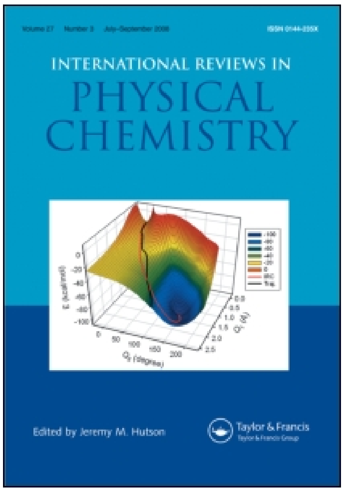

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

# Molecular quantum electrodynamics in the Heisenberg picture: A field theoretic viewpoint

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**To cite this Article** Salam, A.(2008) 'Molecular quantum electrodynamics in the Heisenberg picture: A field theoretic viewpoint', International Reviews in Physical Chemistry, 27: 3, 405 — 448
**To link to this Article: DOI:** 10.1080/01442350802045206
**URL:** http://dx.doi.org/10.1080/01442350802045206

*International Reviews in Physical Chemistry*
Vol. 27, No. 3, July–September 2008, 405–448

# Molecular quantum electrodynamics in the Heisenberg picture: A field theoretic viewpoint

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(*Received 15 February 2008; final version received 6 March 2008*)

Quantum electrodynamics (QED) is the physical theory that describes the interaction of electrons and photons at a fundamental level. Its characteristic feature is that the radiation field, as well as the system of material particles, obeys the postulates of quantum mechanics. A rigorous non-relativistic formulation of this theory applicable to atoms and molecules has also been developed and applied with outstanding success to a number of processes of interest to chemical physicists, being most commonly explicated for a system of charged particles coupled to the electromagnetic field, with the latter second quantized. Calculations are subsequently carried out in the Schrödinger picture. In the last twenty-five years or so, considerable work on Coulomb gauge QED of molecules has been performed in the Heisenberg representation of quantum mechanics by adopting a completely field theoretic point of view. The methods and results of this approach, which offer significant advantages over conventional perturbative techniques for the solution of a number of problems, are reviewed. Beginning with the second quantized multipolar Hamiltonian, the Heisenberg equations of motion for the fermion and boson creation and annihilation operators are obtained. In the electric dipole approximation these are used to evaluate the Maxwell field operators in the proximity of a source in series of powers of the transition moment on iteration. Comparison is then made with the analogous fields computed in the minimal-coupling scheme. Formulae are also given for the fields of a moving source of charge. Two observables of the electromagnetic field associated with a stationary distribution of charge, namely the Poynting vector and the energy density, are then calculated. The source fields are then used in a response theory formalism to calculate the resonant transfer of energy between an excited and an unexcited pair of molecules, and the retarded van der Waals dispersion energy shift between two excited electric dipole polarizable molecules, from which the results when one or both of the pair is in the ground electronic state, are easily derivable. Extension of response theory to many-body dispersion forces is then outlined, with explicit results being given for the retarded correction to the Axilrod–Teller–Muto three-body interaction energy.

**Keywords:** molecular quantum electrodynamics; Heisenberg picture; Maxwell fields; resonance energy transfer; dispersion interactions; many-body forces

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ISSN 0144–235X print/ISSN 1366–591X online

DOI: 10.1080/01442350802045206
http://www.informaworld.com

## Contents

## 1. Introduction

The pre-eminent field theory in modern physics is Quantum Electrodynamics (QED) [1]. Its characteristic feature is the imposition of the principles of quantum mechanics on interacting electron and photon fields. This field theoretic point of view is entirely equivalent to a many-body representation of a system of material particles interacting with quantized particles of light, confirming the underlying duality of the wave–particle descriptions of both radiation and matter. Resting on solid theoretical foundations that allowed novel predictions to be made and tested to unparalleled precision and accuracy – which continues to the present day, QED remains unsurpassed. Added to this is a formalism that permits high-level calculations to be performed on a wide variety of elementary processes for which a conceptual picture and a deep understanding is provided.

QED originated in the 'Dreimännerarbeit' of Born, Heisenberg and Jordan in 1926 [2], who quantized a system of uncoupled harmonic oscillators and showed that this represents the vibrations of a system with infinitely many degrees of freedom, such as the free electromagnetic field. This formalism was then subsequently developed and applied by Dirac in 1927 [3] to the emission and absorption of radiation by charged particles. Since then QED has certainly withstood the test of time. This is due, in no large part, to the considerable efforts of Feynman, Schwinger, Tomonaga and Dyson [4], whose work, along with others, culminated in the construction of a self-consistent and fully covariant formulation of QED [5] in both the particle and field descriptions, in the process overcoming longstanding difficulties associated with the computation of previously divergent observable properties by the introduction of renormalization techniques. Agreement with experiment for quantities such as the Lamb shift and the anomalous magnetic moment of the electron, for example, have been spectacular, at the same time instilling greater confidence in the theory.

For bound particles moving with velocities much less than that of light, such as electrons in atoms and molecules, and for energies considerably below $mc^2$ at which pair-particle production and destruction effects can be neglected, a non-relativistic limiting formulation of QED is obtained and which is the most appropriate for applications in atomic, molecular and optical physics, and theoretical chemistry. Such a formalism has been developed rigorously in its own right, most conveniently in the Coulomb gauge in which the divergence of the vector potential vanishes, and explicated for a charged particle in a radiation field [6,7]. Adopting a canonical quantization scheme beginning with the classical Lagrangian function, so chosen to yield the correct equations of motion when the dynamical variables are subject to the variational calculus, and elevating the particle coordinate, vector potential and their corresponding conjugate momenta to quantum operators, leads to the quantum mechanical Hamiltonian for the coupled radiation–matter system. In the guise of either the minimal-coupling or multipolar framework, the so-called molecular quantum electrodynamics has been developed and applied with considerable success to a large number of radiation–molecule and intermolecular interactions. These include, but are by no means limited to, single- and multi-photon absorption and emission processes, coherent and incoherent scattering of light, optical activity and chiroptical spectroscopy, nonlinear and quantum optics, and resonance energy transfer and retarded van der Waals forces between two- and many-bodies.

Detailed expositions of molecular QED may be found in a handful of highly accessible monographs [8–14] and review articles [15–23]. In each of these publications, the overwhelming majority of the content is presented within the Schrödinger picture of quantum mechanics, in which the dynamical variables are time-independent operators and the states of the system evolve in time according to the time-dependent Schrödinger equation. In this formulation the system of charged particles are subject to the rules of first quantization while the radiation field is second quantized. It is well known [24] that under the transformation theory, quantum mechanics in the Schrödinger picture may be converted to the Heisenberg formalism. The same applies to (molecular) QED. Now states are independent of time but the dynamical variables are time-dependent operators that obey the Heisenberg operator equations of motion. Much work has been done in this framework of QED in the last quarter of a century, but with little appearing in monographs and none in any reviews of the subject. The present contribution remedies this situation.

The review article is organized as follows. In the next section the multipolar Hamiltonian is introduced in second quantized form suitable for later use. In Section 3 the calculation of the time-dependent Maxwell field operators in the proximity of a source molecule is outlined and important features associated with the fields are discussed. Using the Heisenberg operator equations of motion, an iterative solution is obtained for the boson and fermion dynamical variables in series of powers of the leading electric dipole moment, from which power series mode expansions for the electric displacement and magnetic field are generated. The Maxwell fields in the vicinity of a source are then evaluated in the minimal-coupling formalism in Section 4 and compared and contrasted with results presented in the previous section. Expressions are also given for the fields of a moving electric charge in the section that follows. A couple of observable properties derivable from the QED Maxwell fields are then computed in Sections 6 and 7. These include the Poynting vector and the electromagnetic energy density, respectively. A manifestation of the latter occurs in the energy of interaction resulting from a test polarizable molecule placed in the fields of the source that give rise to such energy density. The Poynting vector on the other hand, can be related directly to the rate of flow of radiation from an excited molecule. The form of the interaction Hamiltonian used to treat the contributions arising from higher multipole moments is then discussed briefly in Section 8. In Section 9 the radiation fields of the source are used to calculate a number of intermolecular interactions via a form of response theory. Processes presented and discussed include the resonant transfer of energy between an excited and an unexcited pair of molecules, and the retarded van der Waals dispersion force between two excited species, from which the potentials for one ground and one excited, and two ground state molecules easily follows. Finally, it is shown how the response of one molecule to the fields of $N-1$ other molecules may be used to write down an expression for the non-additive dispersion force in a system comprising $N$ bodies. Explicit results are given for three interacting molecules. As a means for critically assessing the pros and cons of one picture over another, comparison and contrast is made throughout the review with the more familiar Schrödinger formulation and deployment of molecular QED. A brief summary is given in Section 10.

## 2. Second quantized multipolar Hamiltonian

The two most common formulations of the molecular quantum electrodynamical Hamiltonian operator are the minimal-coupling and multipolar versions [6–10, 13,18–20,25–32]. In the classical mechanical treatment, the application of variational principles to the interaction of a charged particle in a radiation field leads directly to the minimal-coupling Lagrangian function, from which the corresponding classical and quantum mechanical minimal-coupling Hamiltonians may be obtained via the familiar canonical quantization prescription. From this starting point, there are three commonly used approaches for obtaining the quantum form of the multipolar Hamiltonian. One is to add a total time derivative of a function $f(\vec{q}, t)$ of the particle coordinates and the time to the classical minimal-coupling Lagrangian, since such an addition causes no change in the equations of motion. If the added function is proportional to the product of the transverse electric polarization field and the vector potential, the multipolar Lagrangian results. From this equivalent Lagrangian, the classical and quantum electrodynamical multipolar Hamiltonians may be derived. A second technique which yields the multipolar form of Hamiltonian is to apply a (quantum) canonical transformation to the (classical) minimal-coupling Hamiltonian. Such a transformation is unitary, leaves the particle and electromagnetic field coordinates unaltered, transforms the corresponding conjugate momenta, but preserves the canonical commutation relations. The explicit form of either $f(\vec{q},t)$, or the generator $S$ which transforms between equivalent Hamiltonians through $H_{mult}=e^{-is}H_{min}e^{is}$, and the connection between them, is known. It is

$$f(\vec{q},t)=\int\vec{p}^{\perp}(\vec{r})\cdot\vec{a}(\vec{r})\mathrm{d}^3\vec{r}, \tag{2.1}$$

with

$$f(\vec{q},t)=-\hbar S. \tag{2.2}$$

In (2.1) $\vec{p}^{\perp}(\vec{r})$ is the transverse polarization field, and $\vec{a}(\vec{r})$ is the vector potential in the Coulomb gauge. When making this selection of gauge, the scalar potential corresponds to the electrostatic potential and the vector potential is purely transverse (in fact $\vec{a}^{\perp}(\vec{r})$ is gauge invariant). A third method of converting between minimal and multipolar formalisms is by effecting a gauge transformation, about which no more will be said. The interested reader is referred to Ref. [33] and Ref. [9] Section 7.3.

When working from the viewpoint of coupled electron and photon wavefields, however, the transformation from the minimal to the multipolar coupling frameworks through the Lagrangian function is effected by a change in the generalized coordinates of the electron field by the transformation [29]

$$\psi(\vec{q})=e^{-iS(\vec{q})}\phi(\vec{q}), \tag{2.3}$$

where $\phi(\vec{q})$ is the electron wavefield, and

$$S(\vec{q})=\frac{1}{\hbar}\int\vec{p}(\vec{r},\vec{q})\cdot\vec{a}^{\perp}(\vec{r})\mathrm{d}^3\vec{r}, \tag{2.4}$$

from which the completely second quantized multipolar Hamiltonian may be constructed in the usual way. As in the case when matter is treated via the method of first quantization and the radiation field is second quantized, the two Hamiltonians are interrelated through a quantum canonical transformation, with the generator analogous to (2.4) being given by

$$\mathrm{S}=\int\bar{\phi}(\vec{q})S(\vec{q})\phi(\vec{q})\mathrm{d}^3\vec{q}=\frac{1}{\hbar}\int\bar{\phi}(\vec{q})\vec{p}(\vec{r},\vec{q})\cdot\vec{a}^{\perp}(\vec{r})\phi(\vec{q})\mathrm{d}^3\vec{q}\mathrm{d}^3\vec{r}, \tag{2.5}$$

and

$$H_{mult}=e^{-i\mathrm{S}}H_{min}e^{i\mathrm{S}}. \tag{2.6}$$

Because Hamiltonians related by canonical transformations are equivalent, identical matrix elements result when either the minimal-coupling or multipolar Hamiltonian is employed in the computation of processes which are energy conserving [6,27,34–36]. For processes off the energy shell, however, different results can ensue [35,36]. This is not too surprising since the unperturbed states of the system, which are used as basis functions in any calculation, refer to different starting Hamiltonians. Hence the states evolve differently in time in the two formalisms and can give rise to non-identical time-dependent probabilities. This is exhibited most clearly in the Heisenberg picture by analysing the time-dependent behaviour of the fermion and boson operators, or equivalently, the Schrödinger or Maxwell fields in both formalisms.

In second quantized form, the multipolar Hamiltonian is

$$\begin{aligned} H_{mult} &= H_{mol} + H_{rad} + H_{int} \\ &= \sum_{n} b_n^{\dagger}(t) b_n(t) E_n + \sum_{\vec{k},\lambda} a^{\dagger(\lambda)}(\vec{k},t) a^{(\lambda)}(\vec{k},t)\hbar\omega - \varepsilon_0^{-1} \sum_{m,n} b_m^{\dagger}(t) b_n(t) \vec{\mu}^{mn} \cdot \vec{d}^{\perp}(\vec{R},t), \end{aligned} \tag{2.7}$$

for an electric dipole $\vec{\mu}$ located at $\vec{R}$, with the self-energy term being neglected, and with the vacuum field energy term, $\frac{1}{2}\hbar ck$ also being omitted since this constant term vanishes when boson operator equations of motion are evaluated. In (2.7) the first term is the molecular Hamiltonian written in terms of $b_n^{\dagger}(t)$ and $b_n(t)$, the time-dependent creation and annihilation operators, respectively, for an electronic state $|n\rangle$ of energy $E_n$, with the electron wavefield defined as

$$\phi(\vec{q},t) = \sum_{n} b_n(t)\phi_n(\vec{q}), \tag{2.8}$$

where $\phi_n(\vec{q})$ is the orthonormal electron field mode. The second term of (2.7) corresponds to the Hamiltonian for the radiation field, expressed more familiarly in terms of the creation and destruction operators for a photon of wavevector $\vec{k}$, circular frequency $\omega = ck$, and index of polarization $\lambda$, $a^{\dagger(\lambda)}(\vec{k},t)$ and $a^{(\lambda)}(\vec{k},t)$, respectively, and which are also dependent on the time. Note that the interaction Hamiltonian, the third term of (2.7), is limited to the leading electric dipole contribution with

$$\vec{\mu}^{mn} = \int \bar{\phi}_m(\vec{q})\vec{\mu}\phi_n(\vec{q})\mathrm{d}^3\vec{q}, \tag{2.9}$$

denoting the transition dipole moment matrix element between states $|m\rangle$ and $|n\rangle$. The addition of higher multipole terms, such as the electric quadrupole, ..., magnetic dipole is straightforward in the multipolar framework, and details are left to Section 8, while explicit formulae for the higher multipole moment fields may be found in Refs. [37–39].

The mode expansion of the transverse electric displacement field, $\vec{d}^{\perp}(\vec{r},t)$, and its analogous magnetic field $\vec{b}(\vec{r},t)$, are given by

$$\vec{d}^{\perp}(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left[\vec{e}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k},t)e^{i\vec{k}\cdot\vec{r}} - \bar{\vec{e}}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k},t)e^{-i\vec{k}\cdot\vec{r}}\right], \tag{2.10}$$

$$\vec{b}(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left[\vec{b}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k},t)e^{i\vec{k}\cdot\vec{r}} - \bar{\vec{b}}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k},t)e^{-i\vec{k}\cdot\vec{r}}\right]. \tag{2.11}$$

In the mode sums (2.10) and (2.11), $\vec{e}^{(\lambda)}(\vec{k})$ and $\vec{b}^{(\lambda)}(\vec{k}) = \hat{k} \times \vec{e}^{(\lambda)}(\vec{k})$, are complex unit electric and magnetic polarization vectors, and $V$ is the box quantization volume.

## 3. Multipolar Maxwell fields emanating from a molecular source

The electric displacement and magnetic field operators in the neighbourhood of a source molecule [37–40] may be obtained from the mode expansions (2.10) and (2.11) by first calculating the time development of the boson and fermion operators $a^{(\lambda)}(\vec{k},t)$ and $b_n(t)$. These are given by the Heisenberg equations of motion

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}a^{(\lambda)}(\vec{k},t)=\left[a^{(\lambda)}(\vec{k},t),H_{mult}\right]_{-} \tag{3.1}$$

and

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}b_n(t)=[b_n(t),H_{mult}]_{+}, \tag{3.2}$$

on using the standard equal-time commutation relation for boson operators,

$$[a^{(\lambda)}(\vec{k},t),a^{\dagger(\lambda')}(\vec{k}',t)]_{-}=\delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'}, \tag{3.3}$$

and the anti-commutation relation for fermion operators,

$$\left[b_m(t),b_n^{\dagger}(t)\right]_{+}=\delta_{mn}. \tag{3.4}$$

Note that the operators in the Schrödinger and Heisenberg pictures are equal at the initial time $t=0$. At this time the electron wavefield acts entirely in the occupation number fermion Fock space while the Maxwell fields operate exclusively in the boson space. For all other positive times, the Heisenberg operators act in the combination space, yielding field operators in the second and higher orders of the multipole moment, for example, that depend on both the photon and fermion creation and destruction operators.

Expressions (3.1) and (3.2) form a pair of coupled integro-differential equations that are solved by iteration. Transforming to the interaction representation via the substitutions $a(t)=\alpha(t)e^{-i\omega t}$, and $b_n(t)=\beta_n(t)e^{-i\omega_n t}$, which removes terms of the form $\hbar\omega a(t)$ and $\hbar\omega_n b_n(t)$ from the equations of motion for $a(t)$ and $b_n(t)$, respectively, where the radiation mode dependence is suppressed for notational brevity, formal integration of (3.1) and (3.2) using (3.3) and (3.4) gives

$$\alpha(t)=\alpha(0)+\frac{1}{\hbar}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\sum_{m,n}\mu_j^{mn}\bar{e}_j e^{-i\vec{k}\cdot\vec{R}}\int_0^t \mathrm{d}t'\,e^{i(\omega_{mn}+\omega)t'}\beta_m^{\dagger}(t')\beta_n(t'), \tag{3.5}$$

and

$$\beta_n(t)=\beta_n(0)-\frac{1}{\hbar}\sum_{\vec{k},\lambda}\sum_{m}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\int_0^t \mathrm{d}t'\,\beta_m(t')\Big[\mu_j^{nm}e_j e^{i\vec{k}\cdot\vec{R}}\alpha(t')e^{-i(\omega_{mn}+\omega)t'} -\mu_j^{nm}\bar{e}_j e^{-i\vec{k}\cdot\vec{R}}\alpha^{\dagger}(t')e^{-i(\omega_{mn}-\omega)t'}\Big], \tag{3.6}$$

where $\omega_{mn} = (E_m - E_n)/\hbar$. Cartesian tensor components are designated by Latin subscripts with an implied summation convention being adopted for repeated suffixes. Hence on expanding in powers of the dipole moment,

$$\alpha(t) = \sum_{m=0}^{\infty} \alpha^{(m)}(t), \tag{3.7}$$

$$\beta_n(t) = \sum_{m=0}^{\infty} \beta_n^{(m)}(t), \tag{3.8}$$

where $m$ is the order of the operator. Thus

$$\alpha^{(0)}(t) = \alpha(0), \tag{3.9}$$

$$\beta_n^{(0)}(t) = \beta_n(0), \tag{3.10}$$

$$\alpha^{(1)}(t) = \frac{1}{i\hbar}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \sum_{m,n} \mu_j^{mn} \bar{e}_j e^{-i\vec{k}\cdot\vec{R}} \beta_m^{\dagger}(0)\beta_n(0)\left(\frac{e^{i(\omega_{mn}+\omega)t} - 1}{(\omega_{mn} + \omega)}\right), \tag{3.11}$$

$$\begin{aligned} \beta_n^{(1)}(t) = \frac{1}{i\hbar} \sum_{\vec{k},\lambda} \sum_p \left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \beta_p(0)\Bigg[\mu_j^{np} e_j e^{i\vec{k}\cdot\vec{R}} \alpha(0)\left(\frac{e^{-i(\omega_{pn}+\omega)t} - 1}{(\omega_{pn} + \omega)}\right) \\ -\mu_j^{np} \bar{e}_j e^{-i\vec{k}\cdot\vec{R}} \alpha^{\dagger}(0)\left(\frac{e^{-i(\omega_{pn}-\omega)t} - 1}{(\omega_{pn} - \omega)}\right)\Bigg], \end{aligned} \tag{3.12}$$

$$\alpha^{(2)}(t) = \frac{1}{\hbar}\sum_{m,n}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \mu_j^{mn} \bar{e}_j e^{-i\vec{k}\cdot\vec{R}} \int_0^t \mathrm{d}t'\, e^{i(\omega_{mn}+\omega)t'} \left[\beta_m^{\dagger(0)}(t')\beta_n^{(1)}(t') + \beta_m^{\dagger(1)}(t')\beta_n^{(0)}(t')\right]. \tag{3.13}$$

Substituting (3.12) and its Hermitian-conjugate into (3.13) leads to

$$\begin{aligned} \alpha^{(2)}(t) = -\frac{1}{\hbar^2} \sum_{\vec{k}',\lambda'} \sum_{m,n,p} \left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \left(\frac{\hbar ck'}{2\varepsilon_0 V}\right)^{1/2} \mu_j^{mn} \bar{e}_j e^{-i\vec{k}\cdot\vec{R}} \\ \times \left[\begin{array}{l} \beta_m^{\dagger}(0)\beta_p(0)\left\{\begin{array}{l} \mu_l^{np} e_l' e^{i\vec{k}'\cdot\vec{R}} \alpha'(0)\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{pn}+\omega')(\omega_{mp}+\omega-\omega')} - \frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pn}+\omega')(\omega_{mn}+\omega)}\right) \\ -\mu_l^{np} \bar{e}_l' e^{-i\vec{k}'\cdot\vec{R}} \alpha'^{\dagger}(0)\left(\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{pn}-\omega')(\omega_{mp}+\omega+\omega')} - \frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pn}-\omega')(\omega_{mn}+\omega)}\right) \end{array}\right\} \\ + \beta_p^{\dagger}(0)\beta_n(0)\left\{\begin{array}{l} \mu_l^{pm} \bar{e}_l' e^{-i\vec{k}'\cdot\vec{R}} \alpha'^{\dagger}(0)\left(\frac{e^{i(\omega_{pn}+\omega+\omega')t}-1}{-(\omega_{pm}+\omega')(\omega_{pn}+\omega+\omega')} - \frac{e^{i(\omega_{mn}+\omega)t}-1}{-(\omega_{pm}+\omega')(\omega_{mn}+\omega)}\right) \\ -\mu_l^{pm} e_l' e^{i\vec{k}'\cdot\vec{R}} \alpha'(0)\left(\frac{e^{i(\omega_{pn}+\omega-\omega')t}-1}{-(\omega_{pm}-\omega')(\omega_{pn}+\omega-\omega')} - \frac{e^{i(\omega_{mn}+\omega)t}-1}{-(\omega_{pm}-\omega')(\omega_{mn}+\omega)}\right) \end{array}\right\} \end{array}\right], \end{aligned} \tag{3.14}$$

which is quadratic in the electric dipole moment. Retaining terms correct to only this order in the series expansion of the source moment is sufficient for the treatment of applications involving the explicit use of Maxwell field operators to be detailed in later sections of this review. Clearly for processes requiring contributions of higher order than the second of the displacement and magnetic field, these can be evaluated using the procedure outlined above. Interestingly, $\alpha^{(2)}(t)$ (and its Hermitian-conjugate) can create as well as destroy photons, being a function of both $\alpha(0)$ and $\alpha^{\dagger}(0)$, in addition to changing the state of the electron, being dependent on fermion creation and annihilation operators also. This is readily apparent from (3.13), noting that (3.12) contains boson raising and lowering operators. The case of $\alpha^{(2)}(t)$ is unlike $\alpha(0)$ which only decreases the number of photons by one, while from (3.11) $\alpha^{(1)}(t)$ is seen to be independent of boson dynamical variables. It is important to point out, however, that second and higher order photon creation and destruction operators act in the composite fermion–boson space.

### 3.1. *Electric displacement field*

Relations (3.7)–(3.14) are then used to obtain the first few terms of the series expansion of the fields (2.10) and (2.11) in powers of the electric dipole moment. For the transverse displacement field,

$$d_i^{\perp}(\vec{r},t) = \sum_{n=0}^{\infty} d_i^{(n)}(\vec{r},t), \tag{3.15}$$

where $n$ is the order of iteration. The first term of (3.15) results on inserting (3.9) into (2.10), and yields the zeroth-order or free field operator,

$$d_i^{(0)}(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar c k \varepsilon_0}{2V}\right)^{1/2}\left[e_i^{(\lambda)}(\vec{k})\alpha^{(0)(\lambda)}(\vec{k},0)e^{i\vec{k}\cdot\vec{r}-i\omega t} - \bar{e}_i^{(\lambda)}(\vec{k})\alpha^{\dagger(0)(\lambda)}(\vec{k},0)e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right], \tag{3.16}$$

which is independent of the source, and operates exclusively in the boson space, increasing or decreasing the photon number by unity. The mode expansion for the transverse displacement field operator correct to first order in the moment is given by

$$d_i^{(1)}(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar c k \varepsilon_0}{2V}\right)^{1/2}\left[e_i^{(\lambda)}(\vec{k})\alpha^{(1)(\lambda)}(\vec{k},t)e^{i\vec{k}\cdot\vec{r}-i\omega t} - \bar{e}_i^{(\lambda)}(\vec{k})\alpha^{\dagger(1)(\lambda)}(\vec{k},t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right], \tag{3.17}$$

whose dependence on particle properties is contained implicitly via $\alpha^{(1)}(t)$. Substituting (3.11) and its Hermitian adjoint into (3.17), carrying out the polarization sum using the identity

$$\sum_{\lambda} e_i^{(\lambda)}(\vec{k})\bar{e}_j^{(\lambda)}(\vec{k}) = \sum_{\lambda} b_i^{(\lambda)}(\vec{k})\bar{b}_j^{(\lambda)}(\vec{k}) = \delta_{ij} - \hat{k}_i\hat{k}_j, \tag{3.18}$$

converting the $\vec{k}$-sum to an integral via the prescription $(1/V)\sum_{\vec{k}} \Rightarrow (1/(2\pi)^3)\int d^3\vec{k}$, transforming the volume element to spherical polar coordinates, and performing the integral over solid angle $\mathrm{d}\Omega$ using the result

$$\frac{1}{4\pi}\int \mathrm{d}\Omega\left(\delta_{ij}-\hat{k}_i\hat{k}_j\right)e^{\pm i\vec{k}\cdot\vec{R}} = \mathrm{Im}[F_{ij}(kR)], \tag{3.19}$$

where

$$\begin{aligned} F_{ij}(kR) &= \frac{1}{k^3}\left(-\nabla^2\delta_{ij}+\nabla_i\nabla_j\right)\frac{e^{ikR}}{R} = \left[-\left(\delta_{ij}-\hat{R}_i\hat{R}_j\right)\frac{1}{kR}+\left(\delta_{ij}-3\hat{R}_i\hat{R}_j\right)\left(\frac{-i}{k^2R^2}+\frac{1}{k^3R^3}\right)\right]e^{ikR} \\ &= f_{ij}(kR)e^{ikR}, \end{aligned} \tag{3.20}$$

yields

$$d_i^{(1)}(\vec{\mu};\vec{\rho},t) = \begin{cases} \dfrac{1}{4\pi}\displaystyle\sum_{m,n}\beta_m^{\dagger}(0)\beta_n(0)\mu_j^{mn}k_{nm}^3 f_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}, & t>\rho/c \\ 0, & t<\rho/c, \end{cases} \tag{3.21}$$

where $\vec{\rho}=\vec{r}-\vec{R}$, with the integral over $k$ being evaluated subject to the causality requirement that the field vanish for $ct<\rho$. Several interesting characteristics emerge from the result (3.21). Firstly, the linear field operates entirely in the electron Fock space, changing only the molecular state of the system. Secondly, the field is strictly causal. Thirdly, (3.21) is the quantum electrodynamical analogue of the classical electric displacement field, exhibiting $\rho^{-3}$ near-zone and $\rho^{-1}$ long-range radiative behaviour, respectively. It is noteworthy that the tensor field $F_{ij}(kR)$ defined in (3.20) appears in the formula for the classical electric field of an oscillating electric dipole [41]. Fourthly, for all field point distances $\rho$, the diagonal matrix element of $d_i^{(1)}(\vec{\mu};\vec{\rho},t)$ is the electrostatic field of a permanent electric dipole.

To evaluate the third term of (3.15), namely the field that is dependent quadratically on the electric dipole moment, (3.14) and its Hermitian-conjugate are substituted into the mode expansion

$$d_i^{(2)}(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left[e_i^{(\lambda)}(\vec{k})\alpha^{(2)(\lambda)}(\vec{k},t)e^{i\vec{k}\cdot\vec{r}-i\omega t}-\bar{e}_i^{(\lambda)}(\vec{k})\alpha^{\dagger(2)(\lambda)}(\vec{k},t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right]. \tag{3.22}$$

Carrying out steps similar to that used in the calculation of the first order displacement field, but this time only performing one of the $\vec{k}$ integrals, results in

$$\begin{aligned} d_i^{(2)}(\vec{\mu}\vec{\mu};\vec{\rho},t) = \frac{i}{4\pi}\sum_{\vec{k},\lambda}\sum_{m,p}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} & \\ \times\Bigg\{ e_k\alpha(0)\beta_m^{\dagger}(0)\beta_p(0)e^{i\vec{k}\cdot\vec{R}} & \\ \times\Bigg[\sum_n\left\{\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}+\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}\right\}(k_{pm}+k)^3 f_{ij}[(k_{pm}+k)\rho]e^{i(k_{pm}+k)(\rho-ct)} & \\ -\sum_n\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}k_{nm}^3 f_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)} & \\ -\sum_n\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}k_{pn}^3 f_{ij}(k_{pn}\rho)e^{ik_{pn}(\rho-ct)}\Bigg]\Bigg\} & \\ +\mathrm{H.C.} & \end{aligned} \tag{3.23}$$

A number of interesting properties are found for the second order field. In contrast to the free and first order fields, the quadratic field operates in the composite boson and fermion space, changing the molecular state, and the number of photons by one. The field (3.23) has no classical counterpart, being nonlinear, a direct result of iterating the Heisenberg equations of motion (3.1) and (3.2) to first order. Again the field is causal. Higher order corrections to the electric displacement field may be evaluated similarly, but produce successively more complicated expressions.

### 3.2. *Magnetic field*

Analogously to the electric field, and continuing to remain in the electric dipole approximation, the magnetic field in the neighbourhood of a source may be expanded as a power series in the electric dipole moment,

$$b_i(\vec{r}, t) = \sum_{n=0}^{\infty} b_i^{(n)}(\vec{r}, t). \tag{3.24}$$

Inserting $\alpha(t) = \alpha(0)$ into the mode expansion (2.11) yields the source free magnetic field operator,

$$b_i^{(0)}(\vec{r}, t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left[b_i^{(\lambda)}(\vec{k})\alpha^{(0)(\lambda)}(\vec{k}, 0)e^{i\vec{k}\cdot\vec{r}-i\omega t} - \bar{b}_i^{(\lambda)}(\vec{k})\alpha^{\dagger(0)(\lambda)}(\vec{k}, 0)e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right]. \tag{3.25}$$

Formulae (3.11) and (3.14) for $\alpha^{(1)}(t)$ and $\alpha^{(2)}(t)$, respectively, are used for the calculation of the linear and quadratic magnetic field as before, and following the steps outlined earlier, but this time making use of the identity

$$\sum_{\lambda} e_i^{(\lambda)}(\vec{k})\bar{b}_j^{(\lambda)}(\vec{k}) = \varepsilon_{ijk}\hat{k}_k, \tag{3.26}$$

for summation over polarizations involving electric and magnetic vectors, where $\varepsilon_{ijk}$ is the third rank Levi-Civita antisymmetric tensor. The angular integral is carried out via

$$\frac{1}{4\pi}\varepsilon_{ijk}\int \hat{k}_k e^{\pm i\vec{k}\cdot\vec{R}}\mathrm{d}\Omega = \pm i\,\mathrm{Re}[G_{ij}(kR)], \tag{3.27}$$

where

$$G_{ij}(kR) = \frac{i}{k^2}\varepsilon_{ijk}\nabla_k\frac{e^{ikR}}{R} = -\varepsilon_{ijk}\hat{R}_k\left[\frac{1}{kR} + \frac{i}{k^2R^2}\right]e^{ikR} = g_{ij}(kR)e^{ikR}. \tag{3.28}$$

The first and second order magnetic fields are found to be

$$b_i^{(1)}(\vec{\mu}; \vec{\rho}, t) = \begin{cases} \dfrac{1}{4\pi\varepsilon_0 c}\displaystyle\sum_{m,n}\beta_m^{\dagger}(0)\beta_n(0)\mu_j^{mn}k_{nm}^3 g_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}, & t > \rho/c \\ 0, & t < \rho/c, \end{cases} \tag{3.29}$$

and

$$b_i^{(2)}(\vec{\mu}\vec{\mu};\vec{\rho},t)=\frac{i}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\sum_{m,p}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}$$

$$\times\left\{\begin{array}{l} e_k\alpha(0)\beta_m^{\dagger}(0)\beta_p(0)e^{i\vec{k}\cdot\vec{R}} \\ \times\left[\begin{array}{l} \sum_n\left\{\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}+\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}\right\}(k_{pm}+k)^3 g_{ij}[(k_{pm}+k)\rho]e^{i(k_{pm}+k)(\rho-ct)} \\ -\sum_n\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}k_{nm}^3 g_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)} \\ -\sum_n\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}k_{pn}^3 g_{ij}(k_{pn}\rho)e^{ik_{pn}(\rho-ct)} \end{array}\right] \end{array}\right\}$$

$$+\mathrm{H.C.} \tag{3.30}$$

Overall properties of the first and second order magnetic fields are similar to those found for the corresponding displacement field, and which were detailed above.

One of the striking consequences of the theory of QED is the zero-point energy associated with the ground state of the radiation field, namely that containing an absence of photons. Such fluctuations of the vacuum electromagnetic field have, over the years, been resorted to in order to understand at one level several well known phenomena in atomic, molecular and optical physics such as spontaneous emission, the Lamb shift, Casimir effects and van der Waals forces [11]. To help bring the role of the vacuum field to the fore in the time-dependent formulation, it is convenient to partition the total Maxwell fields into source independent and dependent parts [35,42,43]. For the displacement and magnetic fields this leads to

$$\vec{d}(\vec{r},t)=\vec{d}^{(0)}(\vec{r},t)+\vec{d}^{(s)}(\vec{r},t), \tag{3.31}$$

and

$$\vec{b}(\vec{r},t)=\vec{b}^{(0)}(\vec{r},t)+\vec{b}^{(s)}(\vec{r},t), \tag{3.32}$$

respectively. The first terms in each of the last two equations denote the vacuum field, and were previously given explicitly by the mode expansions for the free fields (3.16) and (3.25). In the present article the source dependent terms have been expanded in series of powers of the transition moments, with expressions for the linear and quadratic Maxwell field operators being given earlier.

It is worth pointing out that the time-dependent Maxwell fields in the neighbourhood of a source may be evaluated exactly, with causality being introduced automatically, without the need for invoking any special conditions on the evaluation of the wavevector integral. This is achieved by changing the order of integrations over wavevector and time [44]. In the alternate prescription, the former is carried out before the latter, in contrast to that presented earlier in this section. Illustrating for the transverse displacement field, substituting (3.5) into the mode expansion (2.10) produces, on taking $\vec{\mu}^{mn}$ inside the integral over time,

$$d_i(\vec{\mu};\vec{r},t)=\frac{i}{\hbar}\sum_{\vec{k},\lambda}\sum_{m,n}\left(\frac{\hbar ck}{2V}\right)\int_0^t \mathrm{d}t'\mu_j^{mn}(t')\Big[e_i^{(\lambda)}(\vec{k})\bar{e}_j^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}-i\omega t}e^{i(\omega_{mn}+\omega)t'} -\bar{e}_i^{(\lambda)}(\vec{k})e_j^{(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}+i\omega t}e^{-i(-\omega_{mn}+\omega)t'}\Big], \tag{3.33}$$

for a source situated at the origin, where

$$\mu_j^{mn}(t')=\mu_j^{mn}\beta_m^{\dagger}(t')\beta_n(t'). \tag{3.34}$$

Carrying out the polarization sum and converting the wave vector sum to an integral gives for (3.33)

$$d_i(\vec{\mu};\vec{r},t)=\frac{c}{8\pi^2}\sum_{m,n}\left(-\nabla^2\delta_{ij}+\nabla_i\nabla_j\right)\int_0^t \mathrm{d}t'\mu_j^{mn}(t')e^{i\omega_{mn}t'}\int_{-\infty}^{\infty}\frac{1}{r}\left[e^{ik(r-ct+ct')}-e^{-ik(r+ct-ct')}\right]\mathrm{d}k. \tag{3.35}$$

Integration over $k$ is immediate, yielding $\delta$-functions with arguments $(r-ct+ct')$ and $(r+ct-ct')$, respectively,

$$d_i(\vec{\mu};\vec{r},t)=\frac{c}{4\pi}\sum_{m,n}\left(-\nabla^2\delta_{ij}+\nabla_i\nabla_j\right)\int_0^t \mathrm{d}t'\mu_j^{mn}(t')e^{i\omega_{mn}t'}\frac{1}{r}[\delta(r-ct+ct')-\delta(r+ct-ct')]. \tag{3.36}$$

Because $t'=t+r/c$ is outside the range of integration over $t'$, the second delta function does not contribute. There is, however, a contribution from the first term, since $t'=t-r/c$ lies between 0 and $t$, i.e. $t\geq r/c$. Hence the source field (3.36) becomes

$$d_i(\vec{\mu};\vec{r},t)=\frac{1}{4\pi}\sum_{m,n}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\mu_j^{mn}(t-r/c)\frac{e^{i\omega_{mn}(t-r/c)}}{r}. \tag{3.37}$$

In a similar manner, the source dependent magnetic field is

$$b_i(\vec{\mu};\vec{r},t)=\frac{1}{4\pi\varepsilon_0 c}\sum_{m,n}ik_{mn}\varepsilon_{ijk}\nabla_k\mu_j^{mn}(t-r/c)\frac{e^{i\omega_{mn}(t-r/c)}}{r}. \tag{3.38}$$

The expressions for the fields (3.37) and (3.38) are exact. Note that the gradients in the last two expressions operate on the retarded time in addition to *1*/*r*. In the Heisenberg picture it is appropriate to express these operators at $t=0$ in order to evaluate their matrix elements. This necessitates consideration of the time evolution of the dipole moment operator [35] from the Heisenberg equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\mu_i=[\mu_i,H_{mult}]. \tag{3.39}$$

Taking the eigenstates of $H_{mol}$ as base states, then to first order,

$$\mu_i^{(1)}(t) = \sum_{m,n} \mu_i^{mn} e^{i\omega_{mn}t} |m\rangle\langle n|. \tag{3.40}$$

The resulting Maxwell fields linear in the source moment are then identical to (3.21) and (3.29), whose matrix elements are easily evaluated. In the applications that follow, it is sufficient to consider moments that are time-independent, especially in the examination of problems involving stationary states.

## 4. Minimal-coupling Maxwell fields

In a manner similar to that used to calculate the electromagnetic fields – displacement and magnetic – in the multipolar formalism, the Maxwell fields in the minimal-coupling scheme may be evaluated [34–36]. Since in this latter framework the field canonically conjugate to the vector potential is proportional to the transverse electric field rather than to the transverse displacement field as in multipolar coupling, $\vec{e}^{\perp}(\vec{r}, t)$ is calculated instead, along with $\vec{b}(\vec{r}, t)$ in this formalism. The minimal-coupling Hamiltonian for a single particle is

$$H_{min} = H_{mol} + H_{rad} + \frac{e}{m}\vec{p}\cdot\vec{a}(\vec{q}, t) + \frac{e^2}{2m}\vec{a}^2(\vec{q}, t), \tag{4.1}$$

where $\vec{p}$ is the momentum canonically conjugate to the position vector $\vec{q}$, and $\vec{a}(\vec{q}, t)$ is the vector potential, whose mode expansion is

$$\vec{a}(\vec{q}, t) = \sum_{\vec{k},\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\left[\vec{e}^{\,(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k}, t)e^{i\vec{k}\cdot\vec{q}} + \bar{\vec{e}}^{\,(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k}, t)e^{-i\vec{k}\cdot\vec{q}}\right]. \tag{4.2}$$

In the electric dipole approximation the spatial variations of the vector potential may be ignored because the radiation wavelength is large in comparison to molecular dimensions. Hence $\vec{a}(\vec{q}, t)$ can be replaced by $\vec{a}(\vec{R}, t)$, where $\vec{R}$ is a molecular centre, and which can conveniently be chosen as the origin. Hence the interaction terms of (4.1) become

$$H_{min}^{int} = \frac{e}{m}\vec{p}\cdot\vec{a}(0, t) + \frac{e^2}{2m}\vec{a}^2(0, t). \tag{4.3}$$

The time evolution of the boson annihilation operator, for instance, is given by the Heisenberg equation of motion for $a^{(\lambda)}(\vec{k}, t)$

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}a = [a, H_{min}]_- = \hbar\omega a + \frac{e}{m}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}[\vec{p} + e\vec{a}(0, t)]\cdot\bar{\vec{e}}^{\,(\lambda)}(\vec{k}). \tag{4.4}$$

Replacing the minimal-coupling canonical momentum by the kinetic momentum,

$$\frac{\mathrm{d}}{\mathrm{d}t}\vec{q} = \frac{1}{m}[\vec{p} + e\vec{a}], \tag{4.5}$$

and integrating, (4.4) becomes

$$a(t) = a(0)e^{-i\omega t} + \frac{i}{\hbar}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} e^{-i\omega t}\bar{\vec{e}}^{\,(\lambda)}(\vec{k}) \cdot \int_0^t \mathrm{d}t'\, \dot{\vec{\mu}}(t')e^{i\omega t'}, \tag{4.6}$$

where the over-dot denotes differentiation with respect to time. Inserting (4.6) and its Hermitian-adjoint into the mode expansion for the transverse electric field

$$\vec{e}^{\perp}(\vec{r}, t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left[\vec{e}^{\,(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k}, t)e^{i\vec{k}\cdot\vec{r}} - \bar{\vec{e}}^{\,(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k}, t)e^{-i\vec{k}\cdot\vec{r}}\right], \tag{4.7}$$

and carrying out the mode sum produces for the source dependent field,

$$e_i^{\perp}(\vec{r}, t) = \begin{cases} \dfrac{1}{4\pi\varepsilon_0}\left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right)\dfrac{1}{r}[\mu_j(t - r/c) - \mu_j(t)], & t > r/c > 0 \\[2ex] \dfrac{1}{4\pi\varepsilon_0}\left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right)\dfrac{1}{r}[\mu_j(0) - \mu_j(t)], & t < r/c, \end{cases} \tag{4.8}$$

with the gradients operating on the retarded time as well as on $1/r$. Note that for $t < r/c$, this field does not vanish. The total electric field is given by adding the longitudinal component to (4.8), which is itself obtained from the polarization field; in the electric dipole approximation

$$\begin{aligned} \varepsilon_0 e_i^{\parallel}(\vec{r}, t) &= p_i^{\perp}(\vec{r}, t) = -p_i^{\parallel}(\vec{r}, t) = -\mu_j(t)\delta_{ij}^{\perp}(\vec{r}) \\ &= -\frac{1}{4\pi r^3}(\delta_{ij} - 3\hat{r}_i\hat{r}_j)\mu_j(t), \end{aligned} \tag{4.9}$$

so that

$$e_i^{\mathrm{TOT}}(\vec{r}, t) = \begin{cases} \dfrac{1}{4\pi\varepsilon_0}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\dfrac{1}{r}\mu_j(t - r/c), & t > r/c > 0 \\[2ex] \dfrac{1}{4\pi\varepsilon_0}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\dfrac{1}{r}\mu_j(0), & t < r/c, \end{cases} \tag{4.10}$$

where the contribution to the total electric field for $t < r/c$ is the field of a static dipole at the origin.

In identical manner, inserting (4.6) into the mode expansion for the magnetic field yields for the source dependent term the minimal-coupling form,

$$b_i(\vec{r}, t) = \begin{cases} -\dfrac{1}{4\pi\varepsilon_0 c}\varepsilon_{ijk}\nabla_k \dfrac{1}{r}\dfrac{\mathrm{d}}{\mathrm{d}t}\mu_j(t - r/c), & t > r/c > 0 \\ 0, & t < r/c, \end{cases} \tag{4.11}$$

which is identical to the result obtained when starting from the multipolar Hamiltonian, although it should not be forgotten that in (4.11), the dipole moment evolves according to minimal-coupling dynamics. This field is strictly causal.

It is instructive to calculate the transverse and total electric field using the equations of motion for the photon creation and annihilation operators in the multipolar framework. The analogue of (4.6) is

$$a(t) = a(0)e^{-i\omega t} + \frac{1}{\hbar}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} e^{-i\omega t}\vec{\bar{e}}^{(\lambda)}(\vec{k}) \cdot \int_0^t \mathrm{d}t' \vec{\mu}(t')e^{i\omega t'}, \tag{4.12}$$

which when substituted into the mode expansion (4.7) results in

$$e_i^{\perp}(\vec{r}, t) = \begin{cases} \dfrac{1}{4\pi\varepsilon_0}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\dfrac{1}{r}\mu_j(t - r/c) - \dfrac{1}{\varepsilon_0}p_i^{\perp}(\vec{r}, t), & t > r/c > 0 \\ -\dfrac{1}{\varepsilon_0}p_i^{\perp}(\vec{r}, t), & t < r/c, \end{cases} \tag{4.13}$$

which on adding the longitudinal component from (4.9) produces for the total electric field of the source,

$$e_i^{\mathrm{TOT}}(\vec{r}, t) = \begin{cases} \dfrac{1}{4\pi\varepsilon_0}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\dfrac{1}{r}\mu_j(t - r/c), & t > r/c > 0 \\ 0, & t < r/c. \end{cases} \tag{4.14}$$

Now the total electric field is causal, and when multiplied by $\varepsilon_0$ is equal to the source dependent electric displacement field evaluated earlier and given by (3.37). Comparing fields (4.8) and (4.13), and (4.10) and (4.14), for $t > r/c > 0$, it is seen that the respective functional forms are the same, while for $t < r/c$, they differ.

Further insight may be gained into minimal- and multipolar-coupling formalisms by examining the relationships between dynamical variables in the two schemes. Recalling that the quantum canonical transformation used to effect the change from one framework to the other leaves the operators $\vec{q}$ and $\vec{a}(\vec{r})$ invariant, and changes only the canonical momenta $\vec{p}(t)$ and $\vec{\Pi}(\vec{r}, t)$, it is seen that the dipole moment operator $\vec{\mu}(t)$ and the magnetic field $\vec{b}(\vec{r}, t)$ have the same functional form in both constructs as they are both independent of the conjugate momenta.

The annihilation and creation operators in the two formalisms, however, differ since they evolve according to different Hamiltonians, with the canonical momenta also being different. The minimal and multipolar annihilation operators, for example, differ by

$$a_{mult}(t) = a_{min}(t) - i\left(\frac{1}{2\varepsilon_0\hbar ckV}\right)^{1/2}\mu_j(t)\bar{e}_j, \tag{4.15}$$

from which the relationship between the fields in the two formalisms may be derived. Thus

$$\begin{aligned}
\varepsilon_0 e_i^{\mathrm{TOT}(mult)}(\vec{r},t) = d_i(\vec{r},t) &= i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left[e_i a_{mult}(t)e^{i\vec{k}\cdot\vec{r}} - \bar{e}_i a^{\dagger}_{mult}(t)e^{-i\vec{k}\cdot\vec{r}}\right] \\
&= i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left[e_i a_{min}(t)e^{i\vec{k}\cdot\vec{r}} - \bar{e}_i a^{\dagger}_{min}(t)e^{-i\vec{k}\cdot\vec{r}}\right] \\
&\quad + \sum_{\vec{k},\lambda}\frac{1}{2V}\left[e_i\bar{e}_j e^{i\vec{k}\cdot\vec{r}} + \bar{e}_i e_j e^{-i\vec{k}\cdot\vec{r}}\right]\mu_j(t) \\
&= \varepsilon_0 e_i^{\perp(min)}(\vec{r},t) + p_i^{\perp}(\vec{r},t) = \varepsilon_0\left[e_i^{\perp(min)}(\vec{r},t) + e_i^{\parallel}(\vec{r},t)\right] \\
&= \varepsilon_0 e_i^{\mathrm{TOT}(min)}(\vec{r},t),
\end{aligned} \tag{4.16}$$

showing that $\vec{e}^{\,\mathrm{TOT}}(\vec{r},t)$ has identical time development in both formalisms. In contrast, the source free fields give rise to interesting differences. Expressing the free multipolar electric displacement field in terms of minimal boson operators yields

$$\begin{aligned}
d_i^{(0)(mult)}(\vec{r},t) &= i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left[e_i a_{min}(0)e^{i\vec{k}\cdot\vec{r}-i\omega t} - \bar{e}_i a^{\dagger}_{min}(0)e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right] \\
&\quad + \sum_{\vec{k},\lambda}\frac{1}{2V}\left[e_i\bar{e}_j e^{i\vec{k}\cdot\vec{r}-i\omega t} + \bar{e}_i e_j e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right]\mu_j(0) \\
&= \varepsilon_0 e_i^{\perp(0)(min)}(\vec{r},t) + \begin{cases} 0, & t > r/c \\ \dfrac{1}{4\pi}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\dfrac{1}{r}\mu_j(0), & t < r/c \end{cases}.
\end{aligned} \tag{4.17}$$

Similarly,

$$b_i^{(0)(mult)}(\vec{r},t) = b_i^{(0)(min)}(\vec{r},t), r \neq ct. \tag{4.18}$$

The results (4.16) and (4.17) can be expressed succinctly as

$$\vec{d}^{\,(0)(mult)}(\vec{r},t) = \varepsilon_0\vec{e}^{\,\perp(0)(min)}(\vec{r},t) + \begin{cases} 0, & t > r/c > 0 \\ \vec{p}^{\,\perp}(\vec{r},0), & t < r/c \end{cases}, \tag{4.19}$$

and

$$\vec{d}^{\,(mult)}(\vec{r},t) = \varepsilon_0\vec{e}^{\,\perp(min)}(\vec{r},t) + \vec{p}^{\,\perp}(\vec{r},t),\ \forall t, \tag{4.20}$$

demonstrating that the vacuum fields are identical for positive times, and the total fields are identical for *all* times. Note that the static and dynamic polarization fields contribute differently to source and free fields.

It has been well established that for application to atomic and molecular systems, the multipolar form of the quantum electrodynamical Hamiltonian is more efficacious than its minimal-coupling counterpart [6,13,29,34]. In the multipolar scheme, molecules couple directly to electric displacement and magnetic fields through electric and magnetic multipole moments. All of the interaction terms are of one-centre in origin, with intermolecular coupling terms, explicitly present in the minimal-coupling Hamiltonian, having now been eliminated. Photons propagate at their proper speed $c$, with retardation effects automatically accounted for due to the causal nature of the Maxwell fields. Even though the formal expansion of the multipolar interaction terms yields an infinite series, convergence is well established, and the identification of the charge distribution as a sum of electric, magnetic and diamagnetic dipoles, quadrupoles, octupoles, . . . , lends itself naturally to charges grouped into collections of atoms and molecules. This may be contrasted with the minimal-coupling interaction Hamiltonian, which explicitly contains operators for the momentum, vector potential, and the static intermolecular Coulomb interaction. While there are only three terms in the interaction Hamiltonian in minimal-coupling, interpretation using chemically intuitive concepts proves more difficult, notwithstanding calculational difficulties associated with the use of the transverse vector potential, which is non-local. It should be remarked that matrix elements evaluated in minimal-coupling can be converted to their multipolar form, but in many cases this involves a judicious application of identities relating matrix elements of momentum and coordinate operators [34].

## 5. Electromagnetic fields of a moving charge

The expressions for the Maxwell field operators correct up to second order in the transition electric dipole moment presented earlier apply to a stationary source. Recently, the electric and magnetic fields of a charge moving along an arbitrary trajectory have been derived. Interest in this problem surfaced as a result of noticing that only formulae for these fields were given by Feynman in his *Lectures on Physics* [45], with a cautionary remark being made against their derivation. Further, the problem is worthy of study in that its solution may be used to calculate rates of energy and momentum loss from the field of a moving charge, which in turn feature in the explanation of classical bremsstrahlung. It should be remarked that the dynamics of the source, be it a charge, dipole, quadrupole, etc, are not explicitly taken into account since they are not subject to external forces.

For a charge $e$ moving on a trajectory $\vec{q}(t)$, the electric and magnetic fields at a field point $\vec{R}$ at time $t$ are given by

$$\vec{e}(\vec{R},t)=\frac{e}{4\pi\varepsilon_0}\left\{\frac{\hat{e}(t_r)}{r^2(t_r)}+\frac{r(t_r)}{c}\frac{\mathrm{d}}{\mathrm{d}t}\frac{\hat{e}(t_r)}{r^2(t_r)}+\frac{1}{c^2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\hat{e}(t_r)\right\}, \tag{5.1}$$

and

$$\vec{b}(\vec{R},t)=\frac{1}{c}\,\hat{e}(t_r)\times\vec{e}, \tag{5.2}$$

where $\vec{r}(t)=r(t)\hat{e}(t)$ is the relative displacement vector to the field point from the charge at time $t$,

$$\vec{r}(t)=\vec{R}-\vec{q}(t), \tag{5.3}$$

and

$$t_r=t-r(t_r)/c, \tag{5.4}$$

is the retarded time. The three terms of (5.1) each have a simple physical interpretation. The first is the retarded Coulomb field, while the second is a correction to it. The third term is the radiative field, having $r^{-1}$ distance behaviour, and which depends on the acceleration of the charge.

Power and Thirunamachandran [46] used two quite different approaches to derive the fields (5.1) and (5.2). In one mathematically involved method, the classical Maxwell's equations with the moving charge giving rise to a current, were integrated directly. This approach had the following advantages: the electromagnetic potentials were not required to be introduced, thereby avoiding questions of gauge choice and solutions of the wave equations, and the differential equations to be integrated were of first order in time.

In contrast to the method mentioned above in which Maxwell's equations for a moving charge were integrated directly, in a second approach, commonly used in quantum optics, a treatment similar to that outlined earlier in the derivation of the Maxwell fields of a source with zero velocity, was adopted, but now taking account of the motion of the charged particle. For the latter case the Hamiltonian is given by

$$H = \sum_{\vec{k},\lambda} a^{\dagger(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})\hbar ck + e\,\dot{\vec{q}}\cdot\vec{a}(\vec{q}), \tag{5.5}$$

where $\vec{a}(\vec{q})$ is the vector potential, whose explicitly time-dependent mode expansion is

$$\vec{a}(\vec{R},t) = \sum_{\vec{k},\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\left[\vec{e}^{\,(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k},t)e^{i\vec{k}\cdot\vec{R}} + \bar{\vec{e}}^{\,(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k},t)e^{-i\vec{k}\cdot\vec{R}}\right]. \tag{5.6}$$

The introduction of the coupling of the current to the vector potential in (5.5) necessitates the selection of a gauge. One choice frequently adopted in atomic, molecular and optical physics is the radiation or Coulomb gauge, and which has been used thus far. From the Heisenberg equation of motion for the annihilation operator,

$$a(t) = a(0)e^{-i\omega t} - ie\left(\frac{1}{2\varepsilon_0\hbar ckV}\right)^{1/2}\bar{\vec{e}}^{\,(\lambda)}(\vec{k})\cdot\int_0^t \dot{\vec{q}}(t')e^{-i\vec{k}\cdot\vec{q}(t')}e^{-i\omega(t-t')}\mathrm{d}t'. \tag{5.7}$$

Inserting (5.7) into the mode expansion for the transverse electric field,

$$\vec{e}^{\perp}(\vec{R},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left[\vec{e}^{\,(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k},t)e^{i\vec{k}\cdot\vec{R}} - \bar{\vec{e}}^{\,(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k},t)e^{-i\vec{k}\cdot\vec{R}}\right], \tag{5.8}$$

and in the magnetic field $\vec{b}(\vec{R},t) = \nabla\times\vec{a}(\vec{R},t)$, and carrying out the mode sum, the fields (5.1) and (5.2) result after some manipulation. Although this quantum mechanical version requires choosing a gauge, it has the advantage that the fields obtained are properly retarded because the solutions for the Heisenberg operators are valid only for $t - r/c > 0$. Finally, both methods lead straightforwardly to the formulae for the electric and magnetic fields of an oscillating dipole (3.37) and (3.38) when invoking the electric dipole approximation.

In subsequent work [47–50], the fields due to a moving electric dipole were obtained both by direct integration of Maxwell's equations and the quantum electrodynamical method. Extension to include moving higher multipoles was found to be achieved most easily via the quantum mechanical approach, with the fields due to moving electric quadrupole and magnetic dipole moments being derived simply and transparently.

This was achieved by separating the current density into polarization, magnetization and Röntgen current densities. Overall, this body of work demonstrated that analytical techniques used in quantum optics may be used to derive new results in classical electrodynamics.

The electromagnetic fields of a moving source have also been used to further the understanding of the manifestation of the Röntgen current [51]. Röntgen and Eichenwald [52] independently detected a magnetic field in the vicinity of a rotating dielectric, which arose from the coupling of the electric polarization to the velocity of the moving body. One other notable consequence of gross particle motion is the Aharonov–Casher effect [53]. This is generated by a magnetic dipole moment moving relative to a source dependent electric field, and which has been confirmed experimentally [54]. Both the Röntgen and Aharonov–Casher effects are reciprocal to one another, and may be interpreted as special cases of the more general vector Aharonov–Bohm [55] type quantum phase shift phenomenon [56,57].

## 6. Poynting vector

The Maxwell field operators can be used to calculate the energy flux from a molecule in an excited electronic state. This quantity is related directly to the Poynting vector, whose quantum mechanical operator has the Hermitian form

$$\vec{S}(\vec{r},t) = \frac{1}{2}\varepsilon_0 c^2\Big[\vec{e}^{\,\mathrm{TOT}}(\vec{r},t)\times\vec{b}(\vec{r},t) - \vec{b}(\vec{r},t)\times\vec{e}^{\,\mathrm{TOT}}(\vec{r},t)\Big]. \tag{6.1}$$

Noting that for a neutral molecule, $\varepsilon_0\vec{e}^{\,\mathrm{TOT}}(\vec{r},t) = \vec{d}^{\perp}(\vec{r},t)$ outside the source, since $\vec{d}^{\parallel}(\vec{r},t) = 0$ and $\varepsilon_0\vec{e}^{\,\mathrm{TOT}}(\vec{r},t) = \vec{d}(\vec{r},t)$, (6.1) can be written in terms of the transverse displacement field as

$$S_i(\vec{r},t) = \frac{1}{2}c^2\varepsilon_{ijk}\Big[d_j^{\perp}(\vec{r},t)b_k(\vec{r},t) + b_k(\vec{r},t)d_j^{\perp}(\vec{r},t)\Big]. \tag{6.2}$$

For a state $|p;0(\vec{k},\lambda)\rangle$ designating the molecule in the excited electronic state $|p\rangle$ and the radiation field containing no photons, the expectation value of (6.2) is

$$\begin{aligned}
&\langle 0(\vec{k},\lambda);p|S_i(\vec{r},t)|p;0(\vec{k},\lambda)\rangle\\
&= \frac{1}{2}c^2\varepsilon_{ijk}\Big\langle 0(\vec{k},\lambda);p\Big|\Big(d_j^{(0)} + d_j^{(1)} + d_j^{(2)} + \cdots\Big)\Big(b_k^{(0)} + b_k^{(1)} + b_k^{(2)} + \cdots\Big)\Big|p;0(\vec{k},\lambda)\Big\rangle + c.c.\\
&\approx \frac{1}{2}c^2\varepsilon_{ijk}\Big\langle 0(\vec{k},\lambda);p\Big|\Big(d_j^{(1)}b_k^{(1)} + d_j^{(2)}b_k^{(0)} + d_j^{(0)}b_k^{(2)}\Big)\Big|p;0(\vec{k},\lambda)\Big\rangle + c.c.,
\end{aligned} \tag{6.3}$$

where *c.c.* denotes the complex conjugate, and terms proportional to the square of the transition electric dipole moment are retained. Using formulae (3.21) and (3.29), the contribution to (6.3) arising from the product of the first order fields is

$$\frac{c}{32\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_n \mu_l^{pn}\mu_m^{np}k_{pn}^6\big[\bar{f}_{jl}(k_{pn}r)g_{km}(k_{pn}r) + \bar{g}_{km}(k_{pn}r)f_{jl}(k_{pn}r)\big]. \tag{6.4}$$

Note that both upward and downward transitions from $|p\rangle$ appear in the summation of (6.4). At first sight it is somewhat paradoxical that contributions arising from transitions $|n\rangle \leftarrow |p\rangle$, with $E_p < E_n$ show up, since they cannot add to the net energy flow. Since $\vec{d}^{(1)}(\vec{r}, t)$ and $\vec{b}^{(1)}(\vec{r}, t)$ are both Hermitian, it is clear that the $pn$-th matrix element must be equal to the $np$-th one. As was first shown by Power and Thirunamachandran [58], this is resolved by recourse to the terms involving the interference of the vacuum field with the second order field. Evaluating these contributions using expressions (3.16), (3.23), (3.25) and (3.30) produces

$$\frac{c}{32\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_n(\mathrm{sgn}k_{pn})\mu_l^{pn}\mu_m^{np}k_{pn}^6\left[\bar{f}_{jl}(k_{pn}r)g_{km}(k_{pn}r)+\bar{g}_{km}(k_{pn}r)f_{jl}(k_{pn}r)\right]. \tag{6.5}$$

Adding (6.4) to (6.5) yields the result

$$\begin{aligned} S_i(\vec{r}, t) &= \frac{c}{16\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_{\substack{n \\ E_p>E_n}}\mu_l^{pn}\mu_m^{np}k_{pn}^6\left[\bar{f}_{jl}(k_{pn}r)g_{km}(k_{pn}r)+\bar{g}_{km}(k_{pn}r)f_{jl}(k_{pn}r)\right] \\ &= \frac{c}{8\pi^2\varepsilon_0}\sum_{\substack{n \\ E_p>E_n}}\mu_l^{pn}\mu_m^{np}k_{pn}^4(\delta_{lm}-\hat{r}_l\hat{r}_m)\frac{\hat{r}_i}{r^2}, \end{aligned} \tag{6.6}$$

and it is seen that only downward transitions make a net contribution to the Poynting vector. The inverse square dependence of (6.6) is to be expected; it is a reflection of the local conservation of energy requirement that the energy flow across a surface area normal to $\hat{r}$ subtending a solid angle $\mathrm{d}\Omega$ be independent of $r$. The rate of energy loss across a surface of a sphere of radius $r$ is calculated from

$$\int r^2\hat{r}_iS_i(\vec{r}, t)\mathrm{d}\Omega, \tag{6.7}$$

which on using (6.6) becomes

$$\sum_{\substack{n \\ E_p>E_n}}\frac{ck_{pn}^4}{3\pi\varepsilon_0}|\vec{\mu}^{pn}|^2. \tag{6.8}$$

The rate of electromagnetic energy flow from an excited molecule calculated above can be related to the spontaneous emission rate. For a $n \leftarrow p$ transition, let this be denoted by $\Gamma_{n\leftarrow p}$. Then the rate of total energy flow is also given by

$$\sum_n\Gamma_{n\leftarrow p}\hbar ck_{pn}. \tag{6.9}$$

Comparing (6.8) and (6.9) it is seen that

$$\Gamma_{n\leftarrow p} = \frac{k_{pn}^3}{3\pi\varepsilon_0\hbar}|\vec{\mu}^{pn}|^2, \tag{6.10}$$

which is exactly the Einstein A-coefficient computed by standard time-dependent perturbation theory and the Fermi golden rule [13]. The role of Maxwell fields in the radiation of energy by an excited molecule is clearly delineated in the present time-dependent formulation.

## 7. Electromagnetic energy density

The electric and magnetic energy density due to the Maxwell fields is another property of the source fields that may be calculated. The electric part of the energy density may be expressed in terms of the electric displacement field as

$$\frac{1}{2\varepsilon_0}[\vec{d}^{\perp}(\vec{r},t)]^2 = \frac{1}{2\varepsilon_0}\Big[\vec{d}^{(0)} + \vec{d}^{(1)} + \vec{d}^{(2)} + \cdots\Big]^2. \tag{7.1}$$

On squaring, the first term is quadratic in the free-field, being independent of the source. The second and third terms involve the product of the zeroth and first order fields. These two terms do not contribute to the expectation value for a state in which the photon number remains constant. The first contributory terms are proportional to the square of the electric dipole moment and are composed of two types of terms: one involving the product of fields linear in the source moment and a second consisting of the interference of the free and second order fields, namely

$$\frac{1}{2\varepsilon_0}[\vec{d}^{\perp}(\vec{r},t)]^2 \approx \frac{1}{2\varepsilon_0}\Big(\vec{d}^{(1)}\cdot\vec{d}^{(1)} + \vec{d}^{(0)}\cdot\vec{d}^{(2)} + \vec{d}^{(2)}\cdot\vec{d}^{(0)}\Big). \tag{7.2}$$

Because $\vec{d}^{(1)}(\vec{r},t)$ is independent of boson annihilation and creation operators, the first term of (7.2) does not depend on photon occupation number. Its expectation value for a state $|p; 0(\vec{k},\lambda)\rangle$ is

$$\begin{aligned}
&\frac{1}{2\varepsilon_0}\Big\langle 0(\vec{k},\lambda); p|d_i^{(1)}(\vec{r},t)d_i^{(1)}(\vec{r},t)|p; 0(\vec{k},\lambda)\Big\rangle \\
&\quad = \frac{1}{32\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6 \bar{f}_{ij}(k_{pn}r)f_{ik}(k_{pn}r) \\
&\quad = \frac{1}{32\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6\Bigg[(\delta_{jk} - \hat{r}_j\hat{r}_k)\left(\frac{1}{k_{pn}^2r^2} - \frac{2}{k_{pn}^4r^4}\right) \\
&\qquad + (\delta_{jk} + 3\hat{r}_j\hat{r}_k)\left(\frac{1}{k_{pn}^4r^4} + \frac{1}{k_{pn}^6r^6}\right)\Bigg].
\end{aligned} \tag{7.3}$$

In order to evaluate the second and third terms of (7.2), it is recognized that only that part of the quadratic field that is diagonal in the electron space is required because the free field operates only in the boson space. Hence

$$\begin{aligned}
&\frac{1}{2\varepsilon_0}\sum_{\vec{k},\lambda}\Big\langle 0(\vec{k},\lambda); p|d_i^{(0)}d_i^{(2)} + d_i^{(2)}d_i^{(0)}|p; 0(\vec{k},\lambda)\Big\rangle \\
&\quad = \frac{1}{16\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}\frac{\mathrm{PV}}{2\pi i}\int_0^\infty dk k^3 \\
&\qquad \times\left\{\begin{array}{l}
\dfrac{[F_{ik}(kr) - \bar{F}_{ik}(kr)][k^3\bar{F}_{ij}(kr) - (k_{np}^3)\bar{F}_{ij}(k_{np}r)e^{i(k_{np}-k)ct}]}{(k_{np}-k)} \\
\quad + \dfrac{[F_{ik}(kr) - \bar{F}_{ik}(kr)][k^3\bar{F}_{ij}(kr) - (-k_{np}^3)\bar{F}_{ij}(-k_{np}r)e^{-i(k_{np}+k)ct}]}{(k_{np}+k)} - c.c.
\end{array}\right\},
\end{aligned} \tag{7.4}$$

where PV denotes the Cauchy principal value. The integral in (7.4) contains both time-dependent and time-independent terms. For $t \gg r/c$ the former tend to zero because the integrals have exponentially decreasing values. Neglecting these and other transient terms, (7.4) becomes

$$\begin{aligned}&\frac{1}{32\pi^2\varepsilon_0}\sum_n(\mathrm{sgn}\,k_{pn})\mu_j^{pn}\mu_k^{np}k_{pn}^6\bar{f}_{ij}(k_{pn}r)f_{ik}(k_{pn}r)\\&\quad+\frac{1}{16\pi^3\varepsilon_0}\sum_{\substack{n\\ \forall E_n}}\mu_j^{pn}\mu_k^{np}\int_0^\infty\frac{\mathrm{d}u u^6e^{-2ur}}{u^2+k_{pn}^2}k_{pn}f_{ij}(iur)f_{ik}(iur),\end{aligned}\tag{7.5}$$

where $\omega = icu$ is an imaginary frequency. It is worth pointing out that for upward transitions from $|p\rangle$, the first term of (7.5) has opposite sign to (7.3), the contribution arising from the product of the first order fields. Adding (7.5) to (7.3) then yields for the electric energy density the expression

$$\frac{1}{16\pi^2\varepsilon_0}\sum_{\substack{n\\ E_p>E_n}}\mu_j^{pn}\mu_k^{np}k_{pn}^6\bar{f}_{ij}(k_{pn}r)f_{ik}(k_{pn}r)+\frac{1}{16\pi^3\varepsilon_0}\sum_{\substack{n\\ \forall E_n}}\mu_j^{pn}\mu_k^{np}\int_0^\infty\frac{\mathrm{d}u u^6e^{-2ur}}{u^2+k_{pn}^2}k_{pn}f_{ij}(iur)f_{ik}(iur).\tag{7.6}$$

Performing an orientational average [59] on (7.6) leads to the energy density applicable to an isotropic source,

$$\begin{aligned}&\frac{1}{24\pi^2\varepsilon_0r^2}\sum_{\substack{n\\ E_p>E_n}}|\vec{\mu}^{pn}|^2k_{pn}^4\left[1+\frac{1}{k_{pn}^2r^2}+\frac{3}{k_{pn}^4r^4}\right]\\&\quad+\frac{\hbar c}{16\pi^3\varepsilon_0}\int_0^\infty\mathrm{d}u u^6e^{-2ur}\alpha(iu)\left[\frac{1}{u^2r^2}+\frac{2}{u^3r^3}+\frac{5}{u^4r^4}+\frac{6}{u^5r^5}+\frac{3}{u^6r^6}\right],\end{aligned}\tag{7.7}$$

where the analytically continued isotropic dynamic polarizability is defined as

$$\alpha(iu)=\frac{2}{3}\sum_n\frac{E_{np}|\vec{\mu}^{pn}|^2}{E_{np}^2+(\hbar cu)^2}.\tag{7.8}$$

Note that for downward transitions the second term of (7.7) is of opposite sign to that for upward transitions. It is instructive to examine the two terms of (7.7), and their asymptotic limits, separately. In the far-zone, corresponding to field point-molecule separations large compared to reduced characteristic molecular transition wavelengths, the pole term of (7.7) exhibits an inverse square dependence

$$\frac{1}{24\pi^2\varepsilon_0r^2}\sum_{\substack{n\\ E_p>E_n}}|\vec{\mu}^{pn}|^2k_{pn}^4,\tag{7.9}$$

while the $u$-integral term has the limiting form

$$\frac{23\hbar c\alpha(0)}{64\pi^3\varepsilon_0r^7},\tag{7.10}$$

where $\alpha(0)$ is the static polarizability of the source. The result (7.10) is obtained on letting $u=0$ in the expression for the polarizability (7.8), and carrying out the $u$-integral of (7.7) using the standard integral [60]

$$\int_0^\infty x^n e^{-\alpha x}\mathrm{d}x = n!\alpha^{-n-1}, \quad \mathrm{Re}\,\alpha > 0.$$

The overall far-zone density is dominated by (7.9). Hence the far-zone response of a polarizable test molecule to the electric displacement field whose far-zone electric energy density is (7.9), is given by

$$-\frac{1}{24\pi^2\varepsilon_0^2 r^2}\sum_{\substack{n\\E_p>E_n}}|\vec{\mu}^{pn}|^2\alpha_{test}(0)k_{pn}^4. \tag{7.11}$$

Both terms of (7.7) exhibit $r^{-6}$ behaviour in the near-zone, where $|k_{pn}r| \ll 1$. The first term yields

$$\frac{1}{8\pi^2\varepsilon_0 r^6}\sum_{\substack{n\\E_p>E_n}}|\vec{\mu}^{pn}|^2, \tag{7.12}$$

while the second term of (7.7) produces

$$-\frac{1}{16\pi^2\varepsilon_0 r^6}\sum_{\substack{n\\E_p>E_n}}|\vec{\mu}^{pn}|^2 + \frac{1}{16\pi^2\varepsilon_0 r^6}\sum_{\substack{n\\E_p<E_n}}|\vec{\mu}^{pn}|^2, \tag{7.13}$$

both of which are identical to results obtained via conventional electrostatics. At this separation regime, the interaction energy of a polarizable test body to the field producing the limiting densities (7.12) and (7.13) is

$$-\frac{1}{16\pi^2\varepsilon_0^2 r^6}\sum_{\substack{n\\\forall E_n}}|\vec{\mu}^{pn}|^2\alpha_{test}(0), \tag{7.14}$$

which is in agreement with the energy shift calculated using second order perturbation theory and a static dipolar coupling potential.

When the molecule is in the ground electronic state, only the $u$-integral term of (7.7) survives. The asymptotic limits in the far- and near-zones are given by (7.10) and (7.13) as before, but now the transition dipole, which also appears in the polarizability, corresponds to that for the molecular ground state, and contains $|\vec{\mu}^{0n}|^2$. Incidentally, the energy shift resulting from (7.10) is now the familiar far-zone Casimir–Polder potential between a pair of electric dipole polarizable molecules [61].

In a fashion similar to that used to evaluate the electric energy density in the vicinity of an electric dipole source, the magnetic contribution to the electromagnetic energy density can be calculated [58,62]. Correct to second order in the moments, it is given by the expectation value of

$$\frac{1}{2}\varepsilon_0 c^2\left\langle 0(\vec{k},\lambda); p\middle|[\vec{b}(\vec{r},t)]^2\middle|p; 0(\vec{k},\lambda)\right\rangle \approx \frac{1}{2}\varepsilon_0 c^2\left\langle 0(\vec{k},\lambda); p\middle|b_i^{(1)}b_i^{(1)} + b_i^{(2)}b_i^{(0)} + b_i^{(0)}b_i^{(2)}\middle|p; 0(\vec{k},\lambda)\right\rangle. \tag{7.15}$$

Using the magnetic field linear in the moments (3.29), the first term of (7.15) is

$$\frac{1}{32\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6\bar{g}_{ij}(k_{pn}r)g_{ik}(k_{pn}r) = \frac{1}{32\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6(\delta_{jk}-\hat{r}_j\hat{r}_k)\left(\frac{1}{k_{pn}^2r^2}+\frac{1}{k_{pn}^4r^4}\right), \tag{7.16}$$

which on rotational averaging becomes

$$\frac{1}{48\pi^2\varepsilon_0}\sum_n |\vec{\mu}^{pn}|^2k_{pn}^6\left[\frac{1}{k_{pn}^2r^2}+\frac{1}{k_{pn}^4r^4}\right]. \tag{7.17}$$

The last two terms of (7.15) are found to be

$$\frac{1}{32\pi^2\varepsilon_0}\sum_n(\mathrm{sgn}\,k_{pn})\mu_j^{pn}\mu_k^{np}k_{pn}^6\bar{g}_{ij}(k_{pn}r)g_{ik}(k_{pn}r)$$
$$+\frac{1}{16\pi^3\varepsilon_0}\sum_{\substack{n\\ \forall E_n}}\mu_j^{pn}\mu_k^{np}\int_0^\infty\frac{\mathrm{d}u u^6e^{-2ur}}{u^2+k_{pn}^2}k_{np}g_{ij}(iur)g_{ik}(iur). \tag{7.18}$$

Adding (7.16) to (7.18) after performing an orientational average on the latter, the magnetic energy density for an isotropic source is

$$\frac{1}{24\pi^2\varepsilon_0}\sum_{\substack{n\\ E_p>E_n}}|\vec{\mu}^{pn}|^2k_{pn}^6\left[\frac{1}{k_{pn}^2r^2}+\frac{1}{k_{pn}^4r^4}\right]-\frac{\hbar c}{16\pi^3\varepsilon_0}\int_0^\infty \mathrm{d}uu^6e^{-2ur}\alpha(iu)\left[\frac{1}{u^2r^2}+\frac{2}{u^3r^3}+\frac{1}{u^4r^4}\right]. \tag{7.19}$$

When the molecule is electronically excited, both terms of (7.19) contribute to the energy density. At asymptotically large distances, the first term exhibits inverse square behaviour and corresponds to real photon emission,

$$\frac{1}{24\pi^2\varepsilon_0r^2}\sum_{\substack{n\\ E_p>E_n}}|\vec{\mu}^{pn}|^2k_{pn}^4, \tag{7.20}$$

and which dominates over the second term of (7.19), which has the limiting form in the far-zone

$$-\frac{7\hbar c\alpha(0)}{64\pi^3\varepsilon_0r^7}. \tag{7.21}$$

When the source is in the ground state, the first term of (7.19) vanishes, with the ground state polarizability occurring in the remaining second term. Again the energy density manifests itself as an interaction energy between a source and a test polarizable molecule. For a magnetically susceptible test body, $\chi$, in the presence of the magnetic energy density due to the magnetic field, with both source and test in the ground state, the far-zone energy shift is

$$\frac{7\hbar}{64\pi^3\varepsilon_0^2cr^7}\chi_{test}(0)\alpha(0), \tag{7.22}$$

and which is repulsive.

## 8. Contribution from higher multipole moments

The Maxwell field operators dependent on the leading magnetic and diamagnetic interaction terms, as well as the electric quadrupole dependent fields, have also been evaluated [37,38] up to second order in the moments using the method illustrated in Section 3 for the electric dipole coupling term. Now the first few terms of the multipolar interaction Hamiltonian are needed, and they are

$$H_{int} = -\varepsilon_0^{-1}\vec{\mu}\cdot\vec{d}^{\perp}(\vec{r}) - \vec{m}\cdot\vec{b}(\vec{r}) - \varepsilon_0^{-1}Q_{ij}\nabla_j d_i^{\perp}(\vec{r}) + \frac{e^2}{8m}\left(\vec{q}\times\vec{b}(\vec{r})\right)^2, \tag{8.1}$$

where $\vec{m}$ is the magnetic dipole moment operator, $Q_{ij}$ is the electric quadrupole moment tensor, and the last term of (8.1) represents the lowest order diamagnetic interaction. These higher order multipole moment dependent contributions, along with others of a comparable order of magnitude such as electric octupole and magnetic quadrupole coupling, are needed for the correct treatment of a number of intermolecular interactions, such as those occurring between optically active molecules [63,64], between a pair of helium atoms [65,66], and alkali metal dimers [67–69]. The additional electric octupole and magnetic quadrupole coupling terms to be added to the interaction Hamiltonian (8.1) are of the form $-\varepsilon_0^{-1}O_{ijk}\nabla_j\nabla_k d_i^{\perp}(\vec{r})$ and $-m_{ij}\nabla_j b_i(\vec{r})$, respectively, where $O_{ijk}$ is the electric octupole moment tensor, and $m_{ij}$ is the magnetic quadrupole moment tensor. While the magnetic dipole and electric quadrupole moment are both of the same order of magnitude, being a factor of the fine structure constant smaller than the leading electric dipole term, for molecule and field properties proportional to the square of the magnetic field, such as the magnetic energy density due to a magnetic dipole source, and the intermolecular energy shift between electric and magnetic dipole polarizable molecules, the lowest order diamagnetic interaction must be taken into account for consistency [70].

The electromagnetic energy density arising from the last three terms of (8.1) has been evaluated [71], in addition to electric quadrupole and magnetic dipole and their cross-term contributions to the Poynting vector [38,72]. The electric–magnetic dipole contribution to the Poynting vector for example, is crucial in understanding the migration of energy between a pair of chiral molecules. Results similar to that presented for the electric dipole case were found for the higher multipole contributions to the electric displacement and magnetic field operators, the Poynting vector and the Thomson energy density. Also, as expected, an $r^{-2}$ dependence on distance occurred for each of the higher multipole contributions to the Poynting vector that were examined.

In recent work [39] generalized expressions for the Maxwell field operators were obtained correct to first order in an electric or magnetic multipole moment of arbitrary order. This was achieved by employing an interaction Hamiltonian of the form

$$H_{int}^{(m)} = -\varepsilon_0^{-1}\sum_{r,s} b_r^{\dagger}(t)b_s(t)E_{i_1\ldots i_m}^{(m)rs}\nabla_{i_2}\ldots\nabla_{i_m}d_{i_1}^{\perp}(\vec{R},t) - \sum_{r,s} b_r^{\dagger}(t)b_s(t)m_{i_1\ldots i_m}^{(m)rs}\nabla_{i_2}\ldots\nabla_{i_m}b_{i_1}(\vec{R},t), \tag{8.2}$$

where $E_{i_1\ldots i_m}^{(m)rs}$ and $m_{i_1\ldots i_m}^{(m)rs}$ are the $m$-th order transition electric and magnetic multipole moments, respectively, with the operators defined as

$$E_{i_1\ldots i_m}^{(m)} = -\frac{e}{m!}(\vec{q}-\vec{R})_{i_1}\ldots(\vec{q}-\vec{R})_{i_m}, \tag{8.3}$$

and

$$m^{(m)}_{i_1\ldots i_m} = -\frac{em}{M(m+1)!}[(\vec{q}-\vec{R})\times\vec{p}]_{i_1}\ldots(\vec{q}-\vec{R})_{i_m}, \tag{8.4}$$

where $\vec{p}$ is the momentum of the particle whose mass is $M$. These generalized fields correct to first order were used to obtain an expression for the matrix element for the resonant transfer of energy between electric and magnetic systems of arbitrary multipole order.

## 9. Response theory

### 9.1. *Resonance energy transfer*

One of the striking successes of the application of the theory of molecular QED is to the calculation of interactions between molecules, especially those that occur at long ranges of separation [73–75]. At this distance regime, in which the product of the photon wavevector and internuclear distance is much greater than unity, i.e. $kR \gg 1$, the effects of retardation become important, and their automatic inclusion in the theoretical formalism results in significant differences in the functional form of the energy shift or transfer rate over more commonly obtained expressions using molecular quantum mechanics.

One such type of intermolecular interaction is the resonant exchange of excitation energy between a pair of molecules, one of which, say $A$ is initially in an excited electronic state $|n\rangle$ with energy $E_n$, and a second, $B$ which at $t=0$ is in the ground state. After migration of energy, $A$ decays to the ground state and $B$ acquires energy $E_n$. This simplest of coupling processes has been much studied in molecular physics [22,39,44,76–90], especially since the birth of quantum mechanics, having important ramifications on fundamental questions concerning the theory of measurement, the violation or otherwise of Einstein causality, as well as obvious implications regarding the detailed mechanism by which energy is exchanged. More recently, resonance energy transfer has acquired significance in the context of single molecule spectroscopy in biological and macromolecular systems containing numerous functional groups or chromophores, in light harvesting complexes such as the photosynthetic unit, and in dendrimers and nanoscale structures [91]. For non-overlapping centres of charge, use of a static dipolar coupling potential of the form

$$V_{ij}(\vec{R}) = \frac{1}{4\pi\varepsilon_0 R^3}(\delta_{ij} - 3\hat{R}_i\hat{R}_j), \tag{9.1}$$

where $\vec{R} = \vec{R}_B - \vec{R}_A$ is the pair separation distance vector, gives rise to a matrix element for dipole–dipole transfer

$$M = \mu_i^{0n}(A)\mu_j^{n0}(B)V_{ij}(\vec{R}), \tag{9.2}$$

from which the well known inverse sixth power intermolecular separation distance dependence of the isotropic transfer rate is obtained via the Fermi golden rule

$$\Gamma^{Förster} = \frac{\rho}{12\pi\hbar\varepsilon_0^2 R^6}|\vec{\mu}^{0n}(A)|^2|\vec{\mu}^{n0}(B)|^2, \tag{9.3}$$

as first calculated by Förster [77], where $\rho$ is to be regarded as a convolution function that implicitly contains the conservation of energy condition between initial and final states of the system, between which energy is exchanged. Note that the interaction between the two sites is taken to propagate instantaneously. This is clearly unphysical, especially at distances large relative to characteristic reduced transition wavelengths. The correct description and expression for the transfer rate is provided by quantum electrodynamical theory due to the fact that this formulation accounts properly and automatically for the finite speed of propagation of electromagnetic signals. In the second-order diagrammatic perturbation theory calculation of the matrix element [44], energy transfer is viewed as arising from the exchange of a single virtual photon between the pair, and is given by

$$M = \mu_i^{0n}(A)\mu_j^{n0}(B)V_{ij}(k_{n0}, \vec{R}), \tag{9.4}$$

where

$$\begin{aligned} V_{ij}(k, \vec{R}) &= -\frac{1}{4\pi\varepsilon_0}\left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right)\frac{e^{ikR}}{R} \\ &= \frac{1}{4\pi\varepsilon_0 R^3}\left[\left(\delta_{ij} - 3\hat{R}_i\hat{R}_j\right)(1 - ikR) - \left(\delta_{ij} - \hat{R}_i\hat{R}_j\right)k^2R^2\right]e^{ikR}, \end{aligned} \tag{9.5}$$

is the retarded resonant interaction tensor at frequency $\omega = ck$. As expected, the $\omega \to 0$ limit of (9.5) yields (9.1). From the last two equations and the Fermi golden rule the transfer rate for all $R$ beyond wavefunction overlap for freely tumbling $A$ and $B$ is

$$\Gamma = \frac{4\pi\rho}{9\hbar}\frac{1}{(4\pi\varepsilon_0 R^3)^2}|\vec{\mu}^{0n}(A)|^2|\vec{\mu}^{n0}(B)|^2\left[k_{n0}^4R^4 + k_{n0}^2R^2 + 3\right]. \tag{9.6}$$

Evident from the result (9.6) is that the Förster expression does not hold for large values of $R$. At this extreme $k_{n0}R \gg 1$, and the asymptote is

$$\Gamma^{Rad} = \frac{\rho k_{n0}^4}{36\pi\hbar\varepsilon_0^2R^2}|\vec{\mu}^{0n}(A)|^2|\vec{\mu}^{n0}(B)|^2, \tag{9.7}$$

and which exhibits inverse square dependence on $R$. Clearly QED provides a single calculational framework and a unified description for the transfer of energy. From one underlying mechanism which holds for *all* donor–acceptor separation distances beyond orbital overlap, two asymptotically limiting forms of the transfer rate follow, each with differing physical interpretations. On this basis the near-zone limit (9.3) is understood to arise from radiationless transfer, while the long-range rate (9.7) is interpreted as being radiative in origin, corresponding to emission of a photon by the excited donor followed by absorption by the ground state acceptor species.

The matrix element for migration of energy (9.4) may be obtained in an alternative description [39,92] involving the Maxwell fields given earlier. The picture is one in which species $B$ is viewed as a test molecule that responds at the position of $B$, $\vec{R}_B$, to the source electric dipole dependent electric displacement field of excited body $A$, which is undergoing a $0 \leftarrow n$ transition. The interaction energy is

$$-\varepsilon_0^{-1}\mu_j^{n0}(B)e^{-i\omega_{0n}t}d_j^{(1)}(A; \vec{\mu}; \vec{R}_B, t). \tag{9.8}$$

It is interesting to note that to the leading order, the evaluation of the matrix element only requires knowledge of the field linear in the transition dipole moment. From (3.21) its 0–$n$th matrix element is

$$\left\langle 0\middle|d_j^{(1)}(A;\vec{\mu};\vec{R}_B,t)\middle|n\right\rangle = \frac{1}{4\pi}\mu_i^{0n}(A)e^{-ik_{n0}ct}\left(-\nabla^2\delta_{ij}+\nabla_i\nabla_j\right)\frac{e^{ik_{n0}(|\vec{R}_B-\vec{R}_A|)}}{|\vec{R}_B-\vec{R}_A|}, \tag{9.9}$$

which when substituted into (9.8) produces (9.4) on noting the definition of (9.5). This example clearly illustrates the facility of the response formalism. It has recently been generalized to account for transfer between species possessing electric and magnetic multipole moments of arbitrary order by utilizing expressions for the generalized electric displacement and magnetic field operators correct to first order in these moments [39].

### 9.2. *Van der Waals dispersion energy*

Perhaps the best known example illustrating the characteristic features of a fully quantum mechanical treatment when applied to two-body interactions is the celebrated evaluation of the van der Waals dispersion energy shift first performed by Casimir and Polder [61]. In an intricate time-dependent perturbation theory calculation in which the minimal-coupling Hamiltonian was utilized [8,61], they obtained the following formula for the dispersion energy shift between a pair of neutral, non-polar molecules $A$ and $B$ in their ground electronic states,

$$\Delta E = -\frac{\hbar c}{16\pi^3\varepsilon_0^2}\int_0^\infty \mathrm{d}u u^6 e^{-2uR}\alpha(A;iu)\alpha(B;iu)\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]. \tag{9.10}$$

Appearing in (9.10) is the isotropic dynamic electric dipole polarizability of species $\xi$ at the imaginary frequency $\omega = icu$ defined by

$$\alpha(\xi;iu) = \frac{1}{3}\sum_r |\vec{\mu}^{r0}(\xi)|^2\left\{\frac{1}{E_{r0}-i\hbar cu}+\frac{1}{E_{r0}+i\hbar cu}\right\}, \tag{9.11}$$

where $\vec{\mu}^{r0}(\xi)$ is the transition electric dipole moment of particle $\xi$ between electronic states $|r\rangle \leftarrow |0\rangle$, whose difference in energy, $E_{r0}=E_r-E_0$. Expression (9.10) holds for all intermolecular separation distances $\vec{R}=\vec{R}_B-\vec{R}_A$ outside the region of overlap of electronic charge distributions associated with each centre. Easily obtainable from (9.10) is the behaviour of the potential at asymptotic limits of large and small separation distance. In the former case $R$ is much larger than the characteristic reduced transition wavelength, and effecting this approximation leads to the far-zone result

$$\Delta E^{FZ} = -\frac{23\hbar c}{64\pi^3\varepsilon_0^2R^7}\alpha(A;0)\alpha(B;0), \tag{9.12}$$

exhibiting an inverse seventh power dependence on separation distance. Note the presence of static ($\omega \to 0$) atomic/molecular polarizabilities in this energy shift. Contrastingly, in the near-zone, where $kR \ll 1,$ on setting the exponential factor in (9.10) to unity, the leading term is given by [93]

$$\Delta E^{NZ} = -\frac{1}{24\pi^2 \varepsilon_0^2 R^6} \sum_{m,n} \frac{|\vec{\mu}^{m0}(A)|^2 |\vec{\mu}^{n0}(B)|^2}{E_{m0}^A + E_{n0}^B}. \tag{9.13}$$

The result (9.13) is immediately recognizable as the London dispersion energy formula. It is commonly derived using second order perturbation theory with the static dipolar interaction

$$V_{AB} = \frac{1}{4\pi\varepsilon_0 R^3} \mu_i(A)\mu_j(B)(\delta_{ij} - 3\hat{R}_i\hat{R}_j). \tag{9.14}$$

The $R^{-6}$ behaviour of the near-zone limit (9.13) is due to instantaneous propagation of light signals between the pair, and is the viewpoint adopted in the semi-classical picture. With all interparticle interactions being understood as originating from the exchange of electromagnetic influences, the weakening of the potential in the far-zone compared to its behaviour at short-range was attributed to retardation effects. Fluctuations in the dipolar charge distribution at one-centre are felt by the other body at delay times no earlier than $t - R/c$, a redistribution of charge having taken place after a duration of $2R/c$ that no longer coincides with the strength of the interaction at the initial time. Because the concept of the photon arises naturally within the QED formalism, light propagation occurs at the correct speed of $c$.

Since Casimir and Polder's pioneering calculation, considerable effort has been expended to re-evaluating their potential by simpler computational schemes and alternative physical viewpoints. These also help in further understanding the manifestation of dispersion forces. Significant improvement occurred with the adoption of the electric dipole approximated form of the multipolar Hamiltonian [8,13,15], whose interaction term is given by

$$H_{int} = -\varepsilon_0^{-1}\vec{\mu}(A)\cdot\vec{d}^{\perp}(\vec{R}_A) - \varepsilon_0^{-1}\vec{\mu}(B)\cdot\vec{d}^{\perp}(\vec{R}_B). \tag{9.15}$$

Now the result (9.10) is obtained via fourth-order time-dependent perturbation theory by summing over twelve two-photon exchange time-ordered diagrams that each contain four linear in the electric displacement field electron–photon coupling vertices [94].

A further advance in the perturbative calculation was made by Craig and Power [95]. They performed a canonical transformation on the multipolar Hamiltonian containing the interaction Hamiltonian (9.15). This yielded an effective two-photon coupling Hamiltonian of the form

$$H_{eff,\,int} = -\frac{1}{2\varepsilon_0^2} \sum_{\xi} \alpha_{ij}(\xi;0) d_i^{\perp}(\vec{R}_\xi) d_j^{\perp}(\vec{R}_\xi), \xi = A, B. \tag{9.16}$$

Pictorially this corresponds to the collapsing of two, one-photon interaction vertices at each centre to one particle–field coupling term that is quadratic in the electric displacement field operator. Instead of summing over twelve time-ordered diagrams, now only two graphs contribute to the energy shift, with the additional advantage that the leading order of perturbation theory that reproduces the result (9.12) is the second.

A number of other differing calculational approaches have been expounded over the years for the re-calculation of the Casimir–Polder potential, each with a unique physical basis. These include radiation reaction [96], coupling of induced moments [97], calculation in the Lorentz gauge [98], differences in zero-point energy of the electromagnetic field due to the presence and absence of a pair of interacting particles [99,100] and utilizing form factors from scattering theory [101].

One particularly simple conceptual method for the calculation of intermolecular interactions in general, that happens to bear a close resemblance to classical theory, and that utilizes the Maxwell field operators presented in Section 3, is the response formalism. This technique is now applied to the calculation of the retarded van der Waals dispersion force. The physical picture is one in which a test molecule responds, through its frequency dependent polarizability, to the Maxwell source fields of the other body. Both centres simultaneously take on the role of test body and source field. One noteworthy advantage of employing fields in a response theory is that the dispersion potential between electronically excited molecules, as well as for species in the ground state is easily calculated relative to perturbation theory methods. This is due to the facile identification, location and treatment of intermediate state resonances in the former approach. It should be remarked that the concept of an intermolecular interaction energy when one or both of the entities are excited is a valid one provided that the excited states are sufficiently long lived relative to photon propagation times between the two centres.

For electric dipole source and test species, the energy shift is given by

$$\Delta E = -\frac{1}{2\varepsilon_0^2}\alpha_{ij}(A;k)d_i^{\perp}(B;k;\vec{R}_A)d_j^{\perp}(B;k;\vec{R}_A) - \frac{1}{2\varepsilon_0^2}\alpha_{kl}(B;k)d_k^{\perp}(A;k;\vec{R}_B)d_l^{\perp}(A;k;\vec{R}_B), \tag{9.17}$$

with $A$ and $B$ located at $\vec{R}_A$ and $\vec{R}_B$ respectively, and internuclear separation distance vector $\vec{R} = \vec{R}_B - \vec{R}_A$. With $A$ and $B$ initially in excited electronic states $|p\rangle$ and $|q\rangle$, respectively, electric dipole allowed transitions can occur to intermediate states $|m\rangle$ and $|n\rangle$. Recalling that the electric displacement field in the vicinity of a molecule may be expanded in series of powers of the electric dipole moment, the dispersion potential between two electric dipole polarizable molecules is calculated from the expression

$$\begin{aligned}\Delta E = &-\frac{1}{2\varepsilon_0^2}\sum_n \alpha_{ij}(A;k_{qn})d_i^{(1)}(B;\vec{\mu};k_{qn};\vec{R}_A)d_j^{(1)}(B;\vec{\mu};k_{qn};\vec{R}_A)\\ &-\frac{1}{2\varepsilon_0^2}\sum_m \alpha_{kl}(B;k_{pm})d_k^{(1)}(A;\vec{\mu};k_{pm};\vec{R}_B)d_l^{(1)}(A;\vec{\mu};k_{pm};\vec{R}_B)\\ &-\frac{1}{2\varepsilon_0^2}\sum_{\vec{k},\lambda}\alpha_{ij}(A;k)\Big[d_i^{(0)}(k;\vec{R}_A)d_j^{(2)}(B;\vec{\mu}\vec{\mu};k;\vec{R}_A) + d_i^{(2)}(B;\vec{\mu}\vec{\mu};k;\vec{R}_A)d_j^{(0)}(k;\vec{R}_A)\Big]\\ &-\frac{1}{2\varepsilon_0^2}\sum_{\vec{k},\lambda}\alpha_{kl}(B;k)\Big[d_k^{(0)}(k;\vec{R}_B)d_l^{(2)}(A;\vec{\mu}\vec{\mu};k;\vec{R}_B) + d_k^{(2)}(A;\vec{\mu}\vec{\mu};k;\vec{R}_B)d_l^{(0)}(k;\vec{R}_B)\Big],\end{aligned} \tag{9.18}$$

after retaining the appropriate terms correct to second order in the transition electric dipole moments. Note that the product of the zeroth order field does not contribute to the energy shift as it is independent of the source, and is simply the zero-point energy term.

The contribution arising from the product of the vacuum and linear fields can be similarly neglected as its expectation value for the dispersion interaction causes a change in photon number. The first contributing term of (9.18), for instance, represents the response of species $A$ in electronic state $|p\rangle$ via its frequency dependent electric dipole polarizability at the frequency $\omega_{qn} = ck_{qn}$, $\alpha_{ij}(A; k_{qn})$, to the first order electric displacement field of molecule $B$ located at the position of molecule $A$, $\vec{R}_A$ in which the former undergoes an electric dipole allowed transition to intermediate states $|n\rangle$ from the initial state $|q\rangle$,

$$\alpha_{ij}(\xi; k) = \sum_m \left\{ \frac{\mu_i^{pm}(\xi)\mu_j^{mp}(\xi)}{E_{mp} - \hbar ck} + \frac{\mu_j^{pm}(\xi)\mu_i^{mp}(\xi)}{E_{mp} + \hbar ck} \right\}. \tag{9.19}$$

A similar interpretation may be applied to the other three terms in (9.18). Note once again the explicit appearance of the vacuum field in the last two terms of the energy shift, it interfering with the field quadratic in $\vec{\mu}$.

Using the electric displacement field operator linear in the electric dipole moment (3.21), the expectation value of the first two terms of (9.18) over the molecular states $|q\rangle$ and $|p\rangle$ respectively, with the radiation field in the vacuum state, is

$$\begin{aligned} &-\frac{1}{32\pi^2\varepsilon_0^2}\sum_n \alpha_{ij}(A; k_{qn})\mu_k^{qn}(B)\mu_l^{nq}(B)k_{qn}^6 \bar{f}_{ik}(k_{qn}R)f_{jl}(k_{qn}R) \\ &-\frac{1}{32\pi^2\varepsilon_0^2}\sum_m \alpha_{kl}(B; k_{pm})\mu_i^{pm}(A)\mu_j^{mp}(A)k_{pm}^6 \bar{f}_{ki}(k_{pm}R)f_{lj}(k_{pm}R). \end{aligned} \tag{9.20}$$

Examining the first term involving the product of free and second-order fields of $B$ in (9.18), noting that only the diagonal matrix element of the quadratic field (3.23) is required, produces

$$\begin{aligned} &-\frac{1}{2\varepsilon_0^2}\sum_{\vec{k},\lambda} \alpha_{ij}(A; k)d_i^{(0)}(k; \vec{R}_A)d_j^{(2)}(B; \vec{\mu}\vec{\mu}; k; \vec{R}_A) \\ &= \frac{1}{32\pi^2\varepsilon_0^2}\sum_n \mu_k^{qn}(B)\mu_l^{nq}(B)\frac{\mathrm{PV}}{2\pi i}\int_0^\infty \frac{\mathrm{d}kk^3}{k - k_{nq}}\alpha_{ij}(A; k)\big[-k^3 \bar{f}_{il}(kR)\bar{f}_{jk}(kR)e^{-2ikR} \\ &\quad - k_{nq}^3 f_{il}(kR)\bar{f}_{jk}(k_{nq}R)e^{ik(R-ct)}e^{ik_{qn}(R-ct)} + k_{nq}^3 \bar{f}_{il}(kR)\bar{f}_{jk}(k_{nq}R)e^{-ik(R+ct)}e^{ik_{qn}(R-ct)}\big] \\ &\quad - \frac{1}{32\pi^2\varepsilon_0^2}\sum_n \mu_k^{qn}(B)\mu_l^{nq}(B)\frac{\mathrm{PV}}{2\pi i}\int_0^\infty \frac{\mathrm{d}kk^3}{k - k_{qn}}\alpha_{ij}(A; k)\big[-k^3 \bar{f}_{il}(kR)\bar{f}_{jk}(kR)e^{-2ikR} \\ &\quad - k_{qn}^3 f_{il}(kR)\bar{f}_{jk}(k_{qn}R)e^{ik(R-ct)}e^{-ik_{qn}(R-ct)} + k_{qn}^3 \bar{f}_{il}(kR)\bar{f}_{jk}(k_{qn}R)e^{-ik(R+ct)}e^{-ik_{qn}(R-ct)}\big], \end{aligned} \tag{9.21}$$

where $k, l$-index symmetry has been used to eliminate the term without an exponential dependence, and PV denotes the Cauchy principal value. For a state for which $E_q > E_n$, the time-independent part of (9.21) on making the substitution $k = -iu$, is

$$\begin{aligned} &-\frac{1}{64\pi^2\varepsilon_0^2}\sum_n \alpha_{ij}(A; k_{qn})\mu_k^{qn}(B)\mu_l^{nq}(B)k_{qn}^6 \bar{f}_{ik}(k_{qn}R)f_{jl}(k_{qn}R) \\ &+ \frac{\hbar c}{64\pi^3\varepsilon_0^2}\int_0^\infty \mathrm{d}u u^6 e^{-2uR}\alpha_{ij}(A; icu)\alpha_{kl}(B; icu)f_{ik}(iuR)f_{jl}(iuR), \end{aligned} \tag{9.22}$$

while the time-dependent part is given by

$$-\frac{1}{64\pi^2\varepsilon_0^2}\sum_n \mu_k^{qn}(B)\mu_l^{nq}(B)(-k_{qn})^3\int_0^\infty \mathrm{d}u u^3\alpha_{ij}(A;\,icu)\left[\bar{f}_{il}(k_{nq}R)e^{ik_{qn}(R-ct)}f_{jk}(-iuR)\frac{e^{-uc(t-R/c)}}{u+ik_{qn}}\right.$$
$$-\bar{f}_{il}(k_{nq}R)e^{ik_{qn}(R-ct)}\bar{f}_{jk}(-iuR)\frac{e^{-uc(t+R/c)}}{u+ik_{qn}}+\bar{f}_{il}(k_{qn}R)e^{ik_{nq}(R-ct)}f_{jk}(-iuR)\frac{e^{-uc(t-R/c)}}{u-ik_{qn}}$$
$$\left.-\bar{f}_{il}(k_{qn}R)e^{ik_{nq}(R-ct)}\bar{f}_{jk}(-iuR)\frac{e^{-uc(t+R/c)}}{u-ik_{qn}}\right]. \tag{9.23}$$

For $t \gg R/c$ the time-dependent terms tend to zero as the integrals have exponentially decreasing values. Further, the average of (9.23) over a finite time interval tends to zero due to the modulation factors $e^{\pm ik_{qn}ct}$. Returning to (9.21) and evaluating the integral for $k_{nq} > 0$ produces for the time-independent part

$$\frac{1}{64\pi^2\varepsilon_0^2}\sum_n \alpha_{ij}(A;\,k_{qn})\mu_k^{qn}(B)\mu_l^{nq}(B)k_{qn}^6 f_{ik}(k_{qn}R)\bar{f}_{jl}(k_{qn}R)$$
$$+\frac{\hbar c}{64\pi^3\varepsilon_0^2}\int_0^\infty \mathrm{d}u u^6 e^{-2uR}\alpha_{ij}(A;\,icu)\alpha_{kl}(B;\,icu)f_{ik}(iuR)f_{jl}(iuR). \tag{9.24}$$

It is interesting to note that the first term of (9.22) is one-half the contribution of the first term of (9.20), while the first term of (9.24) (the pole contribution) is of opposite sign; the $u$-integral contribution, however, is identical. After calculating the contribution arising from

$$-\frac{1}{2\varepsilon_0^2}\sum_{\vec{k},\lambda}\alpha_{ij}(A;\,k)d_i^{(2)}(B;\,\vec{\mu}\vec{\mu};\,k;\,\vec{R}_A)d_j^{(0)}(k;\,\vec{R}_A)$$

and adding it to (9.22) and (9.24) it is seen that for those states $|n\rangle$ with $E_n > E_q$, the pole contribution has opposite sign to the first term of (9.20) and cancels it, while for states for which $E_n > E_q$, this term is doubled. This addition and cancellation of pole contributions from the zeroth and quadratic fields with terms from the product of the first order fields is identical to that which occurred in the computation of the energy density and Poynting vector presented earlier. Hence the energy shift (9.18) between two excited electric dipole polarizable molecules with fixed relative orientation is

$$\Delta E = -\frac{1}{16\pi^2\varepsilon_0^2}\sum_{\substack{n\\ E_q>E_n}} \alpha_{ij}(A;\,k_{qn})\mu_k^{qn}(B)\mu_l^{nq}(B)k_{qn}^6\bar{f}_{ik}(k_{qn}R)f_{jl}(k_{qn}R)$$
$$-\frac{1}{16\pi^2\varepsilon_0^2}\sum_{\substack{m\\ E_p>E_m}} \alpha_{kl}(B;\,k_{pm})\mu_i^{pm}(A)\mu_j^{mp}(A)k_{pm}^6\bar{f}_{ik}(k_{pm}R)f_{jl}(k_{pm}R)$$
$$+\frac{\hbar c}{32\pi^3\varepsilon_0^2}\int_0^\infty \mathrm{d}u u^6 e^{-2uR}\alpha_{ij}(A;\,icu)\alpha_{kl}(B;\,icu)f_{ik}(iuR)f_{jl}(iuR), \tag{9.25}$$

where the non-resonant (virtual photon) term has been counted only once. For a pair of isotropic molecules, the energy shift (9.25) on orientational averaging becomes [102]

$$\begin{aligned}\Delta E = &-\frac{1}{24\pi^2\varepsilon_0^2}\sum_{\substack{n\\E_q>E_n}}\alpha(A;k_{qn})|\vec{\mu}^{qn}(B)|^2k_{qn}^6\left[\frac{1}{k_{qn}^2R^2}+\frac{1}{k_{qn}^4R^4}+\frac{3}{k_{qn}^6R^6}\right]\\ &-\frac{1}{24\pi^2\varepsilon_0^2}\sum_{\substack{m\\E_p>E_m}}\alpha(B;k_{pm})|\vec{\mu}^{pm}(A)|^2k_{pm}^6\left[\frac{1}{k_{pm}^2R^2}+\frac{1}{k_{pm}^4R^4}+\frac{3}{k_{pm}^6R^6}\right].\\ &-\frac{\hbar c}{16\pi^3\varepsilon_0^2}\int_0^\infty \mathrm{d}u u^6e^{-2uR}\alpha(A;icu)\alpha(B;icu)\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]\end{aligned} \tag{9.26}$$

It is instructive to examine separately the three cases corresponding to both species in the ground electronic state, one molecule excited and one in the ground state, and both molecules excited. When both $A$ and $B$ are in the ground state, the first two terms of (9.26) vanish since only upward transitions from the initial state are now possible, leaving the $u$-integral term as the sole contribution,

$$\begin{aligned}\Delta E = &-\frac{1}{36\pi^3\varepsilon_0^2\hbar c}\sum_{m,n}|\vec{\mu}^{0m}(A)|^2|\vec{\mu}^{0n}(B)|^2\int_0^\infty\frac{\mathrm{d}uu^6e^{-2uR}k_{m0}k_{n0}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)}\\ &\times\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right],\end{aligned} \tag{9.27}$$

which is immediately recognizable as the Casimir–Polder [61] potential, first computed by them using time-dependent perturbation theory and the minimal-coupling Hamiltonian. The $R^{-7}$ far-zone limit is readily obtained from (9.27) by neglecting $u^2$ relative to $k_{m0}$ and $k_{n0}$ in the denominator and carrying out the $u$-integral,

$$-\frac{23\hbar c}{64\pi^3\varepsilon_0^2R^7}\alpha(A;0)\alpha(B;0) \tag{9.28}$$

and which, of course, is identical to the result obtained by evaluating the response of a test polarizable molecule to the field of the source producing the energy density (7.10), as well as to (9.12). At the other extreme of intermolecular separation, the expected London dispersion formula (9.13) results,

$$-\frac{1}{24\pi^2\varepsilon_0^2R^6}\sum_{m,n}\frac{|\vec{\mu}^{0m}(A)|^2|\vec{\mu}^{0n}(B)|^2}{(E_{m0}+E_{n0})}. \tag{9.29}$$

If now molecule $A$ is in the ground electronic state while $B$ remains excited [103], only the first and last terms of (9.26) survive, with the ground state polarizability of $A$ appearing in all of the expressions for the energy shift. At asymptotically large values of $R$ the leading term has an inverse square dependence arising from the pole contribution,

$$-\frac{1}{24\pi^2\varepsilon_0^2R^2}\sum_{\substack{n\\E_q>E_n}}\alpha(A;k_{qn})|\vec{\mu}^{qn}(B)|^2k_{qn}^4, \tag{9.30}$$

and corresponds to emission of a real photon from the excited state. This is the dominant contribution to the interaction energy in the far-zone since the limiting term arising from the $u$-integral has inverse seventh power dependence as in (9.28). When $R$ is much less than reduced characteristic transition wavelengths, the near-zone shift contains contributions from both the first and third terms of (9.26). The former is given by

$$-\frac{1}{8\pi^2\varepsilon_0^2R^6}\sum_{\substack{n\\E_q>E_n}}\alpha(A;k_{qn})|\vec{\mu}^{qn}(B)|^2, \tag{9.31}$$

while that from the $u$-integral term is

$$-\frac{1}{24\pi^2\varepsilon_0^2R^6}\sum_{m,n}\mathrm{sgn}\,(E_{nq})\frac{|\vec{\mu}^{0m}(A)|^2|\vec{\mu}^{qn}(B)|^2}{(E_{m0}+|E_{nq}|)}, \tag{9.32}$$

which on addition gives for the total short-range limit

$$-\frac{1}{24\pi^2\varepsilon_0^2R^6}\sum_{m,n}\frac{|\vec{\mu}^{0m}(A)|^2|\vec{\mu}^{qn}(B)|^2}{(E_{m0}+E_{nq})}, \tag{9.33}$$

and which contains contributions from both real and virtual photon terms.

As noted previously, when both molecules are excited, all three terms of (9.26) are present. This energy shift can be decomposed into three types of terms depending on whether the transitions $m \leftarrow p$ and $n \leftarrow q$ are both upward, one upward and one downward, or both downward. The first two cases have already been dealt with, respectively corresponding to the dispersion interaction when both molecules are in the ground state, and the energy shift between a ground and an excited state molecule. The formulae are the same except for replacement of the appropriate polarizability. The asymptotic limits of the downward transition contribution to the energy shift between two excited molecules are readily obtained from (9.26). The form of the near-zone potential is

$$\begin{aligned}
&-\frac{1}{12\pi^2\varepsilon_0^2\hbar cR^6}\sum_{\substack{n\\E_q>E_n}}k_{mp}\frac{|\vec{\mu}^{pm}(A)|^2|\vec{\mu}^{qn}(B)|^2}{k_{mp}^2-k_{nq}^2}-\frac{1}{12\pi^2\varepsilon_0^2\hbar cR^6}\sum_{\substack{m\\E_p>E_m}}k_{nq}\frac{|\vec{\mu}^{pm}(A)|^2|\vec{\mu}^{qn}(B)|^2}{k_{nq}^2-k_{mp}^2}\\
&-\frac{1}{24\pi^2\varepsilon_0^2\hbar cR^6}\sum_{m,n}(\mathrm{sgn}\,k_{nq})(\mathrm{sgn}\,k_{mp})\frac{|\vec{\mu}^{pm}(A)|^2|\vec{\mu}^{qn}(B)|^2}{(|k_{nq}|+|k_{mp}|)}\\
&\quad=-\frac{1}{24\pi^2\varepsilon_0^2R^6}\sum_{\substack{m,n\\E_q>E_n\\E_p>E_m}}\frac{|\vec{\mu}^{pm}(A)|^2|\vec{\mu}^{qn}(B)|^2}{(E_{mp}+E_{nq})},
\end{aligned} \tag{9.34}$$

exhibiting familiar $R^{-6}$ behaviour. For large $R$ the dominant term is proportional to $R^{-2}$, arising solely from the first two terms of (9.26), and simplifying to

$$-\frac{1}{36\pi^2\varepsilon_0^2(\hbar c)^4R^2}\sum_{\substack{m,n\\E_q>E_n\\E_p>E_m}}\frac{|\vec{\mu}^{pm}(A)|^2|\vec{\mu}^{qn}(B)|^2}{(E_{pm}+E_{qn})}E_{qn}E_{pm}(E_{qn}^2+E_{qn}E_{pm}+E_{pm}^2). \tag{9.35}$$

It is worth pointing out that when one or both of the molecules are excited, the additional contributions to the energy shift arising from the downward transitions dominate, and can result in a repulsive force. The sign of the interaction energy depends on the relative magnitudes of the relevant transition energies of the two molecules involved.

The advantages conferred by employing the quantum electrodynamical Maxwell field operators in a response theory computation of intermolecular energy shifts is clearly evident by the ease with which interactions between ground as well as excited molecules can be obtained in a single formulation. Potentials between electronically excited molecules especially are not easily found by conventional perturbation theory methods due to the presence of intermediate state resonances. In the response formalism the poles are easily isolated and readily accounted for because the source fields automatically include contributions arising from transitions involving a real photon. In addition, the role of the source free radiation field and the necessity of including fields quadratic in the transition moments are brought to the fore in this approach. The method is easily extended to the calculation of intermolecular energy shifts between molecules possessing higher multipole polarizability characteristics such as magnetic dipole susceptible and electric quadrupole polarizable bodies. All that is required are the relevant first and second order electric displacement and magnetic field operators in the vicinity of the source moment, and these are available for the first few lowest order multipole moments [38,39,104] including the contribution from the diamagnetic coupling term [63,64,67–70]. For the response of one molecule $\xi$ to the field of the second $\xi'$, the extension of (9.17) is

$$\begin{aligned}\Delta E = &-\frac{1}{2\varepsilon_0^2}\alpha_{ij}(\xi;k)d_i^{\perp}(\xi';k;\vec{R}_\xi)d_j^{\perp}(\xi';k;\vec{R}_\xi) - \frac{1}{2\varepsilon_0}G_{ij}(\xi;k)d_i^{\perp}(\xi';k;\vec{R}_\xi)b_j(\xi';k;\vec{R}_\xi)\\ &-\frac{1}{2}\chi_{ij}(\xi;k)b_i(\xi';k;\vec{R}_\xi)b_j(\xi';k;\vec{R}_\xi) - \frac{1}{2\varepsilon_0^2}A_{ijk}(\xi;k)d_i^{\perp}(\xi';k;\vec{R}_\xi)\nabla_k d_j^{\perp}(\xi';k;\vec{R}_\xi)\\ &-\frac{1}{2\varepsilon_0^2}\Theta_{ijkl}(\xi;k)\nabla_j d_i^{\perp}(\xi';k;\vec{R}_\xi)\nabla_l d_k^{\perp}(\xi';k;\vec{R}_\xi) + \cdots \end{aligned} \qquad (9.36)$$

where $G_{ij}$ is the mixed electric–magnetic dipole polarizability, the susceptibility $\chi_{ij}$ is the magnetic dipole analogue of $\alpha_{ij}$, $A_{ijk}$ is the mixed electric dipole–quadrupole response tensor, and $\Theta_{ijkl}$ is the pure electric quadrupole polarizability. Many of these higher-order terms have been computed for interactions involving both ground and excited pairs of molecules using the response formalism [104], providing results that agree with perturbation theory methods, but are obtained more efficiently.

### 9.3. *Non-additive dispersion forces*

Forces between particles are called additive if the total interaction energy, $\Delta E$, of an ensemble of $N$ bodies is given by the sum of pairwise contributions $\Delta E_{ij}$, such that

$$\Delta E = \sum_{i>j}^{N} \Delta E_{ij}. \qquad (9.37)$$

This property of additivity is valid as long as each charge remains fixed in space. If, however, the centres of charge distribution are localized but their orientations are allowed to vary, additivity is lost. Non-additivity first appears in the intermolecular interaction between three bodies. In the calculation of the dispersion force of such a triple of particles, the dispersion energy shift is not simply the sum of the dispersion energies of the three pairwise terms, but also includes a non-additive three-body contribution. Inclusion of pair and many-body terms are therefore required for the successful explanation of van der Waals forces as they apply to phenomena such as surface tension of liquids and heats of sublimation of crystals Ref. [74] Chapter 5, [105]. Thus for a system of three interacting molecules $A$, $B$ and $C$, the dispersion energy shift is composed of

$$\Delta E = \Delta E_{AB} + \Delta E_{BC} + \Delta E_{CA} + \Delta E_{ABC}, \tag{9.38}$$

where the first three terms represent the contributions to the interaction energy arising from pairwise interactions between two of the three bodies, and whose evaluation using MQED techniques is well known, with one such approach, namely response theory having been detailed in the last subsection of this review. The last term of (9.38), $\Delta E_{ABC}$, is the non-additive three-body term. This contribution was first computed independently by Axilrod and Teller [106] and by Muto [107]. They used third-order perturbation theory and a static dipolar coupling potential between pairs of particles, extending the calculation of the two-body dispersion energy first performed quantum mechanically by London [93]. $\Delta E$ was evaluated for a variety of three-body configurations such as a triangle (equilateral and right), a collinear arrangement of $A$, $B$ and $C$, and for one molecule far removed from the other two.

For a triangular arrangement of molecules $ABC$, with separation distance $\vec{R}_{AB}$, $\vec{R}_{BC}$, and $\vec{R}_{CA}$, with internal angles $\theta_A$, $\theta_B$, and $\theta_C$ opposite sides $BC$, $CA$ and $AB$, respectively, the triple dipole interaction energy is given by [108]

$$\Delta E_{ABC} = \frac{3\hbar}{\pi(4\pi\varepsilon_0)^2}\int_0^\infty du\,\alpha(A;iu)\alpha(B;iu)\alpha(C;iu)\frac{(1+3\cos\theta_A\cos\theta_B\cos\theta_C)}{R_{AB}^3R_{BC}^3R_{CA}^3}, \tag{9.39}$$

where $\alpha(\xi;iu)$ is the familiar electric dipole polarizability of species $\xi$ at imaginary frequency $\omega = icu$. For most obtuse triangles the sign of (9.39) is negative while for acute triangles the triple dipole dispersion energy is positive. $\Delta E_{ABC}$ is also negative for linear arrangements of $A$, $B$ and $C$. Inclusion of (9.39) in (9.38) was found to be crucial in resolving the large discrepancies observed between experimental third virial coefficients, $C(T)$ and those calculated using only pairwise additive terms, especially for rare gas atoms, for example, with $C(T)$ being more sensitive to the form of the intermolecular potential than the second virial coefficient, $B(T)$. Non-additive three- and many-body terms also make a significant contribution to condensed phase systems where atomic and molecular centres are in close proximity to one another. This was the case for lattice energies of inert gases, where it was found that the Axilrod–Teller–Muto three-body non-additive term could not be ignored. In general, the contribution from the triple dipole correction is positive for the majority of molecular configurations in the liquid and solid state [109].

With retardation effects automatically accounted for in QED, use of an interaction Hamiltonian that is linear in the electric displacement field will double the order of perturbation theory required for the evaluation of pair and three-body contributions to the dispersion energy relative to semi-classical theory. Hence the fourth-order energy shift formula is required for the computation of the Casimir–Polder potential, and the sixth-order result for the calculation of the retardation corrected Axilrod–Teller–Muto triple dipole dispersion energy in the multipolar formalism. The latter was first calculated by Aub and Zienau [110] using S-matrix theory, with the Axilrod–Teller–Muto functional form resulting at short intermolecular separation distances. In an alternative derivation of the three-body dispersion potential including the effects of the finite speed of propagation of light signals, McLachlan [111] accounted for the coupling of $A$ and $B$ with the electromagnetic field and computed the interaction of $C$ to this composite $A+B+$field system using second order perturbation theory. In a variant of this approach, to be presented below, Power and Thirunamachandran [112] used a form of response theory to calculate three- and many-body dispersion potentials by evaluating the response of one molecule to the Maxwell fields produced by an aggregate of remaining $N-1$ species, with each particle in the collection taking on the role of test body.

The advantages offered on using a response theory formalism for the calculation of resonance energy transfer and dispersion forces between a molecular pair has been clearly demonstrated. The same is also true when three and higher non-additive contributions to the dispersion energy are evaluated. Now the response of one molecule to the displacement field of a molecular assembly is calculated with permutational symmetry being invoked to ensure that each species is acting as a test molecule once only.

The displacement field is again expanded as a sum over modes

$$d_i(\vec{r},t) = \frac{i}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left[e_j^{(\lambda)}(\vec{k})\alpha(0)e^{-i\omega t}F_{ij}(\vec{k},\vec{r}) - \bar{e}_j^{(\lambda)}(\vec{k})\alpha^{\dagger}(0)e^{i\omega t}\bar{F}_{ij}(\vec{k},\vec{r})\right], \tag{9.40}$$

with the mode sum satisfying the equation

$$(\nabla^2 + k^2)F_{ij}(\vec{k},\vec{r}) = -\varepsilon_0^{-1}\sum_{\xi}\alpha_{rs}(\xi;k)(-\nabla^2\delta_{is} + \nabla_i\nabla_s)F_{rj}(\vec{k},\vec{r})\delta(\vec{r}-\vec{R}_{\xi}), \tag{9.41}$$

whose solutions are given by

$$F_{ij}(\vec{k},\vec{r}) = F_{ij}^{(0)}(\vec{k},\vec{r}) + \varepsilon_0^{-1}\sum_{\xi}\alpha_{rs}(\xi;k)(-\nabla^2\delta_{is} + \nabla_i\nabla_s)\frac{e^{ik|\vec{r}-\vec{R}_{\xi}|}}{|\vec{r}-\vec{R}_{\xi}|}F_{rj}(\vec{k},\vec{R}_{\xi}), \tag{9.42}$$

where $F_{ij}^{(0)}(\vec{k},\vec{r})$ is the solution of the corresponding homogeneous equation, namely that for the free radiation field

$$F_{ij}^{(0)}(\vec{k},\vec{r}) = \delta_{ij}e^{i\vec{k}\cdot\vec{r}}. \tag{9.43}$$

Iterating (9.42) and inserting into (9.40) generates a power series solution for the displacement field in terms of the polarizabilities.

The extension of (9.17) to $N$ molecules each of which responds to the Maxwell field of the remaining bodies is

$$\begin{aligned}\Delta E &= -\frac{1}{2\varepsilon_0^2 N}\sum_{P}\alpha_{i_1j_1}(P_1;\xi;k)\left\langle 0\middle|d_{i_1}(\vec{R}_{P_1})d_{j_1}(\vec{R}_{P_1})\middle|0\right\rangle\\ &= -\frac{1}{2\varepsilon_0^2 N}\sum_{P}\alpha_{i_1j_1}(P_1;\xi;k)\sum_{\vec{k},\lambda}\frac{1}{16\pi^2}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)e_r^{(\lambda)}(\vec{k})\bar{e}_s^{(\lambda)}(\vec{k})F_{i_1r}(\vec{k},\vec{R}_{P_1})\bar{F}_{j_1s}(\vec{k},\vec{R}_{P_1}),\end{aligned} \tag{9.44}$$

where $\sum_P$ stands for the summation over all permutations

$$P \equiv \begin{bmatrix} 1 & 2 & 3 & \cdots & N \\ P_1 & P_2 & P_3 & \cdots & P_N \end{bmatrix}. \tag{9.45}$$

In the upper line the objects to be permuted are written in their natural order while the second line denotes the order that results on carrying out the permutation in question [113]. Carrying out the polarization sum, converting the wavevector sum to an integral and performing the angular average results in the following expression for the $N$-body energy shift

$$\begin{aligned} \Delta E = &-\frac{\hbar c}{64\pi^3 \varepsilon_0^2 iN} \sum_P \int_0^\infty \mathrm{d}k \alpha_{i_1 j_1}(P_1, k) \alpha_{i_2 j_2}(P_2, k) \ldots \alpha_{i_N j_N}(P_N, k) \\ &\times \left[\gamma_{i_1 j_2}(k) \gamma_{i_2 j_2}(k) \ldots \gamma_{i_N j_1}(k) - \bar{\gamma}_{i_1 j_2}(k) \bar{\gamma}_{i_2 j_2}(k) \ldots \bar{\gamma}_{i_N j_1}(k)\right], \end{aligned} \tag{9.46}$$

where

$$\gamma_{i_a j_b}(k) = \left(-\nabla^2 \delta_{i_a j_b} + \nabla_{i_a} \nabla_{j_b}\right) \frac{e^{ikR_{P_a P_b}}}{R_{P_a P_b}}, \tag{9.47}$$

with $\vec{R}_{P_a P_b} = |\vec{R}_{P_b} - \vec{R}_{P_a}|$, and on which the gradient operators act.

For $N = 2$, formula (9.46) results in the two-body Casimir–Polder potential (9.10). Similarly, for $N = 3$ the retarded three-body non-additive contribution to the dispersion potential follows

$$\begin{aligned} \Delta E^{(3)} = &-\frac{\hbar c}{32\pi^3 \varepsilon_0^2} \left(-\nabla^2 \delta_{ij} + \nabla_i \nabla_j\right)^a \frac{1}{a} \left(-\nabla^2 \delta_{jk} + \nabla_j \nabla_k\right)^b \frac{1}{b} \left(-\nabla^2 \delta_{ik} + \nabla_i \nabla_k\right)^c \frac{1}{c} \\ &\times \int_0^\infty \alpha(A; icu) \alpha(B; icu) \alpha(C; icu) e^{-u(a+b+c)} \mathrm{d}u, \end{aligned} \tag{9.48}$$

where $\vec{a}, \vec{b}$ and $\vec{c}$ denote vector displacements between the molecular centres according to $\vec{a} = \vec{R}_B - \vec{R}_C, \vec{b} = \vec{R}_C - \vec{R}_A,$ and $\vec{c} = \vec{R}_A - \vec{R}_B$. On evaluating the $u$-integral (9.48) becomes

$$\begin{aligned} &-\frac{1}{32\pi^3 \varepsilon_0^2 \hbar^2 c^2} \left(\frac{2}{3}\right)^3 \left(-\nabla^2 \delta_{ij} + \nabla_i \nabla_j\right)^a \frac{1}{a} \left(-\nabla^2 \delta_{jk} + \nabla_j \nabla_k\right)^b \frac{1}{b} \left(-\nabla^2 \delta_{ik} + \nabla_i \nabla_k\right)^c \frac{1}{c} \\ &\times \sum_{r,s,t} |\vec{\mu}^{r0}(A)|^2 |\vec{\mu}^{s0}(B)|^2 |\vec{\mu}^{t0}(C)|^2 \left\{ \frac{k_{s0} k_{t0}}{(k_{s0}^2 - k_{r0}^2)(k_{t0}^2 - k_{r0}^2)} f[k_{r0}(a+b+c)] \right. \\ &\left. + \frac{k_{r0} k_{t0}}{(k_{r0}^2 - k_{s0}^2)(k_{t0}^2 - k_{s0}^2)} f[k_{s0}(a+b+c)] + \frac{k_{r0} k_{s0}}{(k_{r0}^2 - k_{t0}^2)(k_{s0}^2 - k_{t0}^2)} f[k_{t0}(a+b+c)] \right\}, \end{aligned} \tag{9.49}$$

where $r$, $s$, and $t$ are the excited electronic states of $A$, $B$ and $C$ respectively, and the function $f(x)$ is [114]

$$f(x) = ci(x) \sin(x) - si(x) \cos(x). \tag{9.50}$$

After the usual approximations, the asymptotic limits of the energy shift are readily obtained. The far-zone result is of the form

$$\begin{aligned}\Delta E_{FZ}^{(3)} = &-\frac{1}{(4\pi\varepsilon_0)^2}\left(\frac{\hbar c}{\pi}\right)\alpha(A;0)\alpha(B;0)\alpha(C;0)\\ &\times\int_0^\infty[-C(au)\delta_{ij}+D(au)\hat{a}_i\hat{a}_j][-C(bu)\delta_{jk}+D(bu)\hat{b}_j\hat{b}_k]\\ &\times[-C(cu)\delta_{ik}+D(cu)\hat{c}_i\hat{c}_k]e^{-(a+b+c)u}\frac{\mathrm{d}u}{abc},\end{aligned}\tag{9.51}$$

where the static polarizabilities appear, and

$$C(x) = 1 + x + x^2,\tag{9.52}$$

and

$$D(x) = 3 + 3x + x^2.\tag{9.53}$$

In the near-zone, the potential is

$$\begin{aligned}\Delta E_{NZ}^{(3)} &= \frac{\hbar c}{32\pi^3\varepsilon_0^2}(\delta_{ij}-3\hat{a}_i\hat{a}_j)(\delta_{jk}-3\hat{b}_j\hat{b}_k)(\delta_{ik}-3\hat{c}_i\hat{c}_k)\frac{1}{a^3b^3c^3}\int_0^\infty \mathrm{d}u\,\alpha(A;icu)\alpha(B;icu)\alpha(C;icu)\\ &= \frac{1}{72\pi^2\varepsilon_0^2\hbar^2c^2}\sum_{r,s,t}|\vec{\mu}^{r0}(A)|^2|\vec{\mu}^{s0}(B)|^2|\vec{\mu}^{t0}(C)|^2\frac{1}{a^3b^3c^3}\Big[1-3(\hat{b}\cdot\hat{c})(\hat{c}\cdot\hat{a})(\hat{a}\cdot\hat{b})\Big]\\ &\quad\times\frac{(k_{r0}+k_{s0}+k_{t0})}{(k_{r0}+k_{s0})(k_{s0}+k_{t0})(k_{t0}+k_{r0})},\end{aligned}\tag{9.54}$$

which is the Axilrod–Teller–Muto energy shift first calculated using static dipolar coupling potentials. Depending on the geometry, the three-body potential can be either repulsive, as for an equilateral triangle configuration in the far-zone in which $a = b = c = R$, or attractive as in a linear arrangement of three molecules with $2a = 2b = c = R$. This compares with the pairwise dispersion potential which is always attractive for ground state molecules. Explicit results for these situations, as well as for the four-body term including a regular tetrahedral spatial distribution, may be found in Ref. [100], and for the three-body case in Ref. [115].

## 10. Summary

In this review, the quantum field theory formulation of the interaction of electromagnetic radiation with non-relativistic matter – molecular quantum electrodynamics – and applications, have been presented. For the description of electron and photon wavefields, a treatment using the techniques of second quantization, carried out in the Heisenberg representation of quantum mechanics is the most appropriate. This picture allows the two most commonly used quantum electrodynamical Hamiltonians for the coupled system, namely the minimal- and multipolar-coupling versions to be written in terms of fermion and boson creation and annihilation operators, whose time evolution is found by integrating the Heisenberg operator equations of motion. By restricting the analysis to the electric dipole approximation, the Maxwell field operators in the proximity of the source moment are expanded as a power series solution and calculated up to terms quadratic in the transition electric dipole moment. The resulting electromagnetic fields in the two schemes are compared and contrasted, and their properties are discussed. It was shown that the free fields are the same for all times $t > r/c > 0$, while the source dependent minimal- and multipolar-coupling fields are the same for all times, despite the fact that the time-dependent behaviour of the dynamical variables in the two formulations are different because they are governed by different Hamiltonian operators. One notable advantage of working in the Heisenberg picture is the ready evaluation of the Maxwell fields of a moving source, be it a charge, dipole, quadrupole, . . . , over alternative methods involving the direct integration of Maxwell's equations, as detailed in Section 5. A number of observables associated with the QED radiation fields were also calculated from the formulae obtained, and these included the Poynting vector and the electromagnetic energy density. In both cases the importance of including the contribution arising from second order fields was highlighted.

An especially advantageous aspect of the field theoretic approach is in the utilization of the source dependent fields to calculate long-range interactions between molecules using a response theory formalism, in which one species responds through its multipole moments to the Maxwell fields of one or more source molecules. This approach enables energy transfer rates between donor–acceptor pairs and dispersion energy shifts between two polarizable molecules, none, one or both of which may be electronically excited, to be calculated straightforwardly relative to more commonly used diagrammatic perturbation theory methods. When the latter, for example, is employed to calculate the dispersion force, summation over a dozen time-ordered graphs is required, and when one or both entities are in excited states, care must be taken to properly identify and locate poles in the energy denominator expressions corresponding to emission of real photons. The response theory between pairs of molecules has the additional advantage of being easily extended to deal with non-additive contributions to the dispersion potential arising between three-, four- and many-body systems, the leading term giving the retarded correction to the Axilrod–Teller–Muto triple dipole interaction energy.

In all aspects of the formulation of molecular QED in the Heisenberg representation, additional valuable insight is gained into radiation–molecule and molecule–molecule processes over that carried out in the more frequently adopted Schrödinger picture.

## Acknowledgements

This work was (partially) supported by the National Science Foundation through a grant for the Institute for Theoretical Atomic, Molecular and Optical Physics at Harvard University and Smithsonian Astrophysical Laboratory. The author gratefully acknowledges the award of a Visiting Fellowship at ITAMP and the hospitality accorded to him there.

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