mode is emitted or absorbed, however, the particular coefficient will no longer be one so that $j \neq n$, but since n is fixed in value, $n-j$ indices will have vanishing coefficients and are therefore superfluous; hence, no vector representation is necessary in this case. Thus, the truncated set of vectors $I = \{c_1 \vec{i}_1, \dots, c_j \vec{i}_j\}$ represents a subspace of dimension j in the full n -dimensional hyperspace, with the coefficients arranged subject to

$$c_j \geq c_{j-1} \geq \dots \geq c_1 \geq 1. \quad (1.10.3)$$

The initial, final, and intermediate states for a process are then denoted by points in the hyperspace through generation of coordinates (C_1, C_2, \dots, C_j) from the vectors (1.10.1). The scalars C_j take on values $C_j = 0, 1, \dots, c_j$ to accommodate the possible sequencing of I . Because the initial and final states are well defined, they correspond to fixed points on the planar interaction network. The intermediate states, on the other hand, in general require sequence ordering. Taken together, a two-dimensional array of points results, their joining indicating an allowed ordering of photon creation and destruction events.

The points occurring in the interaction plane are designated by the coordinates (k, h) . Those points lying on the vertical axis are termed hyperspace numbers h and are obtained as follows. From the vector coefficient with the highest value is found the numerical base of the space, B , through the relation

$$B = c_j + 1. \quad (1.10.4)$$

The numbers h are found by first converting the hyperspace coordinates to base B and subsequent re-expression in base 10, namely,

$$(C_1, C_2, \dots, C_j) \rightarrow C_1 C_2 \dots C_j|_B \equiv \text{hyperspace number}|_{10} = h. \quad (1.10.5)$$

Meanwhile, the points lying on the horizontal axis, k , are found from

$$k = \sum_{i=1}^j C_i, \quad (1.10.6)$$

with $k = 0, 1, \dots, n$ comprising $n + 1$ subsets of the complete set of $\{(k, h)\}$ points. Each subset is composed of m elements denoted by the vertex r_k^m with the values of m restricted to

$$m = 1, \dots, |r_k|, \quad (1.10.7)$$

from which k can be construed as accounting for the number of steps between point r_k^m and the point representing the initial state $|i\rangle$. Because $|i\rangle$ represents the state of the system before any interaction has occurred, its network coordinate is taken to be the origin $(0, 0)$, since $k = 0$ and $C_i = 0$, and can also be denoted by r_0^1 . In the interaction plane, the coordinate of the final state is denoted by (n, h_f) or r_n^1 since k takes on its maximum value of n . The hyperspace number for f, h_f , corresponds to the situation in which the number of components for each member of the set I is a maximum and is obtained from

$$(c_1, c_2, \dots, c_j) \rightarrow c_1 c_2 \dots c_j |_{B=c_j+1} \equiv h_f |_{10}. \quad (1.10.8)$$

Finally, rules that connect two points in the interaction plane must be formulated, from which all allowed paths between the $|i\rangle$ and $|f\rangle$ termini can be constructed so that the state sequence diagram can ultimately be sketched. For any two vertices r_k^m and $r_{k'}^{m'}$ mapping coordinates (C_1, C_2, \dots, C_i) to $(C'_1, C'_2, \dots, C'_i)$

$$\sum_{i=1}^j |C'_i - C_i| = 1, \quad (1.10.9)$$

which together with equation (1.10.6) results in the linkage rule

$$k' = k \pm 1. \quad (1.10.10)$$

The total number of paths \mathcal{P} permitted between $|i\rangle$ and $|f\rangle$ is given by

$$\mathcal{P} = \frac{n!}{\prod_i (c_i!)} \quad (1.10.11)$$

and represents permutations of interaction indices. Application of this procedure enables the construction of an interaction plane network that serves as a template for the eventual state sequence depiction of all processes of order n involving distinguishable electron–photon coupling events. The number of permutations calculated from (1.10.11) is equal to the number of possible time-ordered sequences of photon absorption and emission events as drawn in separate time-ordered diagrams when a particular process is considered. Hence, it is apparent that the advantage offered by the state sequence approach lies in the information embodied by

the interaction plane network and that one state sequence diagram contains all time orderings.

It proves useful to introduce additional properties associated with the interaction vertices to further aid the drawing and understanding of network planes. One of these is the structure coefficient, defined by

$${}^F T_k^{n,j} = |r_k|. \quad (1.10.12)$$

To aid in the arrangement of vertex sets and to specify the value of m , a partition function F is introduced through

$$F = \{c_1; \dots; c_j\}, \quad (1.10.13)$$

which relates the basis set I (1.10.1) to the structure coefficients. For the specific case in which all of the photon creation and destruction events are distinguishable, namely, all of the indices \vec{i}_j are unique, $F = \{1; \dots; 1\}$, and $n = j$, the values of the structure coefficients (1.10.12) are the binomial coefficients,

$$\{1; \dots; 1\} T_k^{n,n} = \begin{cases} \binom{n}{k} = \frac{n!}{(n-k)!k!}, & 0 \leq k \leq n, \\ 0, & k < 0, k > n. \end{cases} \quad (1.10.14)$$

Hence, a process containing n distinct photonic events will give rise to an interaction plane network and an eventual state sequence diagram partitioned with coefficients generated by the n th row of Pascal's triangle. Furthermore, knowledge of the structure coefficient (1.10.12) for a given value of k enables the structure of an interaction network plane to be predicted via the recursion relation

$$\{c_1; \dots; c_j\} T_k^{n,j} = \sum_{k'=k-c_j}^k \{c_1; \dots; c_j'\} T_{k'}^{n',j'}, \quad (1.10.15)$$

where $n' = n - c_j$ and $j' = j - 1$. Iteration of (1.10.15) creates partitions that contain n -space coefficients greater than unity, enabling degenerate photons also to be treated. Successive application decreases the value of the coefficient, finally bottoming out at $F = \{1; \dots; 1\}$ or the null set, in the process reducing to the result (1.10.14). For the case when $C_j > 1$, the partition function (1.10.13) can be expressed as

$$F = \{c_1; \dots; c_u; \dots c_j\}, \quad (1.10.16)$$

after the introduction of an index u , with $c_j \geq \dots \geq c_u > 1$, and so describes degenerate cases where $n > j$. All structure coefficients can

therefore be expressed through nested sums of binomial coefficients,

$$\{c_1; \dots; c_u; \dots; c_j\} T_k^{n,j} = \sum_{k_1=k-c_j}^k \sum_{k_2=k_1-c_{j-1}}^{k_1} \dots \sum_{k_{j-u+1}=k_{j-u}-c_u}^{k_{j-u}} \binom{u-1}{k_{j-u+1}}. \quad (1.10.17)$$

Formal application of the prescription presented herein to enable drawing of state sequence diagrams for a variety of intermolecular interactions will be undertaken in the chapters to follow as appropriate; these will be compared and contrasted with the commonly used Feynman diagram approach. State sequence diagrams have been employed with success to processes such as second harmonic generation, six-wave mixing, two-photon distributed absorption, energy transfer and pooling in two-, three-, and four-center systems, and laser-induced intermolecular forces.