INTERMOLECULAR INTERACTIONS USING

MOLECULAR QUANTUM ELECTRODYNAMICS

by

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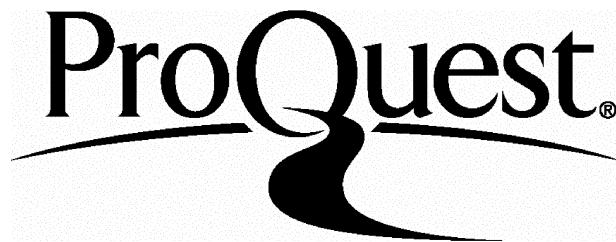
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"Mathematics is the tool specially suited for dealing with abstract concepts of any kind and there is no limit to its power in this field. For this reason a book on the new physics, if not purely descriptive of experimental work, must be essentially mathematical. All the same the mathematics is only a tool and one should learn to hold the physical ideas in one's mind without reference to the mathematical form."

P.A.M. Dirac,
The Principles of Quantum Mechanics,
Oxford University Press, Oxford, 1958.

ABSTRACT

The physical theory describing the interaction of electromagnetic radiation with atoms and molecules, molecular quantum electrodynamics, is applied to problems in intermolecular interactions and optical activity.

After an outline of the basic Coulomb gauge theory in Chapter 1, the quantum electrodynamical Maxwell field operators in the vicinity of a molecule are derived in Chapter 2 in both the multipolar and minimal-coupling frameworks in the Heisenberg picture. The electromagnetic field operators are expanded in powers of the transition moments, correct up to second order in the sources with the interaction Hamiltonian including electric dipole and quadrupole, magnetic dipole and diamagnetic coupling terms.

The Maxwell field operators in the multipolar form are then used in Chapter 3 to calculate the Thompson energy density and the Poynting vector associated with the electromagnetic field. The equivalence of the expectation value of both these operators obtained using the minimal-coupling Maxwell fields in the electric dipole approximation is demonstrated.

The energy of interaction between two neutral molecules in ground or excited electronic states is determined in Chapter 4 using molecular response theory. The response of a polarisable test body to the electric displacement and magnetic fields of a second source molecule is calculated. Discriminatory interaction energies dependent upon the handedness of the pair of molecules are found. The energy shift is expressed in terms of pure and mixed multipole polarisabilities and is valid for all separation distances beyond overlap of electronic wavefunctions for molecules with fixed relative and random orientations.

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The near- and far-zone behaviour is also examined.

In the final Chapter a theory for the chiroptical phenomenon molecule induced circularly polarised luminescence is presented. The difference in the rate of emission of a left-/right-circularly polarised photon from an achiral molecule through intermolecular interaction with a chiral species is calculated.

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CONTENTS

CHAPTER 1

COULOMB GAUGE QUANTUM ELECTRODYNAMICS

1.1 INTRODUCTION

Quantum electrodynamics (QED) is the physical theory that describes the interaction of matter with electromagnetic fields and the interaction between atoms and molecules.

The origins of QED lie in the fundamental paper by Dirac [1] in which the radiation field is treated quantum mechanically. This process, known as second quantisation, gives rise to the quantised particle of radiation called the photon. The need for a quantum field theory arose from the singular failure of semi-classical theory to account for spontaneous emission. The quantum theory of radiation not only enabled the Einstein A- and B-coefficients to be derived in a straightforward manner, but further accounted for previously inexplicable phenomena such as the anomalous magnetic moment of the electron, and the Lamb shift, where the agreement between theory and experiment has been excellent. Of the theories currently available, QED, either formulated using traditional field theory or the alternative space-time approach due to Feynman [2,3], provides the most accurate description of photon-electron interactions known so far.

The characteristic feature of QED is that the electromagnetic field, as well as the system of particles, is quantised, so that light and matter together constitute a closed dynamical system that is subject to quantum mechanical rules. Instead of considering an atom or molecule and the radiation field with which it interacts as two distinct entities, a single system is examined whose total energy is given by the energy of the atom alone, the electromagnetic energy of the radiation

field alone and a small term representing the coupling energy of the particles and the field.

In chemical physics, where the problem is the coupling of radiation with particles of low energy, a non-covariant formulation of QED is sufficient. A theory of the emission and absorption of radiation and of the reaction of the radiation field on the system has been built up on the basis of a dynamics which is not relativistic [1,4]. This is on account of the time being treated throughout as a c-number instead of symmetrically with the space coordinates. Molecular QED is the non-relativistic limit of QED, and is applied to systems involving bound electrons of low binding energies moving with velocities insignificant to that of light, making it ideally suited to the study of problems of chemical interest. To facilitate the use of molecular QED in the non-covariant version, the Coulomb gauge condition is employed throughout, allowing separation of the dynamic and static aspects of the sources of the field.

QED may be formulated in either the Schrödinger or Heisenberg representations. Almost all the applications of molecular QED to date have been investigated in the more familiar Schrödinger picture. In this thesis, the alternative Heisenberg viewpoint is employed in dealing with radiation-molecule interactions.

A wide range of applications of molecular QED to problems in theoretical chemistry have not only provided new results but also important insight into fundamental physical processes. These include, amongst others, light scattering, intermolecular forces, and with the recent advent of laser sources as probes of atomic and molecular structure, non-linear optical phenomena and quantum optics. These and various other applications, as well as the theoretical foundations of the subject have been discussed in texts and review articles such as

those by Power [5], Craig and Thirunamachandran [6,7], Healy [8], Andrews *et al.* [9], Woolley [10], Cohen-Tannoudji *et al.* [11] and the compilation by Schwinger [12].

After a brief outline of the basic QED theory in the subsequent Section, a detailed exposition in the Heisenberg framework is given in Chapter 2.

1.2 BASIC THEORY

Consider a collection of slowly moving charged particles α of charge e_α, mass m_α with position $\vec{q}_\alpha$ and velocity $\dot{\vec{q}}_\alpha$, interacting with the radiation field of vector potential $\vec{a}(\vec{r})$ subject to the Coulomb gauge condition

$$\vec{\nabla}.\vec{a}(\vec{r}) = 0. \tag{1.2.1}$$

Classically, the total system is described by the Lagrangian [13]

$$L = 1/2\sum_\alpha m_\alpha \dot{\vec{q}}_\alpha^2 - V + \frac{\varepsilon_0}{2}\int\left\{\dot{\vec{a}}(\vec{r})^2 - c^2(\vec{\nabla}\times\vec{a}(\vec{r}))^2\right\}d^3\vec{r} + \int\vec{j}^\perp(\vec{r}).\vec{a}(\vec{r})d^3\vec{r} \tag{1.2.2}$$

in which V is the electrostatic potential energy and $\vec{j}^\perp(\vec{r})$ is the transverse part of the total current density

$$\vec{j}(\vec{r}) = \sum_\alpha e_\alpha \dot{\vec{q}}_\alpha \delta(\vec{r}-\vec{q}_\alpha). \tag{1.2.3}$$

The Lagrangian is expressed as the sum of three terms, one each for the particles, for the field and for the interaction between them. The

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Lagrangian is a function of the coordinates and velocities of the particle and a functional of the corresponding field "coordinates and velocities". In the absence of interaction, only the particles Lagrangian and the free field Lagrangian remain, with the dynamics of one system not affecting that of the other. The two systems move independently and have equations of motion that are not coupled to one another. When the particles and field interact, the coupling appears as an interaction term in the Lagrangian. The specific choice of Lagrangian is such that it leads to the correct equations of motion. By invoking Hamilton's principle through the calculus of variations, the solutions of which are Lagrange's equations of motion [14], it can be shown, that in this case the equations of motion lead to the Lorentz force for particles (1.2.4) and to Maxwell's equations, with sources, for the radiation field (1.2.5).

$$m_\alpha \ddot{q}_{i\alpha} = - \frac{\partial V}{\partial q_{i\alpha}} + e_\alpha (e_i^\perp(\vec{q}_\alpha) + [\dot{\vec{q}}_\alpha \times \vec{b}(\vec{q}_\alpha)]_i) \qquad (1.2.4)$$

$$\vec{\nabla} \cdot \vec{e}(\vec{r}) = \frac{\rho(\vec{r})}{\varepsilon_0}$$

$$\vec{\nabla} \cdot \vec{b}(\vec{r}) = 0$$

$$\qquad (1.2.5)$$

$$\vec{\nabla} \times \vec{e}(\vec{r}) = - \frac{\partial \vec{b}(\vec{r})}{\partial t}$$

$$c^2 \vec{\nabla} \times \vec{b}(\vec{r}) = \frac{\partial \vec{e}(\vec{r})}{\partial t} + \frac{1}{\varepsilon_0} \vec{j}(\vec{r}).$$

The electric and magnetic field vectors $\vec{e}(\vec{r})$ and $\vec{b}(\vec{r})$ are related to the vector potential through the relations

$$\vec{e}^{\perp}(\vec{r}) = -\dot{\vec{a}}(\vec{r}) \tag{1.2.6}$$

$$\vec{b}(\vec{r}) = \vec{\nabla} \times \vec{a}(\vec{r}). \tag{1.2.7}$$

The transverse component of $\vec{e}(\vec{r})$ is a consequence of the gauge condition (1.2.1). The charge density is

$$\rho(\vec{r}) = \sum_{\alpha} e_{\alpha} \delta(\vec{r} - \vec{q}_{\alpha}). \tag{1.2.8}$$

The equations of motion may be written in an alternative manner by starting from an arbitrary gauge with the introduction of the electromagnetic potentials [15,16], which also aid the subsequent quantisation of the electromagnetic field. From the second equation of (1.2.5) it is seen that the definition of the vector potential (1.2.7) still holds. Substituting this into the third equation of (1.2.5) and noting that a vector whose curl is zero can be defined as the gradient of a scalar function,

$$\vec{e}(\vec{r}) + \dot{\vec{a}}(\vec{r}) = -\vec{\nabla}\phi(\vec{r}) , \tag{1.2.9}$$

where $\phi(\vec{r})$ is the scalar potential. The electromagnetic potentials as defined by (1.2.6) and (1.2.7) are not unique, being determined up to an additive gauge function χ, expressed in the gauge transformation

$$\left.\begin{array}{l} \vec{a}(\vec{r}) \Rightarrow \vec{a}(\vec{r}) + \vec{\nabla}\chi \\[2mm] \phi(\vec{r}) \Rightarrow \phi(\vec{r}) - \dfrac{\partial \chi}{\partial t} \end{array}\right\} , \tag{1.2.10}$$

a substitution which leaves the fields $\vec{e}(\vec{r})$ and $\vec{b}(\vec{r})$ invariant. Since

the treatment of atoms and molecules requires an explicit Coulomb potential term in the Hamiltonian, the choice of χ given by

$$\nabla^2 \chi = -\vec{\nabla}.\vec{a}(\vec{r}) \qquad (1.2.11)$$

leads to the Coulomb gauge defined earlier. The equations of motion in terms of the potentials are obtained from the remaining Maxwell equations after decomposition of the electric field into longitudinal and transverse parts [17], and are

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{a}(\vec{r}) = -\frac{1}{\varepsilon_0 c^2}\vec{j}^{\perp}(\vec{r}) \qquad (1.2.12)$$

$$\nabla^2 \phi(\vec{r}) = -\rho(\vec{r})/\varepsilon_0. \qquad (1.2.13)$$

The choice of Coulomb gauge thus separates the Coulombic fields from the transverse fields;

$$\vec{e}^{\perp}(\vec{r}) = -\dot{\vec{a}}(\vec{r}) \quad ; \quad \vec{e}''(\vec{r}) = -\vec{\nabla}\phi(\vec{r}). \qquad (1.2.14)$$

The electrostatic field due to the charged particles is given by $\vec{e}''(\vec{r})$ and described by the scalar potential while the radiation field $\vec{e}^{\perp}(\vec{r})$ is described by the transverse vector potential.

The Lagrangian function expressed in terms of the electromagnetic potentials which leads to the equations of motion (1.2.12) and (1.2.13) is

$$L = 1/2\sum_{\alpha} m_{\alpha}\dot{\vec{q}}_{\alpha}^2 + \frac{\varepsilon_0}{2}\int\left\{\vec{e}^2(\vec{r}) - c^2\vec{b}^2(\vec{r})\right\}d^3\vec{r} + \int\vec{j}^{\perp}(\vec{r}).\vec{a}(\vec{r})d^3\vec{r} - \int\rho(\vec{r})\phi(\vec{r})d^3\vec{r}$$

$$(1.2.15)$$

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and is known as the Coulomb gauge Lagrangian. The scalar potential $\phi(\vec{r})$ may be eliminated from (1.2.15) in favour of the electrostatic potential energy V by employing the relationship of the latter to the longitudinal electric field. This results in the Lagrangian (1.2.2), which is known as the minimal-coupling Lagrangian.

It is possible in an alternative formulation to describe the equations of motion using the Hamiltonian function [14], defined in terms of the Lagrangian by

$$H = \sum_{\alpha} \vec{p}_{\alpha} \cdot \dot{\vec{q}}_{\alpha} + \int \vec{\Pi}(\vec{r}) \cdot \dot{\vec{a}}(\vec{r}) d^3\vec{r} - L. \qquad (1.2.16)$$

The dynamical variables are then the generalised coordinates and the canonically conjugate momenta, which for particles and field are respectively given by

$$\vec{p}_{\alpha} = \frac{\partial L}{\partial \dot{\vec{q}}_{\alpha}} \quad ; \quad \vec{\Pi}(\vec{r}) = \frac{\partial \mathcal{L}}{\partial \dot{\vec{a}}} \quad , \qquad (1.2.17)$$

where the functional $\mathcal{L}$ is the Lagrangian density. For conservative systems the Hamiltonian represents the total energy. The Hamiltonian is written in terms of the canonically conjugate variables, which are the coordinates and the conjugate momenta for field and particles. By grouping the charges to form electrically neutral aggregates, atoms and molecules labelled ζ, the minimal-coupling Lagrangian (1.2.2) when substituted in (1.2.16) results in the minimal-coupling Hamiltonian H_{MIN}. The quantum mechanical version [18] of the Hamiltonian operator is obtained by the replacement of the classical variables with quantum operators subject to the canonical commutation relations

$$\left[q_{i(\alpha)}(\zeta), p_{j(\beta)}(\zeta')\right] = i\hbar\delta_{ij}\delta_{\alpha\beta}\delta_{\zeta\zeta'} \qquad (1.2.18)$$

$$\left[a_i(\vec{r}), \Pi_j(\vec{r}')\right] = i\hbar\delta^{\perp}_{ij}(\vec{r}-\vec{r}'), \qquad (1.2.19)$$

where $\delta^{\perp}_{ij}(\vec{r}-\vec{r}')$ is the transverse delta-dyadic [5]. Thus the minimal-coupling Hamiltonian [6]

$$H_{MIN} = \sum_{\zeta} H_{MOL}(\zeta) + H_{RAD} + \sum_{\zeta} H_{INT}(\zeta) + V_{INTER}, \qquad (1.2.20)$$

with

$$H_{MOL}(\zeta) = \sum_{\alpha} \frac{1}{2m_\alpha}\vec{p}^2_\alpha(\zeta) + V(\zeta) \qquad (1.2.21)$$

$$H_{RAD} = \frac{1}{2}\int\left\{\frac{\vec{\Pi}^2(\vec{r})}{\epsilon_0} + \epsilon_0 c^2(\vec{\nabla}\times\vec{a}(\vec{r}))^2\right\}d^3\vec{r} \qquad (1.2.22)$$

$$H_{INT}(\zeta) = -\sum_{\alpha}\frac{e_\alpha}{m_\alpha}\vec{p}_\alpha(\zeta).\vec{a}(\vec{q}_\alpha(\zeta)) + \sum_{\alpha}\frac{e^2_\alpha}{2m_\alpha}\vec{a}^2(\vec{q}_\alpha(\zeta)) \qquad (1.2.23)$$

and

$$V_{INTER} = \sum_{\zeta<\zeta'} V(\zeta,\zeta'). \qquad (1.2.24)$$

The quantised radiation field Hamiltonian [19], H_{RAD}, corresponds to a set of independent quantised harmonic oscillators confined to a box of volume V on which periodic boundary conditions are imposed. The photon is the resulting quantised particle. The linear term in the interaction Hamiltonian depends on the product of the particle momentum with the

vector potential while the second order term, quadratic in the electric charge depends on the square of the vector potential. The potential term appears explicitly in the Hamiltonian and is separated into intra- and inter-molecular contributions.

The application of molecular QED to problems in chemical physics is facilitated by the use of the multipolar Hamiltonian [20]. In this framework radiation-molecule interactions are described solely by the coupling of molecular multipoles to the electric displacement and magnetic fields. The multipolar Lagrangian, used to determine the multipolar Hamiltonian, is obtained from the minimal-coupling Lagrangian by the addition of a total time derivative of a function of the coordinates [21]. The transformation uses the property that the equations of motion derived from a Lagrangian are unaltered by just such an addition. Lagrangians so related are said to be equivalent, but give rise to Hamiltonians differing in form. Thus

$$L_{MULT} = L_{MIN} - \frac{d}{dt}\int \vec{p}^{\perp}(\vec{r}).\vec{a}(\vec{r})d^3\vec{r} \qquad (1.2.25)$$

where $\vec{p}(\vec{r})$ is the electric polarisation field and is a function of the particle coordinates. The multipolar Lagrangian is then written as

$$L_{MULT} = \sum_{\zeta}\left\{\frac{1}{2}\sum_{\alpha} m_{\alpha}\dot{\vec{q}}_{\alpha}^2(\zeta) - V(\zeta)\right\} + \frac{\varepsilon_0}{2}\int\left\{\dot{\vec{a}}(\vec{r})^2 - c^2(\vec{\nabla}\times\vec{a}(\vec{r}))^2\right\}d^3\vec{r}$$
$$-\int \vec{p}^{\perp}(\vec{r}).\dot{\vec{a}}(\vec{r})d^3\vec{r} + \int\left\{\vec{\nabla}\times\vec{M}(\vec{r})\right\}.\vec{a}(\vec{r})d^3\vec{r} - \sum_{\zeta<\zeta'} V_{INTER}(\zeta,\zeta') \qquad (1.2.26)$$

where $\vec{p}(\vec{r})$, and the magnetisation field $\vec{M}(\vec{r})$, are defined by

$$\vec{p}(\vec{r}) = \sum_{\zeta} \vec{p}(\zeta;\vec{r}); \qquad \vec{M}(\vec{r}) = \sum_{\zeta} \vec{M}(\zeta;\vec{r}) \qquad (1.2.27)$$

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with

$$\vec{p}(\zeta;\vec{r}) = \sum_{\alpha} e_{\alpha}(\vec{q}_{\alpha}(\zeta)-\vec{R}_{\zeta})\int_{0}^{1}\delta(\vec{r}-\vec{R}_{\zeta}-\lambda(\vec{q}_{\alpha}(\zeta)-\vec{R}_{\zeta}))d\lambda \quad , \qquad (1.2.28)$$

and

$$\vec{M}(\zeta;\vec{r}) = \sum_{\alpha} e_{\alpha}\left\{(\vec{q}_{\alpha}(\zeta)-\vec{R}_{\zeta})\times\dot{\vec{q}}_{\alpha}(\zeta)\right\}\int_{0}^{1}\lambda\delta(\vec{r}-\vec{R}_{\zeta}-\lambda(\vec{q}_{\alpha}(\zeta)-\vec{R}_{\zeta}))d\lambda \quad . \qquad (1.2.29)$$

These fields allow the total charge density associated with each ensemble to be partitioned into true and polarisation charge densities, and the total current density into true, polarisation and magnetisation current densities [22,23]. This division of the sources necessitates the introduction of a reference vector $\vec{R}_{\zeta}$, which may conveniently be taken as the centre of mass, an inversion centre or a local chromophore centre.

The multipolar Hamiltonian [24], evaluated in the usual manner gives

$$H_{MULT} = \sum_{\zeta} H_{MOL}(\zeta) + H_{RAD} + \sum_{\zeta} H_{INT}(\zeta) + H_{SELF} \qquad (1.2.30)$$

with $H_{MOL}(\zeta)$ unchanged from (1.2.21)

$$H_{RAD} = \frac{1}{2}\int\left\{\frac{\vec{d}^{\perp 2}(\vec{r})}{\varepsilon_{0}} + \varepsilon_{0}c^{2}\vec{b}^{2}(\vec{r})\right\}d^{3}\vec{r} \qquad (1.2.31)$$

$$H_{SELF} = \frac{1}{2\varepsilon_{0}}\int \sum_{\zeta}|\vec{p}^{\perp}(\zeta;\vec{r})|^{2}d^{3}\vec{r} \qquad (1.2.32)$$

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and the interaction terms now given by

$$H_{INT}(\zeta) = -\varepsilon_0^{-1} \int \vec{p}(\vec{r}) \cdot \vec{d}^\perp(\vec{r}) d^3\vec{r} - \int \vec{m}(\vec{r}) \cdot \vec{b}(\vec{r}) d^3\vec{r}$$

$$+ \frac{1}{2} \int O_{ij}(\vec{r}, \vec{r}') b_i(\vec{r}) b_j(\vec{r}') d^3\vec{r} d^3\vec{r}' . \qquad (1.2.33)$$

It should be noted that in the multipolar framework it is the transverse electric displacement vector field $\vec{d}^\perp(\vec{r})$ that appears explicitly, rather than the transverse electric field $\vec{e}^\perp(\vec{r})$ as found in H_{MIN}. The displacement vector is defined as

$$\vec{d}(\vec{r}) = \varepsilon_0 \vec{e}(\vec{r}) + \vec{p}(\vec{r}). \qquad (1.2.34)$$

The quantum mechanical mode expansions for the electromagnetic fields $\vec{d}^\perp(\vec{r})$ and $\vec{b}(\vec{r})$ are

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

$$(1.2.35)$$

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

$$(1.2.36)$$

with $\vec{e}^{(\lambda)}(\vec{k})$ the electric polarisation of wavevector $\vec{k}$, index of polarisation λ and with $a^{(\lambda)}(\vec{k})$ and $a^{+(\lambda)}(\vec{k})$ respectively annihilation and creation operators of a photon of mode $(\vec{k},\lambda)$. $\vec{b}^{(\lambda)}(\vec{k})$ is defined through

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$$\vec{b}^{(\lambda)}(\vec{k}) = \hat{\vec{k}} \times \vec{e}^{(\lambda)}(\vec{k}).$$

(1.2.37)

The creation and annihilation operators are subject to the commutation relation

$$\left[a^{(\lambda)}(\vec{k}), a^{+(\lambda')}(\vec{k}') \right] = \delta_{\lambda\lambda'} \delta_{\vec{k}\vec{k}'}.$$

(1.2.38)

The first term of (1.2.33) denotes the interaction of the electric multipoles with the transverse electric displacement field. The second term represents the interaction of the magnetic multipoles with the magnetic field. The modified magnetisation field is defined as

$$\vec{m}(\vec{r}) = \sum_{\zeta} \vec{m}(\zeta;\vec{r})$$

(1.2.39)

with

$$\vec{m}(\zeta;\vec{r}) = \sum_{\alpha} \frac{1}{2m_{\alpha}} \left\{ \vec{n}_{\alpha}(\zeta;\vec{r}) \times \vec{p}_{\alpha}(\zeta) - \vec{p}_{\alpha}(\zeta) \times \vec{n}_{\alpha}(\zeta;\vec{r}) \right\}.$$

(1.2.40)

In (1.2.40) the vector field $\vec{n}(\zeta;\vec{r})$ for a molecule ζ is given by

$$\vec{n}(\vec{r}) = \sum_{\zeta} \vec{n}(\zeta;\vec{r})$$

(1.2.41)

$$\vec{n}_{\alpha}(\zeta,\vec{r}) = \sum_{\alpha} e_{\alpha}(\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta}) \int_{0}^{1} \lambda \delta(\vec{r} - \vec{R}_{\zeta} - \lambda(\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta})) d\lambda .$$

(1.2.42)

The final term of (1.2.33) is the diamagnetisation interaction and is quadratic in the electric charge and in the magnetic field. It is

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defined as

$$O_{ij}(\vec{r},\vec{r}') = \sum_{\zeta,\zeta'} O_{ij}(\zeta,\zeta';\vec{r},\vec{r}') \tag{1.2.43}$$

$$O_{ij}(\zeta,\zeta';\vec{r},\vec{r}') = \varepsilon_{ik\ell}\varepsilon_{jm\ell}\sum_{\alpha}\frac{1}{m_{\alpha}}n_{k(\alpha)}(\vec{r})n_{m(\alpha)}(\vec{r}'). \tag{1.2.44}$$

The term H_{SELF} is independent of the electromagnetic field and does not play an important role in radiative processes and for this reason is usually neglected. It must however be incorporated into self energy calculations as in the treatment of the Lamb shift.

The particular choice of the total time derivative in (1.2.25) leads to the elimination of the intermolecular Coulomb interactions in the resulting multipolar Hamiltonian describing neutral systems, a characteristic feature of this approach. Molecules couple entirely to the electric displacement and magnetic fields and all intermolecular interactions are mediated by the exchange of transverse photons. Thus retardation is a natural occurrence in the multipolar formalism with signals propagating at the speed of light.

It has been demonstrated how the multipolar Hamiltonian may be obtained from the minimal coupling Lagrangian by the addition of a total time derivative followed by the construction of the Hamiltonian H_{MULT} from L_{MULT}. An alternative method of obtaining H_{MULT} is to start with the minimal coupling Hamiltonian H_{MIN} found from L_{MIN} and then to apply a canonical transformation [20,25-29] on H_{MIN} to find H_{MULT}. Hamiltonians related by canonical transformations are termed equivalent. In the quantum theory canonical transformations form part of the general class of unitary transformations which preserve the canonical commutation relations and the operator equations of motion. They are the

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quantum analogues of contact transformations in classical theory [14,18]. The transformation which results in H_{MULT} when applied to H_{MIN} is

$$H_{MULT} = e^{-iS}H_{MIN}e^{iS} ,$$
(1.2.45)

with the particular choice of generator

$$S = 1/\hbar \int \vec{p}^{\perp}(\vec{r}) \cdot \vec{a}(\vec{r})d^3\vec{r} .$$
(1.2.46)

It is clear that $\vec{q}$ and $\vec{a}(\vec{r})$ remain unaltered by the transformation with only the corresponding momenta changing. The resulting multipolar Hamiltonian is that given by (1.2.30). It should be noted that although the partitioning of the minimal- and multipolar-coupling Hamiltonians is different in both cases, identical matrix elements are obtained for processes where conservation of energy hold. This is a consequence of the two forms of Hamiltonian being equivalent, thus giving equal matrix elements "on the energy shell".

The interaction term of the Hamiltonian (1.2.33) is conveniently expanded in terms of multipole moments to simplify its subsequent use in the applications to be considered. The leading contributions to the multipolar series of the polarisation and magnetisation fields, and the ones employed in this thesis are

$$p_i(\zeta;\vec{r}) = (\mu_i(\zeta) - Q_{ij}(\zeta)\nabla_j + \dots)\delta(\vec{r}-\vec{R}_\zeta)$$
(1.2.47)

$$m_i(\zeta;\vec{r}) = (m_i(\zeta) + \dots)\delta(\vec{r}-\vec{R}_\zeta)$$
(1.2.48)

and the first term of the diamagnetisation interaction may be written

$$H_{DIA}(\zeta) = \sum_{\alpha} \frac{e_{\alpha}^2}{8m_{\alpha}} \left\{ (\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta}) \times \vec{b}(\vec{R}_{\zeta}) \right\}^2 . \tag{1.2.49}$$

In (1.2.47) and in the rest of this thesis, the Einstein summation convention is used. The electric dipole, electric quadrupole and magnetic dipole moments of molecule ζ are respectively given by

$$\mu_i(\zeta) = \sum_{\alpha} e_{\alpha} (\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta})_i \tag{1.2.50}$$

$$Q_{ij}(\zeta) = \frac{1}{2} \sum_{\alpha} e_{\alpha} (\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta})_i (\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta})_j \tag{1.2.51}$$

$$m_i(\zeta) = \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \left\{ (\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta}) \times \vec{p}_{\alpha} \right\}_i . \tag{1.2.52}$$

Using the definitions above in (1.2.33) and performing the volume integral, the multipolar interaction Hamiltonian becomes

$$H_{INT}(\zeta) = - \varepsilon_0^{-1} \vec{\mu}(\zeta) . \vec{d}^{\perp}(\vec{R}_{\zeta}) - \varepsilon_0^{-1} Q_{ij}(\zeta) \nabla_j d_i^{\perp}(\vec{R}_{\zeta}) - \vec{m}(\zeta) . \vec{b}(\vec{R}_{\zeta})$$

$$+ \sum_{\alpha} \frac{e_{\alpha}^2}{8m_{\alpha}} \left\{ (\vec{q}_{\alpha}(\zeta) - \vec{R}_{\zeta}) \times \vec{b}(\vec{R}_{\zeta}) \right\}^2 \tag{1.2.53}$$

including all terms of a similar origin. Assuming that the coupling between radiation and matter is small enough to be considered as a perturbation on the system, both the minimal-coupling and the multipolar Hamiltonians may be suitably divided as

$$H = H_0 + H_{INT} \tag{1.2.54}$$

with

$$H_O = \sum_\zeta H_{MOL}(\zeta) + H_{RAD} \qquad (1.2.55)$$

$$H_{INT} = \sum_\zeta H_{INT}(\zeta) + V_{INTER}, \qquad (1.2.56)$$

remembering that V_{INTER} is absent in the multipolar case. The base states are then given by the eigenstates of H_O which are the products of the eigenstates of the unperturbed molecular and radiation field Hamiltonians, whose solutions are taken to be known. For processes dependent upon time, the perturbation causes transitions between the unperturbed states. The transition rate is given by the Fermi golden rule

$$\Gamma = (2\pi/h)|M_{fi}|^2 \rho \qquad (1.2.57)$$

with ρ the density of final states, where M_{fi} is the matrix element linking the initial state $|i\rangle$ and the final state $|f\rangle$, and is given by

$$M_{fi} = \langle f|H_{INT}|i\rangle$$

$$-\sum_I \frac{\langle f|H_{INT}|I\rangle\langle I|H_{INT}|i\rangle}{(E_I - E_i)} + \sum_{II}\sum_I \frac{\langle f|H_{INT}|II\rangle\langle II|H_{INT}|I\rangle\langle I|H_{INT}|i\rangle}{(E_{II} - E_i)(E_I - E_i)}$$

$$-\sum_{III}\sum_{II}\sum_I \frac{\langle f|H_{INT}|III\rangle\langle III|H_{INT}|II\rangle\langle II|H_{INT}|I\rangle\langle I|H_{INT}|i\rangle}{(E_{III} - E_i)(E_{II} - E_i)(E_I - E_i)} + \ldots$$

$$(1.2.58)$$

1.3 APPLICATIONS

In the preceding Section, the construction of the minimal-coupling and more commonly used multipolar Hamiltonians of molecular QED originating from the classical charged particle-electromagnetic field Lagrangian function, was described. Both forms of Hamiltonian are applied to the resolution of problems occurring in the areas of intermolecular forces and optical activity.

In the following Chapter the Heisenberg representation of QED is employed in the determination of the Maxwell fields in the vicinity of a molecule in both the multipolar and minimal-coupling frameworks. In this treatment both the radiation and electron wavefields are second quantised with the fermion and boson operators explicitly dependent upon the time. The electromagnetic radiation field operators are evaluated in series of powers of the transition moments and the derivation given is correct up to second order in the sources with the interaction Hamiltonian including electric quadrupole and magnetic dipole couplings, in addition to the electric dipole interaction term.

The electric displacement and magnetic field operators of the multipolar formalism are then applied in Chapter 3 to the calculation of the Thompson energy density and the Poynting vector associated with the electromagnetic field. The equivalence of the matrix element obtained for both these processes in the electric dipole approximation of the minimal-coupling approach is demonstrated. The rate of flow of electromagnetic energy is then compared with the spontaneous power.

In the fourth Chapter, the Maxwell fields are applied to the study of the intermolecular interaction of two polarisable neutral molecules using a response formalism. The response of a polarisable test body to the field of the source leads to the energy of interaction between two species in the ground electronic state, the dispersion potential, and

the interaction energy of molecules in electronically excited levels. Results valid for all separation distances beyond electronic overlap for molecules with fixed relative orientations and possessing a variety of multipole polarisability characteristics, are obtained. The limiting near- and far-zone behaviour of molecules in the fluid phase is also examined. This work is compared and contrasted with previous studies carried out in the Schrödinger picture.

In the final Chapter, a theory of molecule induced circularly polarised luminescence is presented. The polarisation characteristics of luminescence are altered by the presence of a chiral species. This is interpreted in terms of the interaction between achiral and chiral molecules. The differential emission rate is evaluated using the Schrödinger and Heisenberg pictures.

CHAPTER 2

ELECTROMAGNETIC FIELDS IN THE NEIGHBOURHOOD OF A MOLECULE

2.1 INTRODUCTION

As in quantum mechanics [18], QED may be formulated in, and calculations carried out in, either the Schrödinger or Heisenberg points of view. The time development in the former is governed by Schrödinger's wave equation and its solutions are time-dependent wavefunctions. In the Heisenberg picture the states correspond to fixed vectors and the dynamical variables to moving linear operators. The variation with time of any dynamical variable is governed by the Heisenberg equation of motion for the operator. The two representations are related by a time-dependent unitary transformation and identical results are obtained with the use of each formalism.

In Chapter 1 the quantum mechanical minimal-coupling Hamiltonian was obtained from its classical origins through the use of the Lagrangian function and the principle of minimal-electromagnetic interaction, and its relationship to the multipolar Hamiltonian was discussed. The minimal-coupling form of the theory was converted to its multipolar counterpart by the addition of a total time derivative to the Lagrangian, or by the application of a quantum canonical transformation to the Hamiltonian. Similarities and differences between the two approaches were examined by treating the charges within the framework of first quantisation.

QED with non-relativistic sources in Heisenberg form with both radiation and matter placed on an equal footing was elucidated in a series of papers by Power and Thirunamachandran [30-34] with both the electron field and the radiation field being second quantised. A

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consequence of second quantisation was the resulting change in the equations of motion for the total system. The electron wave-field now had Schrödinger's equations in the presence of the electromagnetic field. This was in direct contrast to the conventional particle description of matter, where the equation of motion for the charges was given by the Lorentz force law. The electromagnetic fields themselves obeyed Maxwell's equations in both cases. The multipolar form of the theory, advantageous for situations involving bound systems as sources of the electromagnetic field, was then shown to follow from the underlying quantum electrodynamical theory based on the principle of minimal-electromagnetic coupling.

In the Heisenberg approach L_{MULT} was obtained from L_{MIN} by a change in the generalised coordinate of the electron field, amounting to the application of a point transformation. H_{MIN} however, was converted directly into H_{MULT} through the application of a quantum canonical transformation. After extension of the theory to include molecular assemblies, it was found that the elimination of the intermolecular electrostatic terms in the multipolar Hamiltonian in favour of couplings via the exchange of transverse photons was again possible, a characteristic feature of the multipolar formalism as noted previously. Maxwell fields in the vicinity of the sources were then derived within the electric dipole approximation. Applications using the Heisenberg picture included the study of intermolecular interactions and energy transport phenomena.

In this Chapter, the electromagnetic fields in the proximity of a molecule are obtained using both the minimal-coupling and multipolar formalisms in the Heisenberg framework. In QED the use of the Heisenberg formalism provides additional insight into processes conventionally described by the more familiar Schrödinger picture.

2.2 MAXWELL FIELDS FROM MULTIPOLAR HAMILTONIAN

The electromagnetic field in the proximity of a molecule is first determined using the multipolar formalism of non-relativistic QED in Heisenberg form. The multipolar Hamiltonian describing the radiation-molecule and molecule-molecule interactions is written in second quantised form. The theory is extended by including the interaction term electric dipole, magnetic dipole, electric quadrupole and diamagnetic couplings. The Maxwell fields of atoms and molecules are found in the Heisenberg picture, in which the operators contain all the time dependence. The electric displacement and magnetic field operators are conveniently expanded in power series involving the transition moments. A complete derivation of the Maxwell fields to second order in the sources correct to diamagnetic coupling and including all terms of comparable order, is presented. This provides an extension of the theory by going beyond the electric dipole approximation in the evaluation of the quadratic fields [31] and the earlier work by Thirunamachandran [35] where the higher order multipole moments were used to obtain the first order fields only. The importance of the inclusion of higher multipole moments is seen when applications involving chiral molecular species are examined.

The Heisenberg field operators are found to be complicated functions of the creation and annihilation operators for both electrons and photons. Consequently the Maxwell field operators can either act solely in the fermion space, or solely in the boson space or in unison in the composite photon-electron space. The fields derived exhibit the expected causal behaviour for distances $r > ct$, r being the distance from the source of the field point.

The natural starting point for the evaluation of the Maxwell fields in the vicinity of a molecule is the multipolar Hamiltonian [31,35]

$$H_{MULT} = \int \bar{\phi}(\vec{q})\left[-\frac{\hbar^2}{2m}(\vec{\nabla}^{(\vec{q})})^2 + V(\vec{q})\right]\phi(\vec{q})d^3\vec{q} + \frac{\epsilon}{2}_0\int\left(\frac{\vec{d}^{\perp 2}(\vec{r})}{\epsilon_0^2} + c^2\vec{b}^2(\vec{r})\right)d^3\vec{r} +$$

$$\int \bar{\phi}(\vec{q})\left[-\epsilon_0^{-1}\vec{\mu}.\vec{d}^\perp(\vec{r}')-\epsilon_0^{-1}Q_{ij}\nabla_i d_j^\perp(\vec{r}')-\vec{m}.\vec{b}(\vec{r}') + \frac{e^2}{8m}(\vec{q}\times\vec{b}(\vec{r}'))^2\right]\phi(\vec{q})d^3\vec{q}$$

(2.2.1)

correct up to the first diamagnetic coupling term, with self energies being ignored, and with the point molecular multipoles located at position $\vec{r}'$. In the second quantised form the electron wavefield is expressed as

$$\phi(\vec{q},t) = \sum_n b_n(t)\phi_n(\vec{q})$$

(2.2.2)

where $\phi_n(\vec{q})$ is the orthonormal electron field mode and $b_n(t)$ is the time-dependent fermion annihilation operator for the state $|n\rangle$, of energy E_n. The time-dependent mode expansions of the electromagnetic fields are

$$\vec{d}^\perp(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\epsilon_0}{2V}\right)^{1/2}\left\{\vec{e}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k},t)e^{i\vec{k}.\vec{r}} - \vec{e}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k},t)e^{-i\vec{k}.\vec{r}}\right\}$$

(2.2.3)

$$\vec{b}(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\left\{\vec{b}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k},t)e^{i\vec{k}.\vec{r}} - \vec{b}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k},t)e^{-i\vec{k}.\vec{r}}\right\}$$

(2.2.4)

where $a^{(\lambda)}(\vec{k},t)$ and $a^{\dagger(\lambda)}(\vec{k},t)$ are now time-dependent annihilation and creation operators for a photon of mode $(\vec{k},\lambda)$ with $\vec{e}^{(\lambda)}(\vec{k})$ and $\vec{b}^{(\lambda)}(\vec{k})$ as defined previously. The boson operators obey the standard equal-time quantum mechanical commutation relation

$$\left[a^{(\lambda)}(\vec{k},t), a^{+(\lambda')}(\vec{k'},t)\right]_{-} = \delta_{\vec{k}\vec{k'}} \, \delta_{\lambda\lambda'} \tag{2.2.5}$$

while the fermion operators satisfy the anticommutation relation

$$\left[b_m(t), b_n^{+}(t)\right]_{+} = \delta_{mn}. \tag{2.2.6}$$

With the aid of the expansions (2.2.2)-(2.2.4) the second quantised multipolar Hamiltonian becomes

$$
\begin{aligned}
H_{MULT} = & \sum_n b_n^{+} b_n E_n + \sum_{\vec{k},\lambda} a^{+} a \hbar\omega \\
& -i\sum_{\vec{k},\lambda}\sum_{m,n} \left(\frac{\hbar c k}{2 V \varepsilon_0}\right)^{1/2} b_m^{+} b_n \, \vec{\mu}^{mn} \cdot (\vec{e} a e^{i\vec{k}\cdot\vec{r}'} - \vec{e} a^{+} e^{-i\vec{k}\cdot\vec{r}'}) \\
& -i\sum_{\vec{k},\lambda}\sum_{m,n} \left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} b_m^{+} b_m \, \vec{m}^{mn} \cdot (\vec{b} a e^{i\vec{k}\cdot\vec{r}'} - \vec{b} a^{+} e^{-i\vec{k}\cdot\vec{r}'}) \\
& -i\sum_{\vec{k},\lambda}\sum_{m,n} \left(\frac{\hbar c k}{2 V \varepsilon_0}\right)^{1/2} b_m^{+} b_n \, \vec{Q}^{mn} : ((i\vec{k})\vec{e} a e^{i\vec{k}\cdot\vec{r}'} - (-i\vec{k})\vec{e} a^{+} e^{-i\vec{k}\cdot\vec{r}'}) \\
& -\frac{e^2}{8m} \varepsilon_{ijn} \varepsilon_{k\ell n} \sum_{\vec{k'},\lambda'} \sum_{\vec{k},\lambda} \sum_{m,n} \left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} \left(\frac{\hbar k'}{2\varepsilon_0 c V}\right)^{1/2} b_m^{+} b_n (q_i q_k)^{mn} \times
\end{aligned}
$$

$$(b_j a e^{i\vec{k}\cdot\vec{r}'} - b_j a^{+} e^{-i\vec{k}\cdot\vec{r}'})(b_\ell a' e^{i\vec{k'}\cdot\vec{r}'} - b_\ell a'^{+} e^{-i\vec{k'}\cdot\vec{r}'}) \tag{2.2.7}$$

where the time dependence of the electron and photon operators is implicit as is the $\vec{k},\lambda$-dependence of the electric and magnetic polarisation vectors and the radiation field operators. The primed superscript on these vectors and operators signifies the photon mode $(\vec{k'},\lambda')$. In (2.2.7) the transition dipole moment matrix element is given by

$$\vec{\mu}^{mn} = \int \vec{\phi}_m(\vec{q})\vec{\mu}\phi_n(\vec{q})d^3\vec{q} \tag{2.2.8}$$

with similar definitions for the matrix elements for the magnetic dipole and electric quadrupole transition moments.

The time development of the operators a and b_n are found from the Heisenberg equations of motion

$$i\hbar\dot{a} = [a,H_{MULT}]_- \tag{2.2.9}$$

and

$$i\hbar\dot{b}_n = [b_n,H_{MULT}]_- . \tag{2.2.10}$$

Using the Hamiltonian (2.2.7), the relations (2.2.5) and (2.2.6) and introducing the operators $\alpha(t)$ and $\beta_n(t)$ in the interaction representation through the substitutions $a(t) = \alpha(t)e^{-i\omega t}$ and $b_n(t) = \beta_n(t)e^{-i\omega_n t}$, and after performing the time integral, it follows that

$$\alpha(t) = \alpha(0) + \frac{1}{\hbar}\left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2}\sum_{m,n}(\mu_j^{mn-}e_j + \frac{1}{c}m_j^{mn-}\bar{b}_j + (-ik_\ell)Q_{j\ell}^{mn-}e_j)e^{-i\vec{k}.\vec{r}'}\times$$

$$\int_0^t dt' e^{i(\omega_{mn}+\omega)t'}\beta_m^+(t')\beta_n(t')$$

$$-\frac{ie^2}{4\hbar m}\epsilon_{ijn}\epsilon_{\ell\ell n}\sum_{\vec{k}',\lambda'}\sum_{m,n}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\left(\frac{\hbar k'}{2\epsilon_0 cV}\right)^{1/2}(q_i q_\ell)^{mn-}\bar{b}_j\int_0^t dt' e^{i(\omega_{mn}+\omega)t'}\times$$

$$e^{-i\vec{k}.\vec{r}'}\beta_m^+(t')\beta_n(t')(b_\ell'\alpha'(t')e^{i\vec{k}'.\vec{r}'-i\omega't'}-\bar{b}_\ell'\alpha'^+(t')e^{-i\vec{k}'.\vec{r}'+i\omega't'})$$

$$\tag{2.2.11}$$

and

$$\beta_n(t) = \beta_n(0) -$$

$$\frac{1}{\hbar}\sum_{\substack{\vec{k},\lambda \\ m}} \left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2} \int_0^t dt'\, \beta_m(t')\left[(\mu_j^{nm}e_j+\frac{1}{c}m_j^{nm}\bar{b}_j+(ik_\ell)Q_{j\ell}^{nm}e_j)\alpha(t')e^{i\vec{k}\cdot\vec{r}'-i(\omega_{mn}+\omega)t'}\right.$$

$$\left. - (\mu_j^{nm-}e_j+\frac{1}{c}m_j^{nm-}\bar{b}_j+(-ik_\ell)Q_{j\ell}^{nm-}e_j)\alpha^\dagger(t')e^{-i\vec{k}\cdot\vec{r}'-i(\omega_{mn}-\omega)t'}\right]$$

$$+ \frac{ie^2}{8\hbar m}\epsilon_{ijn}\epsilon_{k\ell n}\sum_{\substack{\vec{k}',\lambda' \\ \vec{k},\lambda,m}}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\left(\frac{\hbar k'}{2\epsilon_0 cV}\right)^{1/2}(q_i q_\ell)^{nm}\int_0^t dt'\,\beta_m(t')\times$$

$$(b_j\alpha(t')e^{i\vec{k}\cdot\vec{r}'-i(\omega_{mn}+\omega)t'} - \bar{b}_j\alpha^\dagger(t')e^{-i\vec{k}\cdot\vec{r}'-i(\omega_{mn}-\omega)t'})\times$$

$$(b'_\ell\alpha'(t')e^{i\vec{k}'\cdot\vec{r}'-i(\omega_{mn}+\omega')t'} - \bar{b}'_\ell\alpha'^\dagger(t')e^{-i\vec{k}'\cdot\vec{r}'-i(\omega_{mn}-\omega')t'}).$$

$$(2.2.12)$$

For the present the diamagnetic contribution is ignored but will be considered separately later. The calculation of the electric displacement field is given first with the derivation of the magnetic field following.

The transverse electric displacement vector $d_i^\perp$ at time t in the Heisenberg picture is

$$d_i^\perp(\vec{r},t) = i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck\epsilon_0}{2V}\right)^{1/2}[e_i\alpha(t)e^{i\vec{k}\cdot\vec{r}-i\omega t}-e_i\alpha^\dagger(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}] \qquad (2.2.13)$$

which is evaluated as a power series in the transition moments as

$$d_i^\perp(\vec{r},t) = d_i^{(0)}(\vec{r},t) + d_i^{(1)}(\vec{r},t) + d_i^{(2)}(\vec{r},t) + \ldots \qquad (2.2.14)$$

by expanding the operators $\alpha(t)$ and $\beta_n(t)$. The first term arises when $\alpha(t)$ and $\beta_n(t)$ take on their initial values at $t = 0$, so that

$$d_\lambda^{(0)}(\vec{r},t) = i\sum_{\vec{k},\lambda} \left(\frac{\hbar c k \varepsilon_0}{2V}\right)^{1/2} [e_\lambda \alpha(0)e^{i\vec{k}\cdot\vec{r}-i\omega t} - \bar{e}_\lambda \alpha^\dagger(0)e^{-i\vec{k}\cdot\vec{r}+i\omega t}]. \qquad (2.2.15)$$

This is the free field operator independent of the source. It can create or destroy a single photon, operating entirely in the boson space. The term linear in the transition moments is

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

$$(2.2.16)$$

$\alpha^{(1)}(t)$ is found by integrating (2.2.11) with respect to t' subject to $\beta_m^\dagger(t') = \beta_m^\dagger(0)$ and $\beta_n(t') = \beta_n(0)$, giving

$$\alpha^{(1)}(t) = \frac{1}{\hbar}\left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2}\sum_{m,n}(\mu_j^{mn-}e_j + \frac{1}{c}m_j^{mn-}\bar{b}_j + (-ik_\ell)Q_{j\ell}^{mn-}e_j)e^{-i\vec{k}\cdot\vec{r}'} \times$$

$$\beta_m^\dagger(0)\beta_n(0)\left(\frac{e^{i(\omega_{mn}+\omega)t}-1}{i(\omega_{mn}+\omega)}\right). \qquad (2.2.17)$$

This is inserted into (2.2.16) to obtain

$$d_\lambda^{(1)}(\vec{r},t) = \frac{i}{\hbar}\sum_{\substack{\vec{k},\lambda \\ m,n}} \left(\frac{\hbar c k}{2V}\right)[\beta_m^\dagger(0)\beta_n(0)e_\lambda e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}[\mu_j^{mn-}e_j+\frac{1}{c}m_j^{mn-}\bar{b}_j+(-ik_\ell)Q_{j\ell}^{mn-}e_j] \times$$

$$\left(\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{i(\omega_{mn}+\omega)}\right) + H.C.]. \qquad (2.2.18)$$

Two necessary and key steps repeatedly used in the evaluation of the Maxwell fields and subsequently in applications throughout the rest of this thesis are the polarisation and wavevector summations and the evaluation of angular integrals. For the former, by exploiting the transverse nature of electromagnetic radiation with the use of complex

polarisation vectors and the definition (1.2.37), it can be shown that the following polarisation sums hold [6]

$$\sum_\lambda e_i^{(\lambda)}(\vec{k})\overline{e}_j^{(\lambda)}(\vec{k}) = \sum_\lambda b_i^{(\lambda)}(\vec{k})\overline{b}_j^{(\lambda)}(\vec{k}) = \delta_{ij}-\hat{k}_i\hat{k}_j \qquad (2.2.19)$$

and

$$\sum_\lambda e_i^{(\lambda)}(\vec{k})\overline{b}_j^{(\lambda)}(\vec{k}) = \varepsilon_{ij\ell}\hat{k}_\ell . \qquad (2.2.20)$$

In the continuum approximation, the number of allowed values of $\vec{k}$ is dense enough for the mode sum to be replaced by the integral

$$\frac{1}{V}\sum_{\vec{k}} \xrightarrow[V\to\infty]{} \int\frac{d^3\vec{k}}{(2\pi)^3} \qquad (2.2.21)$$

with $d^3\vec{k} = k^2 dk d\Omega$ in spherical polar coordinates with $d\Omega$ an element of solid angle. The angular integrals which are given below and are used in the rest of this work are derived by noting that

$$\frac{1}{4\pi}\int e^{\pm i\vec{k}\cdot\vec{r}}d\Omega = \frac{\sin kr}{kr} \qquad (2.2.22)$$

and by using the relation

$$\frac{1}{k}\nabla_i\int e^{\pm i\vec{k}\cdot\vec{r}}d\Omega = \pm i\int\hat{k}_i e^{\pm i\vec{k}\cdot\vec{r}}d\Omega. \qquad (2.2.23)$$

Thus

$$\frac{1}{4\pi}\int(\delta_{ij}-\hat{k}_i\hat{k}_j)e^{\pm i\vec{k}\cdot\vec{r}}d\Omega = \frac{1}{2i}[F_{ij}(kr)-\overline{F}_{ij}(kr)] \qquad (2.2.24)$$

$$\frac{1}{4\pi}\int \epsilon_{ij\ell}\hat{k}_\ell e^{\pm i\vec{k}\cdot\vec{r}}d\Omega = \mp\frac{1}{2i}[G_{ij}(kr)+\bar{G}_{ij}(kr)] \qquad (2.2.25)$$

$$\frac{1}{4\pi}\int (\delta_{ij}-\hat{k}_i\hat{k}_j)\hat{k}_\ell e^{\pm i\vec{k}\cdot\vec{r}}d\Omega = \mp\frac{1}{2}[H_{ij\ell}(kr)-\bar{H}_{ij\ell}(kr)] \qquad (2.2.26)$$

$$\frac{1}{4\pi}\int \epsilon_{ij\ell}\hat{k}_\ell\hat{k}_\ell e^{\pm i\vec{k}\cdot\vec{r}}d\Omega = \frac{1}{2i}[J_{ij\ell}(kr)-\bar{J}_{ij\ell}(kr)]. \qquad (2.2.27)$$

The Cartesian tensors used above are defined by

$$F_{ij}(kr) = \frac{1}{k^3}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{ikr}}{r} = f_{ij}(kr)e^{ikr} \qquad (2.2.28)$$

$$G_{ij}(kr) = \frac{i}{k^2}\epsilon_{ij\ell}\nabla_\ell\frac{e^{ikr}}{r} = g_{ij}(kr)e^{ikr} \qquad (2.2.29)$$

$$H_{ij\ell}(kr) = \frac{1}{k}\nabla_\ell F_{ij}(kr) = \frac{1}{k^4}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_\ell\frac{e^{ikr}}{r} = h_{ij\ell}(kr)e^{ikr} \qquad (2.2.30)$$

$$J_{ij\ell}(kr) = \frac{i}{k}\nabla_\ell G_{ij}(kr) = -\frac{1}{k^3}\epsilon_{ij\ell}\nabla_\ell\nabla_\ell\frac{e^{ikr}}{r} = j_{ij\ell}(kr)e^{ikr}. \qquad (2.2.31)$$

The geometric tensors defined above are also repeatedly used in subsequent applications and their explicit forms are given in an Appendix at the end of this Chapter.

Returning to (2.2.18) and performing the appropriate polarisation sum and angular integral using the relations given above,

$$d_i^{(1)}(\vec{\rho},t) = \frac{1}{4\pi^2}\sum_{m,n}\beta_m^\dagger(0)\beta_n(0)\int_0^\infty dk\left\{\frac{k^3}{2i}\mu_j^{mn}[F_{ij}(k\rho)-\bar{F}_{ij}(k\rho)]-\right.$$

$$\left.\frac{k^3}{2ic}m_j^{mn}[G_{ij}(k\rho)+\bar{G}_{ij}(k\rho)]-\frac{k^4}{2i}Q_{j\ell}^{mn}[H_{ij\ell}(k\rho)-\bar{H}_{ij\ell}(k\rho)]\right\}\frac{(e^{-ik_{nm}ct}-e^{-ikct})}{k-k_{nm}}$$

$$+ \text{ H.C.} \qquad (2.2.32)$$

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where $\vec{\rho} = \vec{r} - \vec{r}'$. Since the replacement of k by -k in the Hermitian-conjugate term gives essentially the same contribution as the first term but with the limits $(-\infty, 0)$, the limits of the integral can be changed from $(0, \infty)$ to $(-\infty, \infty)$. Illustrating explicitly for the $\vec{\mu}$-dependent part of (2.3.32)

$$\frac{1}{8\pi^2 i} \sum_{m,n} \mu_j^{mn} \beta_m^\dagger(0) \beta_n(0) \int_{-\infty}^{\infty} \frac{dk k^3}{k - k_{nm}} \left[f_{ij}(k\rho) e^{ik\rho} e^{-ik_{nm}ct} - f_{ij}(k\rho) e^{ik(\rho - ct)} \right.$$

$$\left. - \bar{f}_{ij}(k\rho) e^{-ik\rho} e^{-ik_{nm}ct} + \bar{f}_{ij}(k\rho) e^{-ik(\rho + ct)} \right]$$

$$= \frac{1}{4\pi} \sum_{m,n} \mu_j^{mn} \beta_m^\dagger(0) \beta_n(0) k_{nm}^3 f_{ij}(k_{nm}\rho) e^{ik_{nm}(\rho - ct)}, \qquad (2.2.33)$$

the contribution obtained being independent of the way the pole is displaced. The other source-dependent terms are similarly evaluated with the result that the first order electric displacement field, linear in the transition moments is

$$d_i^{(1)}(\vec{\rho}, t) = \frac{1}{4\pi} \sum_{m,n} \beta_m^\dagger(0) \beta_n(0) [\mu_j^{mn} k_{nm}^3 f_{ij}(k_{nm}\rho) - \frac{1}{c} m_j^{mn} k_{nm}^3 g_{ij}(k_{nm}\rho)$$

$$- Q_{j\ell}^{mn} k_{nm}^4 h_{ij\ell}(k_{nm}\rho)] e^{ik_{nm}(\rho - ct)}, \qquad t > \rho/c$$

$$= 0, \qquad t < \rho/c, \qquad (2.2.34)$$

and is strictly causal. Retardation is a natural occurrence of the formalism with signals propagating at the speed of light. It is seen that the first order field is the analogue of the classical field [15]. It operates entirely in the electron Fock space, changing only the molecular state.

In the procedure outlined above, the operator equation of motion is

first integrated with respect to t' as in (2.2.17), substituted into the field mode expansion (2.2.16), followed by the conversion of the mode sum to an integral over dk, which finally results in (2.2.34). It should be noted however, that it is possible to evaluate $\vec{d}^{\perp}(\vec{r},t)$ by changing the order of integration. The first order field (2.2.34) can be obtained by inserting (2.2.11) directly into the mode expansion (2.2.16), carrying out the sum over modes and then finally performing the time integral. This also leads to the introduction of causality without the need for any further assumption [36].

The transverse displacement vector $\vec{d}^{\perp}(\vec{r},t)$ has higher order contributions and the second order term that depends quadratically on the transition moments is now evaluated. This takes the form

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

(2.2.35)

To determine $\alpha^{(2)}(t)$ it is necessary to use the solution (2.2.12) in addition to (2.2.11). Thus

$$\alpha^{(2)}(t) = \frac{1}{\hbar}\sum_{m,n} \left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2} (\mu_j^{mn-}e_j + \frac{1}{c}m_j^{mn-}\bar{b}_j + (-ik_\ell)Q_{j\ell}^{mn-}e_j)e^{-i\vec{k}\cdot\vec{r}}$$

$$\times \int_0^t dt' e^{i(\omega_{mn}+\omega)t'} [\beta_m^{\dagger(0)}(t')\beta_n^{(1)}(t') + \beta_m^{\dagger(1)}(t')\beta_n^{(0)}(t')], \qquad (2.2.36)$$

$$\beta_n^{(1)}(t) = -\frac{1}{\hbar}\sum_{\vec{k}',\lambda'}\sum_p \left(\frac{\hbar c k'}{2\varepsilon_0 V}\right)^{1/2} \beta_p(0)\left[(\mu_j^{np}e_j' + \frac{1}{c}m_j^{np}b_j' + (ik_\ell')Q_{j\ell}^{np}e_j') \times \right.$$

$$e^{i\vec{k}'\cdot\vec{r}'}\alpha'(0)\frac{e^{-i(\omega_{pn}+\omega')t}-1}{-i(\omega_{pn}+\omega')}$$

$$\left. -(\mu_j^{np-}e_j' + \frac{1}{c}m_j^{np-}b_j' + (-ik_\ell')Q_{j\ell}^{np-}e_j')e^{-i\vec{k}'\cdot\vec{r}'}\alpha'^{\dagger}(0)\frac{e^{-i(\omega_{pn}-\omega')t}-1}{-i(\omega_{pn}-\omega')}\right] \qquad (2.2.37)$$

and taking the Hermitian conjugate of (2.2.37)

$$\beta_n^{+(1)}(t) = -\frac{1}{\hbar}\sum_{\substack{\vec{k}',\lambda' \\ p}}\left(\frac{\hbar ck'}{2\epsilon_0 V}\right)^{1/2}\beta_p^+(0)\left[(\mu_j^{pn-}e_j'+\frac{1}{c}m_j^{pn-}b_j'+(-ik_\ell')Q_{j\ell}^{pn-}e_j')\times\right.$$

$$e^{-i\vec{k}'\cdot\vec{r}'}\alpha'^+(0)\frac{e^{i(\omega_{pn}+\omega')t}-1}{i(\omega_{pn}+\omega')}$$

$$\left.-(\mu_j^{pn}e_j'+\frac{1}{c}m_j^{pn}b_j'+(ik_\ell')Q_{j\ell}^{pn}e_j')e^{i\vec{k}'\cdot\vec{r}'}\alpha'(0)\frac{e^{i(\omega_{pn}-\omega')t}-1}{i(\omega_{pn}-\omega')}\right]. \qquad (2.2.38)$$

The last two expressions are substituted into (2.2.36) and after integrating with respect to t', $\alpha^{(2)}(t)$ is found to be

$$\alpha^{(2)}(t) = -\frac{1}{\hbar^2}\sum_{\substack{\vec{k}',\lambda' \\ m,p,n}}\left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2}\left(\frac{\hbar ck'}{2\epsilon_0 V}\right)^{1/2}[\mu_j^{mn-}e_j+\frac{1}{c}m_j^{mn-}b_j+(-ik_\ell)Q_{j\ell}^{mn-}e_j]e^{-i\vec{k}\cdot\vec{r}'}$$

$$\left\{\beta_m^+(0)\beta_p(0)\left[[\mu_\ell^{np}e_\ell'+\frac{1}{c}m_\ell^{np}b_\ell'+(ik_m')Q_{\ell m}^{np}e_\ell']e^{i\vec{k}'\cdot\vec{r}'}\alpha'(0)\times\right.\right.$$

$$\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{pn}+\omega')(\omega_{mp}+\omega-\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pn}+\omega')(\omega_{mn}+\omega)}\right)$$

$$-[\mu_\ell^{np-}e_\ell'+\frac{1}{c}m_\ell^{np-}b_\ell'+(-ik_m')Q_{\ell m}^{np-}e_\ell']e^{-i\vec{k}'\cdot\vec{r}'}\alpha'^+(0)\times$$

$$\left.\left(\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{pn}-\omega')(\omega_{mp}+\omega+\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pn}-\omega')(\omega_{mn}+\omega)}\right)\right]$$

$$+\beta_p^+(0)\beta_n(0)\left[[\mu_\ell^{pm-}e_\ell'+\frac{1}{c}m_\ell^{pm-}b_\ell'+(-ik_m')Q_{\ell m}^{pm-}e_\ell']e^{-i\vec{k}'\cdot\vec{r}'}\alpha'^+(0)\times\right.$$

$$\left(\frac{e^{i(\omega_{pn}+\omega+\omega')t}-1}{-(\omega_{pm}+\omega')(\omega_{pn}+\omega+\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{-(\omega_{pm}+\omega')(\omega_{mn}+\omega)}\right)$$

$$-[\mu_\ell^{pm}e_\ell'+\frac{1}{c}m_\ell^{pm}b_\ell'+(ik_m')Q_{\ell m}^{pm}e_\ell']e^{i\vec{k}'\cdot\vec{r}'}\alpha'(0)\times$$

$$\left.\left.\left(\frac{e^{i(\omega_{pn}+\omega-\omega')t}-1}{-(\omega_{pm}-\omega')(\omega_{pn}+\omega-\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{-(\omega_{pm}-\omega')(\omega_{mn}+\omega)}\right)\right]\right\}$$

$$(2.2.39)$$

with $\alpha^{+(2)}(t)$ given by the Hermitian conjugate of (2.2.39). Substituting for $\alpha^{(2)}(t)$ into (2.2.35)

$$d_i^{(2)}(\vec{p},t) = -\frac{i}{\hbar^2}\sum_{\substack{\vec{k}',\lambda',n \\ \vec{k},\lambda,m,p}}\left(\frac{\hbar c k}{2V}\right)\left(\frac{\hbar c k'}{2\epsilon_0 V}\right)^{1/2}\alpha'(0) \times$$

$$\left\{\left[[e_i\bar{e}_j\mu_j^{mn}+\frac{1}{c}e_i\bar{b}_j m_j^{mn}-ie_i\bar{e}_j k_\ell Q_{j\ell}^{mn}][\mu_\ell^{np}e_\ell'+\frac{1}{c}m_\ell^{np}b_\ell'+(ik_m')Q_{\ell m}^{np}e_\ell']\beta_m^\dagger(0)\beta_p(0)\times\right.\right.$$

$$\left.\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{pn}+\omega')(\omega_{mp}+\omega-\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pn}+\omega')(\omega_{mn}+\omega)}\right)e^{i\vec{k}'.\vec{r}'}e^{i\vec{k}.\vec{p}-i\omega t}\right]$$

$$+\left[[\mu_\ell^{pm}e_\ell'+\frac{1}{c}m_\ell^{pm}b_\ell'+(ik_m')Q_{\ell m}^{pm}e_\ell'][e_i\bar{e}_j\mu_j^{mn}+\frac{1}{c}e_i\bar{b}_j m_j^{mn}-ie_i\bar{e}_j k_\ell Q_{j\ell}^{mn}]\beta_p^\dagger(0)\beta_n(0)\times\right.$$

$$\left.\left(\frac{e^{i(\omega_{pn}+\omega-\omega')t}-1}{(\omega_{pm}-\omega')(\omega_{pn}+\omega-\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pm}-\omega')(\omega_{mn}+\omega)}\right)e^{i\vec{k}'.\vec{r}'}e^{i\vec{k}.\vec{p}-i\omega t}\right]$$

$$+\left[[\mu_\ell^{pn}e_\ell'+\frac{1}{c}m_\ell^{pn}b_\ell'+(ik_m')Q_{\ell m}^{pn}e_\ell'][e_i\bar{e}_j\mu_j^{nm}+\frac{1}{c}e_i\bar{b}_j m_j^{nm}+ie_i\bar{e}_j k_\ell Q_{j\ell}^{nm}]\beta_p^\dagger(0)\beta_m(0)\times\right.$$

$$\left.\left(\frac{e^{-i(\omega_{mp}+\omega+\omega')t}-1}{-(\omega_{pn}-\omega')(\omega_{mp}+\omega+\omega')}-\frac{e^{-i(\omega_{mn}+\omega)t}-1}{-(\omega_{pn}-\omega')(\omega_{mn}+\omega)}\right)e^{i\vec{k}'.\vec{r}'}e^{-i\vec{k}.\vec{p}+i\omega t}\right]$$

$$+\left[[e_i\bar{e}_j\mu_j^{nm}+\frac{1}{c}e_i\bar{b}_j m_j^{nm}+ie_i\bar{e}_j k_\ell Q_{j\ell}^{nm}][\mu_\ell^{mp}e_\ell'+\frac{1}{c}m_\ell^{mp}b_\ell'+(ik_m')Q_{\ell m}^{mp}e_\ell']\beta_n^\dagger(0)\beta_p(0)\times\right.$$

$$\left.\left.\left(\frac{e^{-i(\omega_{pn}+\omega+\omega')t}-1}{-(\omega_{pm}+\omega')(\omega_{pn}+\omega+\omega')}-\frac{e^{-i(\omega_{mn}+\omega)t}-1}{-(\omega_{pm}+\omega')(\omega_{mn}+\omega)}\right)e^{i\vec{k}'.\vec{r}'}e^{-i\vec{k}.\vec{p}+i\omega t}\right]\right\}\right. + \text{H.C.}$$

(2.2.40)

Carrying out the polarisation sum and angular average on (2.2.40) using the relations given earlier and by extending the limits of integration as before, since replacing k by -k in the final two terms above gives essentially the same contribution as the first two, and also similarly for the Hermitian conjugate term, only the first two terms of (2.2.40) need be retained. Thus

$$d_i^{(2)}(\vec{\rho},t) = \frac{-ic}{4\pi\hbar} \sum_{\vec{k}',\lambda'} \sum_{m,n,p} \left(\frac{\hbar ck'}{2\epsilon_0 V}\right)^{1/2} \alpha'(0) e^{i\vec{k}'\cdot\vec{r}'} \frac{1}{2\pi i} \int_{-\infty}^{\infty} dk\, e^{-i\omega t} \left\{ \beta_m^+(0)\beta_p(0)\times \right.$$

$$\left[k^3 [F_{ij}(k\rho)-\overline{F}_{ij}(k\rho)]\mu_j^{mn} - \frac{k^3}{c}[G_{ij}(k\rho)+\overline{G}_{ij}(k\rho)]m_j^{mn} - k^4[H_{ij\ell}(k\rho)-\overline{H}_{ij\ell}(k\rho)]Q_{j\ell}^{mn} \right]$$

$$\times [\mu_\ell^{np}e_\ell' + \frac{1}{c}m_\ell^{np}b_\ell' + (ik_m')Q_{\ell m}^{np}e_\ell'] \left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{pn}+\omega')(\omega_{mp}+\omega-\omega')} - \frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pn}+\omega')(\omega_{mn}+\omega)} \right) +$$

$$\beta_p^+(0)\beta_n(0)[\mu_\ell^{pm}e_\ell' + \frac{1}{c}m_\ell^{pm}b_\ell' + (ik_m')Q_{\ell m}^{pm}e_\ell']\times$$

$$\left[k^3 [F_{ij}(k\rho)-\overline{F}_{ij}(k\rho)]\mu_j^{mn} - \frac{k^3}{c}[G_{ij}(k\rho)+\overline{G}_{ij}(k\rho)]m_j^{mn} - k^4[H_{ij\ell}(k\rho)-\overline{H}_{ij\ell}(k\rho)]Q_{j\ell}^{mn} \right]$$

$$\left. \times \left(\frac{e^{i(\omega_{pn}+\omega-\omega')t}-1}{(\omega_{pm}-\omega')(\omega_{pn}+\omega-\omega')} - \frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pm}-\omega')(\omega_{mn}+\omega)} \right) \right\}$$

$$+ \text{ H.C.} \qquad (2.2.41)$$

The molecular state labels are now changed so that $\beta_m^+(0)\beta_p(0)$ is common. From (2.2.41) are extracted the $F_{ij}(k\rho)$ dependent terms as follows

$$-\frac{1}{8\pi^2\hbar c} \sum_{\vec{k}',\lambda'} \sum_{m,n,p} \left(\frac{\hbar ck'}{2\epsilon_0 V}\right)^{1/2} \beta_m^+(0)\beta_p(0)\alpha'(0) e^{i\vec{k}'\cdot\vec{r}'} \times$$

$$\left\{ \mu_j^{mn}[\mu_\ell^{np}e_\ell' + \frac{1}{c}m_\ell^{np}b_\ell' + (ik_m')Q_{\ell m}^{np}e_\ell'] \int_{-\infty}^{\infty} dk\, k^3 \left[f_{ij}(k\rho)\left(\frac{e^{i(k_{mp}-k')ct}e^{ik\rho}-e^{ik(\rho-ct)}}{(k_{pn}+k')(k_{mp}-k'+k)} \right) \right. \right.$$

$$- \overline{f}_{ij}(k\rho)\left(\frac{e^{i(k_{mp}-k')ct}e^{-ik\rho}-e^{-ik(\rho+ct)}}{(k_{pn}+k')(k_{mp}-k'+k)} \right)$$

$$- f_{ij}(k\rho)\left(\frac{e^{ik_{mn}ct}e^{ik\rho}-e^{ik(\rho-ct)}}{(k_{pn}+k')(k_{mn}+k)} \right) + \overline{f}_{ij}(k\rho)\left(\frac{e^{ik_{mn}ct}e^{-ik\rho}-e^{-ik(\rho+ct)}}{(k_{pn}+k')(k_{mn}+k)} \right) \right] +$$

$$[\mu_\ell^{mn}e_\ell' + \frac{1}{c}m_\ell^{mn}b_\ell' + (ik_m')Q_{\ell m}^{mn}e_\ell']\mu_j^{np} \int_{-\infty}^{\infty} dk\, k^3 \left[f_{ij}(k\rho)\left(\frac{e^{i(k_{mp}-k')ct}e^{ik\rho}-e^{ik(\rho-ct)}}{(k_{mn}-k')(k_{mp}-k'+k)} \right) \right.$$

$$- \overline{f}_{ij}(k\rho)\left(\frac{e^{i(k_{mp}-k')ct}e^{-ik\rho}-e^{-ik(\rho+ct)}}{(k_{mn}-k')(k_{mp}-k'+k)} \right)$$

$$\left. \left. - f_{ij}(k\rho)\left(\frac{e^{ik_{np}ct}e^{ik\rho}-e^{ik(\rho-ct)}}{(k_{mn}-k')(k_{np}+k)} \right) + \overline{f}_{ij}(k\rho)\left(\frac{e^{ik_{np}ct}e^{-ik\rho}-e^{-ik(\rho+ct)}}{(k_{mn}-k')(k_{np}+k)} \right) \right] \right\}$$

$$+ \text{ H.C.} \qquad (2.2.42)$$

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Integrating the above with respect to k for $\rho < ct$ and with $m = p$ gives

$$\frac{-i}{4\pi\hbar c}\sum_{\substack{\bar{m},\bar{n}\\\bar{k},\lambda}}\left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2}\beta_m^\dagger(0)\beta_m(0)\alpha(0)e^{i\vec{k}\cdot\vec{r}'}\left\{\mu_j^{mn}[\mu_\ell^{nm}e_\ell+\frac{1}{c}m_\ell^{nm}b_\ell+(ik_m)Q_{\ell m}^{nm}e_\ell]\times\right.$$

$$\left[-\frac{k^3 f_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}-k}+\frac{k_{nm}^3 f_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}}{k_{nm}-k}\right]+$$

$$[\mu_\ell^{mn}e_\ell+\frac{1}{c}m_\ell^{mn}b_\ell+(ik_m)Q_{\ell m}^{mn}e_\ell]\mu_j^{nm}\times$$

$$\left[-\frac{k^3 f_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}+k}+\frac{k_{nm}^3 f_{ij}(-k_{nm}\rho)e^{-ik_{nm}(\rho-ct)}}{k_{nm}+k}\right]\right\}+\text{ H.C. }\qquad(2.2.43)$$

Returning to (2.2.41) and picking up the G_{ij} terms, changing the molecular labels and performing the k-integral subject to the usual conditions results in

$$\frac{i}{4\pi\hbar c}\sum_{\substack{\bar{m},\bar{n}\\\bar{k},\lambda}}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\beta_m^\dagger(0)\beta_m(0)\alpha(0)e^{i\vec{k}\cdot\vec{r}'}\left\{m_j^{mn}[\mu_\ell^{nm}e_\ell+\frac{1}{c}m_\ell^{nm}b_\ell+(ik_m)Q_{\ell m}^{nm}e_\ell]\times\right.$$

$$\left[-\frac{k^3 g_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}-k}+\frac{k_{nm}^3 g_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}}{k_{nm}-k}\right]+$$

$$[\mu_\ell^{mn}e_\ell+\frac{1}{c}m_\ell^{mn}b_\ell+(ik_m)Q_{\ell m}^{mn}e_\ell]m_j^{nm}\times$$

$$\left[-\frac{k^3 g_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}+k}+\frac{k_{nm}^3 g_{ij}(-k_{nm}\rho)e^{-ik_{nm}(\rho-ct)}}{k_{nm}+k}\right]\right\}+\text{ H.C. }\qquad(2.2.44)$$

and repeating for the H_{ijk} terms,

$$\frac{i}{4\pi\hbar c}\sum_{\substack{m,n \\ \vec{k},\lambda}} \left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2}\beta_m^\dagger(0)\beta_m(0)\alpha(0)e^{i\vec{k}\cdot\vec{r}'}\left\{Q_{jk}^{mn}[\mu_\ell^{nm}e_\ell+\frac{1}{c}m_\ell^{nm}b_\ell+(ik_m)Q_{\ell m}^{nm}e_\ell]\times\right.$$

$$\left[-\frac{k^4 h_{ijk}(k\rho)e^{ik(\rho-ct)}}{k_{nm}-k}+\frac{k_{nm}^4 h_{ijk}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}}{k_{nm}-k}\right]+$$

$$[\mu_\ell^{mn}e_\ell+\frac{1}{c}m_\ell^{mn}b_\ell+(ik_m)Q_{\ell m}^{mn}e_\ell]Q_{jk}^{nm}\times$$

$$\left.\left[-\frac{k^4 h_{ijk}(k\rho)e^{ik(\rho-ct)}}{k_{nm}+k}+\frac{k_{mn}^4 h_{ijk}(k_{mn}\rho)e^{-ik_{nm}(\rho-ct)}}{k_{nm}+k}\right]\right\}+\text{H.C.} \qquad (2.2.45)$$

The total electric displacement field to this order is obtained by adding the last three expressions. For the applications considered later on it is useful to write the second order field as quadratic in the transition moments. Extracting the individual terms for a source located at the origin so that $\vec{r}' = 0$ and $\vec{\rho} = \vec{r}$,

$$d_i^{(2)}(\vec{\mu\mu};\vec{r},t) = \frac{i}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2}\left\{e_\ell\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times\right.$$

$$\left[\sum_n\left(\frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)k^3 f_{ij}(kr)e^{ik(r-ct)}\right.$$

$$\left.\left.-\sum_n\frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}k_{nm}^3 f_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)}-\sum_n\frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}k_{mn}^3 f_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}$$

$$+\text{H.C.} \qquad (2.2.46)$$

$$d_i^{(2)}(\vec{\mu m};\vec{r},t) = \frac{i}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\left\{\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times\right.$$

$$\left[b_\ell\left[\sum_n\left(\frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega}+\frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)k^3 f_{ij}(kr)e^{ik(r-ct)}\right.\right.$$

$$\left.\left.\left.-\sum_n\frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega}k_{nm}^3 f_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)}-\sum_n\frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}k_{mn}^3 f_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right]\right\}+$$

$$
\left[e_{k}\left[-\sum_{n}\left(\frac{m_{j}^{mn}\mu_{k}^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_{k}^{mn}m_{j}^{nm}}{E_{nm}+\hbar\omega}\right)k^{3}g_{ij}(kr)e^{ik(r-ct)}\right.\right.
$$

$$
\left.\left.+\sum_{n}\frac{m_{j}^{mn}\mu_{k}^{nm}}{E_{nm}-\hbar\omega}k_{nm}^{3}g_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)}+\sum_{n}\frac{\mu_{k}^{mn}m_{j}^{nm}}{E_{nm}+\hbar\omega}k_{mn}^{3}g_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right]\right\}
$$

$$
+\text{ H.C.}\qquad(2.2.47)
$$

$$
d_{i}^{(2)}(\vec{mm};\vec{r},t)=\frac{-i}{4\pi c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_{0}cV}\right)^{1/2}\left\{b_{k}\alpha(0)\beta_{m}^{\dagger}(0)\beta_{m}(0)\times\right.
$$

$$
\left[\sum_{n}\left(\frac{m_{j}^{mn}m_{k}^{nm}}{E_{nm}-\hbar\omega}+\frac{m_{k}^{mn}m_{j}^{nm}}{E_{nm}+\hbar\omega}\right)k^{3}g_{ij}(kr)e^{ik(r-ct)}\right.
$$

$$
\left.\left.-\sum_{n}\frac{m_{j}^{mn}m_{k}^{nm}}{E_{nm}-\hbar\omega}k_{nm}^{3}g_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)}-\sum_{n}\frac{m_{k}^{mn}m_{j}^{nm}}{E_{nm}+\hbar\omega}k_{mn}^{3}g_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}
$$

$$
+\text{ H.C.}\qquad(2.2.48)
$$

$$
d_{i}^{(2)}(\vec{\mu Q};\vec{r},t)=\frac{-1}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_{0}V}\right)^{1/2}\left\{k_{\ell}e_{k}\alpha(0)\beta_{m}^{\dagger}(0)\beta_{m}(0)\times\right.
$$

$$
\left[\sum_{n}\left(\frac{\mu_{j}^{mn}Q_{k\ell}^{nm}}{E_{nm}-\hbar\omega}+\frac{Q_{k\ell}^{mn}\mu_{j}^{nm}}{E_{nm}+\hbar\omega}\right)k^{3}f_{ij}(kr)e^{ik(r-ct)}\right.
$$

$$
\left.\left.-\sum_{n}\frac{\mu_{j}^{mn}Q_{k\ell}^{nm}}{E_{nm}-\hbar\omega}k_{nm}^{3}f_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)}-\sum_{n}\frac{Q_{k\ell}^{mn}\mu_{j}^{nm}}{E_{nm}+\hbar\omega}k_{mn}^{3}f_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}
$$

$$
\frac{-i}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_{0}V}\right)^{1/2}\left\{e_{j}\alpha(0)\beta_{m}^{\dagger}(0)\beta_{m}(0)\times\right.
$$

$$
\left[\sum_{n}\left(\frac{Q_{k\ell}^{mn}\mu_{j}^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_{j}^{mn}Q_{k\ell}^{nm}}{E_{nm}+\hbar\omega}\right)k^{4}h_{ik\ell}(kr)e^{ik(r-ct)}\right.
$$

$$
\left.\left.-\sum_{n}\frac{Q_{k\ell}^{mn}\mu_{j}^{nm}}{E_{nm}-\hbar\omega}k_{nm}^{4}h_{ik\ell}(k_{nm}r)e^{ik_{nm}(r-ct)}-\sum_{n}\frac{\mu_{j}^{mn}Q_{k\ell}^{nm}}{E_{nm}+\hbar\omega}k_{mn}^{4}h_{ik\ell}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}
$$

$$
+\text{ H.C.}\qquad(2.2.49)
$$

$$d_i^{(2)}(m\vec{Q};\vec{r},t) = \frac{1}{4\pi c}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left\{k_\ell e_\ell\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times\right.$$

$$\left[\sum_n\left\{\frac{m_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{\ell\ell}^{mn}m_j^{nm}}{E_{nm}+\hbar\omega}\right\}k^3 g_{ij}(kr)e^{ik(r-ct)}\right.$$

$$\left.-\sum_n\frac{m_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}-\hbar\omega}k_{nm}^3 g_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_n\frac{Q_{\ell\ell}^{mn}m_j^{nm}}{E_{nm}+\hbar\omega}k_{mn}^3 g_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}$$

$$\frac{-i}{4\pi c}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left\{b_j\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times\right.$$

$$\left[\sum_n\left\{\frac{Q_{\ell\ell}^{mn}m_j^{nm}}{E_{nm}-\hbar\omega} + \frac{m_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}+\hbar\omega}\right\}k^4 h_{i\ell\ell}(kr)e^{ik(r-ct)}\right.$$

$$\left.-\sum_n\frac{Q_{\ell\ell}^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}k_{nm}^4 h_{i\ell\ell}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_n\frac{m_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}+\hbar\omega}k_{mn}^4 h_{i\ell\ell}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}$$

$$+ \text{ H.C.} \qquad (2.2.50)$$

$$d_i^{(2)}(QQ;\vec{r},t) = \frac{1}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left\{e_\ell k_m\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times\right.$$

$$\left[\sum_n\left\{\frac{Q_{jk}^{mn}Q_{\ell m}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{\ell m}^{mn}Q_{jk}^{nm}}{E_{nm}+\hbar\omega}\right\}k^4 h_{ijk}(kr)e^{ik(r-ct)}\right.$$

$$\left.-\sum_n\frac{Q_{jk}^{mn}Q_{\ell m}^{nm}}{E_{nm}-\hbar\omega}k_{nm}^4 h_{ijk}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_n\frac{Q_{\ell m}^{mn}Q_{jk}^{nm}}{E_{nm}+\hbar\omega}k_{mn}^4 h_{ijk}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}$$

$$+ \text{ H.C.} \qquad (2.2.51)$$

This completes the evaluation of the second order electric displacement field in the neighbourhood of a molecule which is quadratic in the transition moments. This operator, in contrast to $\vec{d}^{(0)}$ and $\vec{d}^{(1)}$, operates in the composite photon and electron field spaces. It changes the photon number by one, and in general changes the electron state. The procedure outlined in the derivation above may of course be extended in a similar manner to include higher powers of the multipole moments for

the evaluation of higher order terms in the expansion of $\vec{d}(\vec{r},t)$.

The magnetic field $b_\iota(\vec{r},t)$ for a source of charges and currents can also be found in the Heisenberg picture. The mode expansion for the magnetic field is

$$b_\iota(\vec{r},t) = i \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left\{b_\iota\alpha(t)e^{i\vec{k}\cdot\vec{r}-i\omega t}-\bar{b}_\iota\alpha^\dagger(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right\} \qquad (2.2.52)$$

and like the electric displacement field, may also be expanded as a series in powers of the transition moments

$$b_\iota(\vec{r},t) = b_\iota^{(0)}(\vec{r},t) + b_\iota^{(1)}(\vec{r},t) + b_\iota^{(2)}(\vec{r},t) + \ldots \qquad (2.2.53)$$

The first term $b_\iota^{(0)}(\vec{r},t)$ is obtained from (2.2.52) by making the substitution $\alpha(t) = \alpha(0)$, and is the free field operator. The first and second order magnetic field terms are determined in a manner identical to that used to obtain the displacement fields with $\alpha^{(1)}(t)$ and $\alpha^{(2)}(t)$ derived earlier and respectively given by the expressions (2.2.17) and (2.2.39) being re-employed. The results are now given with only the most important steps highlighted.

For the term linear in the moments, the first order magnetic field is obtained by inserting (2.2.17) into (2.2.52)

$$b_\iota^{(1)}(\vec{r},t) = \frac{i}{\hbar} \sum_{\substack{\vec{k},\lambda \\ m,n}} \left(\frac{\hbar k}{2\varepsilon_0 V}\right) [\beta_m^\dagger(0)\beta_n(0)b_\iota e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}[\mu_j^{mn-}e_j+\frac{1}{c}m_j^{mn-}\bar{b}_j+(-ik_\ell)Q_{j\ell}^{mn-}e_j]\times$$
$$\frac{(e^{i\omega_{mn}t}-e^{-i\omega t})}{i(\omega_{mn}+\omega)} + \text{H.C.}]. \qquad (2.2.54)$$

After performing polarisation sums and angular integrals and integrating with respect to k

$$b_i^{(1)}(\vec{\rho},t) = \frac{1}{4\pi\varepsilon_0 c}\sum_{m,n}\beta_m^\dagger(0)\beta_n(0)[\mu_j^{mn}k_{nm}^3 g_{ij}(k_{nm}\rho) + \frac{1}{c}m_j^{mn}k_{nm}^3 f_{ij}(k_{nm}\rho)$$

$$-iQ_{j\ell}^{mn}k_{nm}^4 J_{ij\ell}(k_{nm}\rho)]e^{ik_{nm}(\rho-ct)} \quad , \qquad t > \rho/c$$

$$= 0 \quad , \qquad t < \rho/c. \tag{2.2.55}$$

It is seen that the first order magnetic field (2.2.55) is the quantum analogue of the familiar classical field. Further, comparing (2.2.55) with the first order displacement field (2.2.34), the associated symmetry between the two becomes apparent: the electric field of a magnetic dipole is the negative of the magnetic field of an electric dipole and the electric field of an electric dipole is the same as the magnetic field of a magnetic dipole, with $\vec{\mu}^{mn}$ replaced by $\vec{m}^{mn}$ in both cases.

For the second order magnetic field, after substituting (2.2.39) into (2.2.53) and performing the usual polarisation sums and angular averages, the analogue of (2.2.41) is

$$b_i^{(2)}(\vec{\rho},t) = \frac{-i}{4\pi\varepsilon_0\hbar c}\sum_{\substack{\vec{k}',\lambda'\\m,n,p}}\left(\frac{\hbar ck'}{2\varepsilon_0 V}\right)^{1/2}\alpha'(0)e^{i\vec{k}'\cdot\vec{r}'}\frac{1}{2\pi i}\int_{-\infty}^{\infty}dke^{-i\omega t}\left\{\beta_m^\dagger(0)\beta_p(0)\times\right.$$

$$\left[k^3[G_{ij}(k\rho)+\bar{G}_{ij}(k\rho)]\mu_j^{mn}+\frac{k^3}{c}[F_{ij}(k\rho)-\bar{F}_{ij}(k\rho)]m_j^{mn}\right.$$

$$\left.-ik^4[J_{ij\ell}(k\rho)-\bar{J}_{ij\ell}(k\rho)]Q_{j\ell}^{mn}\right][\mu_\ell^{np}e_\ell'+\frac{1}{c}m_\ell^{np}b_\ell'+(ik_m')Q_{\ell m}^{np}e_\ell']\times$$

$$\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{pn}+\omega')(\omega_{mp}+\omega-\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pn}+\omega')(\omega_{mn}+\omega)}\right)+$$

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$$\beta_p^+(0)\beta_n(0)[\mu_\ell^{pm}e'_\ell+\tfrac{1}{c}m_\ell^{pm}b'_\ell+(ik'_m)Q_{\ell m}^{pm}e'_\ell] \times$$

$$\left[k^3[G_{ij}(k\rho)+\bar{G}_{ij}(k\rho)]\mu_j^{mn}+\frac{k^3}{c}[F_{ij}(k\rho)-\bar{F}_{ij}(k\rho)]m_j^{mn}\right.$$

$$\left.-ik^4[J_{ijk}(k\rho)-\bar{J}_{ijk}(k\rho)]Q_{jk}^{mn}\right]\left(\frac{e^{i(\omega_{pn}+\omega-\omega')t}-1}{(\omega_{pm}-\omega')(\omega_{pn}+\omega-\omega')}-\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{pm}-\omega')(\omega_{mn}+\omega)}\right)\right\}$$

$$+ \text{ H.C.} \qquad (2.2.56)$$

By changing the molecular state labels as before to ensure that $\beta_m^+(0)\beta_p(0)$ is common and performing the k-integral subject to the usual requirements, the following g_{ij}, f_{ij} and j_{ijk} dependent terms are obtained

$$\frac{-i}{4\pi\epsilon_0\hbar c}\sum_{\bar{m},\bar{n}}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\beta_m^+(0)\beta_m(0)\alpha(0)e^{i\vec{k}\cdot\vec{r}'}\left\{\mu_j^{mn}[\mu_\ell^{nm}e_\ell+\tfrac{1}{c}m_\ell^{nm}b_\ell+(ik_m)Q_{\ell m}^{nm}e_\ell]\times\right.$$

$$\left[-\frac{k^3 g_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}-k}+\frac{k_{nm}^3 g_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}}{k_{nm}-k}\right]+$$

$$[\mu_\ell^{mn}e_\ell+\tfrac{1}{c}m_\ell^{mn}b_\ell+(ik_m)Q_{\ell m}^{mn}e_\ell]\mu_j^{nm}\times$$

$$\left[-\frac{k^3 g_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}+k}+\frac{k_{nm}^3 g_{ij}(-k_{nm}\rho)e^{-ik_{nm}(\rho-ct)}}{k_{nm}+k}\right]\right\}+ \text{ H.C.} \qquad (2.2.57)$$

$$\frac{-i}{4\pi\epsilon_0\hbar c^2}\sum_{\bar{m},\bar{n}}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\beta_m^+(0)\beta_m(0)\alpha(0)e^{i\vec{k}\cdot\vec{r}'}\left\{m_j^{mn}[\mu_\ell^{nm}e_\ell+\tfrac{1}{c}m_\ell^{nm}b_\ell+(ik_m)Q_{\ell m}^{nm}e_\ell]\times\right.$$

$$\left[-\frac{k^3 f_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}-k}+\frac{k_{nm}^3 f_{ij}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}}{k_{nm}-k}\right]+$$

$$[\mu_\ell^{mn}e_\ell+\tfrac{1}{c}m_\ell^{mn}b_\ell+(ik_m)Q_{\ell m}^{mn}e_\ell]m_j^{nm}\times$$

$$\left[-\frac{k^3 f_{ij}(k\rho)e^{ik(\rho-ct)}}{k_{nm}+k} + \frac{k_{mn}^3 f_{ij}(-k_{nm}\rho)e^{-ik_{nm}(\rho-ct)}}{k_{nm}+k} \right] \right\} + \text{H.C.} \tag{2.2.58}$$

$$\frac{-1}{4\pi\varepsilon_0 \hbar c} \sum_{\substack{m,n \\ \vec{k},\lambda}} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} \beta_m^\dagger(0)\beta_m(0)\alpha(0)e^{i\vec{k}\cdot\vec{r}'} \left\{ Q_{jk}^{mn}[\mu_\ell^{nm}e_\ell + \tfrac{1}{c}m_\ell^{nm}b_\ell + (ik_m)Q_{\ell m}^{nm}e_\ell] \times \right.$$

$$\left[-\frac{k^4 j_{ijk}(k\rho)e^{ik(\rho-ct)}}{k_{nm}-k} + \frac{k_{nm}^4 j_{ijk}(k_{nm}\rho)e^{ik_{nm}(\rho-ct)}}{k_{nm}-k} \right] +$$

$$[\mu_\ell^{mn}e_\ell + \tfrac{1}{c}m_\ell^{mn}b_\ell + (ik_m)Q_{\ell m}^{mn}e_\ell]Q_{jk}^{nm} \times$$

$$\left[-\frac{k^4 j_{ijk}(k\rho)e^{ik(\rho-ct)}}{k_{nm}+k} + \frac{k_{mn}^4 j_{ijk}(-k_{nm}\rho)e^{-ik_{nm}(\rho-ct)}}{k_{nm}+k} \right] \right\} + \text{H.C.} \tag{2.2.59}$$

The total magnetic field to this order is obtained by adding (2.2.57)-(2.2.59). As for the displacement operator, the individual source fields quadratic in the moments are extracted for a source situated at the origin, and are

$$b_i^{(2)}(\vec{\mu\mu};\vec{r},t) = \frac{i}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} \left\{ e_\ell \alpha(0)\beta_m^\dagger(0)\beta_m(0) \times \right.$$

$$\left[\sum_n \left\{ \frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega} + \frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega} \right\} k^3 g_{ij}(kr)e^{ik(r-ct)} \right.$$

$$\left. -\sum_n \frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega} k_{nm}^3 g_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)} -\sum_n \frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega} k_{mn}^3 g_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)} \right] \right\}$$

$$+ \text{H.C.} \tag{2.2.60}$$

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$$b_i^{(2)}(\vec{\mu m};\vec{r},t) = \frac{i}{4\pi\varepsilon_0 c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left\{\alpha(0)\beta_m^+(0)\beta_m(0)\times\right.$$

$$\left[b_\ell\left[\sum_n\left\{\frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega} + \frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}k^3 g_{ij}(kr)e^{ik(r-ct)}\right.\right.$$

$$\left.\left.- \sum_n\frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega}k_{nm}^3 g_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_n\frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}k_{mn}^3 g_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right] +$$

$$\left[e_\ell\left[\sum_n\left\{\frac{m_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega} + \frac{\mu_\ell^{mn}m_j^{nm}}{E_{nm}+\hbar\omega}\right\}k^3 f_{ij}(kr)e^{ik(r-ct)}\right.\right.$$

$$\left.\left.\left.- \sum_n\frac{m_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}k_{nm}^3 f_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_n\frac{\mu_\ell^{mn}m_j^{nm}}{E_{nm}+\hbar\omega}k_{mn}^3 f_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right]\right\}$$

$$+ \text{H.C.} \qquad\qquad (2.2.61)$$

$$b_i^{(2)}(\vec{mm};\vec{r},t) = \frac{i}{4\pi\varepsilon_0 c^2}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left\{b_\ell\alpha(0)\beta_m^+(0)\beta_m(0)\times\right.$$

$$\left[\sum_n\left\{\frac{m_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega} + \frac{m_\ell^{mn}m_j^{nm}}{E_{nm}+\hbar\omega}\right\}k^3 f_{ij}(kr)e^{ik(r-ct)}\right.$$

$$\left.\left.- \sum_n\frac{m_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega}k_{nm}^3 f_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_n\frac{m_\ell^{mn}m_j^{nm}}{E_{nm}+\hbar\omega}k_{mn}^3 f_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\}$$

$$+ \text{H.C.} \qquad\qquad (2.2.62)$$

$$b_i^{(2)}(\vec{\mu Q};\vec{r},t) = \frac{1}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left\{e_\ell k_m\alpha(0)\beta_m^+(0)\beta_m(0)\times\right.$$

$$\left[-\sum_n\left\{\frac{\mu_j^{mn}Q_{\ell m}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{\ell m}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}k^3 g_{ij}(kr)e^{ik(r-ct)}\right.$$

$$\left.\left.+ \sum_n\frac{\mu_j^{mn}Q_{\ell m}^{nm}}{E_{nm}-\hbar\omega}k_{nm}^3 g_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)} + \sum_n\frac{Q_{\ell m}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}k_{mn}^3 g_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\right]\right\} +$$

$$\frac{1}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left\{e_\ell\alpha(0)\beta_m^+(0)\beta_m(0)\times\right.$$

$$\left[\sum_n\left\{\frac{Q_{j\ell}^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega} + \frac{\mu_\ell^{mn}Q_{j\ell}^{nm}}{E_{nm}+\hbar\omega}\right\}k^4 j_{ij\ell}(kr)e^{ik(r-ct)}\right.$$

$$-\sum_{\bar{n}} \frac{Q_{j\mathit{k}}^{mn}\mu_{\mathit{l}}^{nm}}{E_{nm}-\hbar\omega}\, k_{nm}^4 j_{ij\mathit{k}}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_{\bar{n}} \frac{\mu_{\mathit{l}}^{mn}Q_{j\mathit{k}}^{nm}}{E_{nm}+\hbar\omega}\, k_{mn}^4 j_{ij\mathit{k}}(k_{mn}r)e^{ik_{mn}(r-ct)}\Big]\Big\}$$

$$+ \text{ H.C.} \qquad\qquad (2.2.63)$$

$$b_i^{(2)}(\vec{m}\vec{Q};\vec{r},t) = \frac{1}{4\pi\varepsilon_0 c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\Big\{ e_{\mathit{l}}k_{m}\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times$$

$$\Big[-\sum_{\bar{n}}\Big\{\frac{m_{\mathit{j}}^{mn}Q_{\mathit{l}m}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{\mathit{l}m}^{mn}m_{\mathit{j}}^{nm}}{E_{nm}+\hbar\omega}\Big\}k^3 f_{ij}(kr)e^{ik(r-ct)}$$

$$+ \sum_{\bar{n}}\frac{m_{\mathit{j}}^{mn}Q_{\mathit{l}m}^{nm}}{E_{nm}-\hbar\omega}\, k_{nm}^3 f_{ij}(k_{nm}r)e^{ik_{nm}(r-ct)} + \sum_{\bar{n}}\frac{Q_{\mathit{l}m}^{mn}m_{\mathit{j}}^{nm}}{E_{nm}+\hbar\omega}\, k_{mn}^3 f_{ij}(k_{mn}r)e^{ik_{mn}(r-ct)}\Big]\Big\} +$$

$$\frac{1}{4\pi\varepsilon_0 c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\Big\{ b_{\mathit{l}}\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times$$

$$\Big[\sum_{\bar{n}}\Big\{\frac{Q_{j\mathit{k}}^{mn}m_{\mathit{l}}^{nm}}{E_{nm}-\hbar\omega} + \frac{m_{\mathit{l}}^{mn}Q_{j\mathit{k}}^{nm}}{E_{nm}+\hbar\omega}\Big\}k^4 j_{ij\mathit{k}}(kr)e^{ik(r-ct)}$$

$$- \sum_{\bar{n}}\frac{Q_{j\mathit{k}}^{mn}m_{\mathit{l}}^{nm}}{E_{nm}-\hbar\omega}\, k_{nm}^4 j_{ij\mathit{k}}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_{\bar{n}}\frac{m_{\mathit{l}}^{mn}Q_{j\mathit{k}}^{nm}}{E_{nm}+\hbar\omega}\, k_{mn}^4 j_{ij\mathit{k}}(k_{mn}r)e^{ik_{mn}(r-ct)}\Big]\Big\}$$

$$+ \text{ H.C.} \qquad\qquad (2.2.64)$$

$$b_i^{(2)}(\vec{Q}\vec{Q};\vec{r},t) = \frac{i}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\Big\{ e_{\mathit{l}}k_{m}\alpha(0)\beta_m^\dagger(0)\beta_m(0)\times$$

$$\Big[\sum_{\bar{n}}\Big\{\frac{Q_{j\mathit{k}}^{mn}Q_{\mathit{l}m}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{\mathit{l}m}^{mn}Q_{j\mathit{k}}^{nm}}{E_{nm}+\hbar\omega}\Big\}k^4 j_{ij\mathit{k}}(kr)e^{ik(r-ct)}$$

$$- \sum_{\bar{n}}\frac{Q_{j\mathit{k}}^{mn}Q_{\mathit{l}m}^{nm}}{E_{nm}-\hbar\omega}\, k_{nm}^4 j_{ij\mathit{k}}(k_{nm}r)e^{ik_{nm}(r-ct)} - \sum_{\bar{n}}\frac{Q_{\mathit{l}m}^{mn}Q_{j\mathit{k}}^{nm}}{E_{nm}+\hbar\omega}\, k_{mn}^4 j_{ij\mathit{k}}(k_{mn}r)e^{ik_{mn}(r-ct)}\Big]\Big\}$$

$$+ \text{ H.C.} \qquad\qquad (2.2.65)$$

Returning now to the diamagnetic coupling terms and examining the electromagnetic fields arising from this interaction, it is found from (2.2.11), that for a source located at the origin,

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$$\alpha^{DIA}(t) = \alpha(0) -$$

$$\frac{ie^2}{4\hbar m}\varepsilon_{ij\eta}\varepsilon_{k\ell\eta}\sum_{\substack{\vec{k},\lambda \\ m,n \\ \vec{k}',\lambda'}}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left(\frac{\hbar k'}{2\varepsilon_0 cV}\right)^{1/2}(q_i q_\ell)^{mn}\beta_m^\dagger(0)\beta_n(0)\bar{b}_j \times$$

$$\left[b_\ell'\alpha'(0)\left(\frac{e^{i(\omega_{mn}+\omega-\omega')t}-1}{i(\omega_{mn}+\omega-\omega')}\right) - \bar{b}_\ell'\alpha'^{\dagger}(0)\left(\frac{e^{i(\omega_{mn}+\omega+\omega')t}-1}{i(\omega_{mn}+\omega+\omega')}\right)\right] . \qquad (2.2.66)$$

It should be noted that in the diamagnetic contribution there is no term linear in the molecular variables, the leading molecular dependent part being quadratic in the electric charge. Substituting (2.2.66) into the mode expansion for $d_i^\perp(\vec{r},t)$, the diamagnetic coupling contribution to the electric displacement vector is

$$d_i^{\perp(DIA)}(\vec{r},t) = \frac{e^2}{4\hbar m}\varepsilon_{jk\eta}\varepsilon_{\ell m\eta}\sum_{\substack{m,n \\ \vec{k}',\lambda' \\ \vec{k},\lambda}}\left(\frac{\hbar k}{2V}\right)\left(\frac{\hbar k'}{2\varepsilon_0 cV}\right)^{1/2}e_i\bar{b}_\ell e^{i\vec{k}.\vec{r}}(q_j q_\ell)^{mn} \times$$

$$\beta_m^\dagger(0)\beta_n(0)\alpha'(0)b_m'\left(\frac{e^{i(\omega_{mn}-\omega')t}-e^{-i\omega t}}{i(\omega_{mn}+\omega-\omega')}\right) + H.C. \qquad (2.2.67)$$

After performing the usual sum over polarisations and angular average

$$d_i^{\perp(DIA)}(\vec{r},t) = \frac{e^2}{16\pi^2 mc}\varepsilon_{jk\eta}\varepsilon_{\ell m\eta}\sum_{\substack{m,n \\ \vec{k}',\lambda'}}\left(\frac{\hbar k'}{2\varepsilon_0 cV}\right)^{1/2}(q_j q_\ell)^{mn}\beta_m^\dagger(0)\beta_n(0)\alpha'(0)b_m' \times$$

$$\int_0^\infty dk\, k^3[G_{i\ell}(kr)+\bar{G}_{i\ell}(kr)]\left(\frac{e^{i(k_{mn}-k')ct}-e^{-ikct}}{(k_{mn}+k-k')}\right) + H.C. \qquad (2.2.68)$$

Integrating subject to the usual restrictions results in

$$d_i^{\perp(DIA)}(\vec{r},t) = \frac{ie^2}{8\pi mc}\varepsilon_{jk\eta}\varepsilon_{\ell m\eta}\sum_{\substack{m,n \\ \vec{k},\lambda}}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}(q_j q_\ell)^{mm}\beta_m^\dagger(0)\beta_m(0) \times$$

$$\alpha(0)b_m k^3 g_{i\ell}(kr)e^{ik(r-ct)} + H.C. \qquad (2.2.69)$$

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Similarly, for the diamagnetic contribution to the magnetic field, after substituting (2.2.66) into the mode expansion for $\vec{b}(\vec{r},t)$ and following the usual procedure,

$$b_i^{(DIA)}(\vec{r},t) = \frac{-ie^2}{8\pi\varepsilon_0 mc^2} \varepsilon_{jkn} \varepsilon_{\ell mn} \sum_{\substack{\bar{m},\bar{n} \\ \vec{k},\lambda}} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} (q_j q_\ell)^{mm} \beta_m^\dagger(0)\beta_m(0) \times$$

$$\alpha(0)b_m k^3 f_{i\ell}(kr) e^{ik(r-ct)} + H.C. \qquad (2.2.70)$$

This completes the formal derivation of the time-dependent electric displacement and magnetic field operators correct to second order in the transition moments and including all interaction terms of a comparable order, in the Heisenberg picture of multipolar QED. The Maxwell fields were expanded as power series in the molecular multipole moments and found to be complicated functions of the boson and fermion operators. The source-independent field acts solely in the photon space, simply creating or destroying a single quantum of light. In contrast, the first order electromagnetic fields, linear in the transition moments, operates exclusively in the space of the fermion field, leading to changes of molecular state. The first order field was shown to be the quantum electrodynamical analogue of the classical multipole radiation field emitted by an excited source. The second order Maxwell fields, quadratic in the sources, however, operate in both the photon and electron Fock spaces, changing both the photon number by unity and the state of electronic excitation. As expected all the fields exhibit causal behaviour, vanishing for t < r/c. The extension to even higher terms of the multipolar series and powers of the radiation fields is straightforward, but leads to progressively more complicated expressions.

2.3 MAXWELL FIELDS FROM MINIMAL-COUPLING HAMILTONIAN

In this Section, the minimal-coupling version of the quantum electrodynamical radiation-molecule Hamiltonian is used as the starting point in the derivation of the Maxwell fields in the neighbourhood of a molecule. As mentioned previously, in minimal-coupling the momentum conjugate to the vector potential is proportional to the transverse component of the electric field. This is in contrast to the multipolar case where the conjugate momentum is proportional to the transverse component of the displacement vector field [30]. Therefore, instead of evaluating the displacement field in the vicinity of a molecule as in the multipolar case, in the minimal-coupling approach the transverse electric field operator is determined. Further, for a neutral system the total electric field is equal to the transverse displacement field outside the source since the longitudinal component of the displacement field is zero. Also, since the transverse electric polarisation field is non-local, $\vec{d}^{\perp}(\vec{r}) \neq \varepsilon_0 \vec{e}^{\perp}(\vec{r})$ outside the sources. From (1.2.34) it is seen that $\vec{d}^{TOT}(\vec{r}) = \varepsilon_0 \vec{e}^{TOT}(\vec{r}) + \vec{p}^{TOT}(\vec{r})$. This has the important consequence that $\vec{e}^{\perp}(\vec{r})$ is unretarded, in contrast to $\vec{e}^{TOT}(\vec{r})$ which is fully retarded [31]. The "static" contributions manifest themselves as poles at $k = 0$ in the evaluation of the k-integral. These additional poles are absent in the multipolar treatment. A retarded result for $\vec{e}^{TOT}(\vec{r})$ is finally obtained after cancellation of the static contributions arising from $\vec{p}^{\perp}(\vec{r})$ with those from $\vec{e}^{\perp}(\vec{r})$. Although the equations of motion for the magnetic field remain unaltered in both frameworks, the magnetic fields derived in the previous Section using the multipolar approach do not remain valid in the minimal-coupling case as the operator equations of motion are different. Hence $\vec{b}(\vec{r},t)$ is also determined in minimal-coupling.

This treatment extends previous work in which the total electric field was obtained to first order within the electric dipole approximation [31], by including magnetic dipole and electric quadrupole couplings, and by the evaluation of the magnetic field. The derivation given takes into account the leading correction terms arising from the inclusion of the first derivative of the vector potential. The evaluation of the field operators is similar to that of the preceding Section, but with several important and subtle differences which will be indicated where they occur.

The starting point in the derivation of the Maxwell fields is the minimal-coupling Hamiltonian in second quantised form

$$
H_{MIN} = \sum_n b_n^\dagger b_n E_n + \sum_{\vec{k},\lambda} a^\dagger a \hbar\omega +
$$

$$
\frac{e}{m} \sum_{\substack{\vec{k},\lambda \\ m,n}} \left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} b_m^\dagger b_n \left\{ e_j a [p_j^{mn} + ik_\ell (p_j q_\ell)^{mn}] + \bar{e}_j a^\dagger [p_j^{mn} - ik_\ell (p_j q_\ell)^{mn}] \right\} +
$$

$$
\frac{e^2}{2m} \sum_{\substack{\vec{k}',\lambda',m \\ \vec{k}'',\lambda'',n}} \left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2} \left(\frac{\hbar}{2\varepsilon_0 ck''V}\right)^{1/2} b_m^\dagger b_n [e_j' e_j'' a' a'' (1 + ik_\ell' q_\ell^{mn} + ik_\ell'' q_\ell^{mn}) +
$$

$$
e_j' \bar{e}_j'' a' a''^\dagger (1 + ik_\ell' q_\ell^{mn} - ik_\ell'' q_\ell^{mn}) + \bar{e}_j' e_j'' a'^\dagger a'' (1 - ik_\ell' q_\ell^{mn} + ik_\ell'' q_\ell^{mn}) +
$$

$$
\bar{e}_j' \bar{e}_j'' a'^\dagger a''^\dagger (1 - ik_\ell' q_\ell^{mn} - ik_\ell'' q_\ell^{mn})]
$$

$$(2.3.1)$$

where use has been made of the mode expansion of the vector potential

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

$$(2.3.2)$$

The time dependence of the boson and fermion operators in (2.3.1) is implicit as is the mode dependence of the photon creation and annihilation operators and electric polarisation vectors. It should be noted that in the Hamiltonian (2.3.1), the spatial variations of the vector potential to first order have been partially accounted for by including the first derivative of $\vec{a}(\vec{q})$. This is essential for the inclusion of magnetic dipole and electric quadrupole moments in the evaluation of the electromagnetic radiation fields. In previous studies [31] within the electric dipole approximation, where the radiation wavelength is large compared with molecular dimensions, the variation of the vector potential over the extent of the molecules is ignored. Thus $\vec{a}(\vec{q})$ is replaced by $\vec{a}(\vec{R})$, $\vec{R}$ being the molecular centre, usually taken to be the origin, so that the electric dipole is the only resulting molecular multipole interaction term. By taking the first derivative, the field derived will include electric quadrupole and magnetic dipole couplings as well as the contribution from the electric dipole interaction term.

The Heisenberg equations of motion for the electron and photon field operators are evaluated using the analogues of (2.2.9) and (2.2.10) along with the relations (2.2.5) and (2.2.6). Thus

$$
i\hbar \dot{a} = [a, H_{MIN}]
$$

$$
= \hbar\omega a + \frac{e}{m} \sum_{m,n} \left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} b_m^\dagger b_n \bar{e}_j [p_j^{mn} - ik_\ell(p_j q_\ell)^{mn}] +
$$

$$
\frac{e^2}{m} \sum_{\substack{\vec{k}',\lambda' \\ m;n}} \sum \left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} \left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2} b_m^\dagger b_n \bar{e}_j \times
$$

$$
[e_j' a' (1 + ik_\ell' q_\ell^{mn} - ik_\ell q_\ell^{mn}) + \bar{e}_j' a'^\dagger (1 - ik_\ell' q_\ell^{mn} - ik_\ell q_\ell^{mn})] \qquad (2.3.3)
$$

and

$$i\hbar \dot{b}_n = [b_n, H_{MIN}]$$

$$= \hbar\omega_n b_n + \frac{e}{m}\sum_{\vec{k},\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} b_m\left\{e_j a[p_j^{nm}+ik_\ell(p_j q_\ell)^{nm}]+\bar{e}_j a^\dagger[p_j^{nm}-ik_\ell(p_j q_\ell)^{nm}]\right\}.$$

(2.3.4)

In (2.3.4) the term of order e^2 has been ignored since this will not be required in the derivation of the fields for terms up to $\vec{\mu}$, $\vec{m}$, and $\vec{Q}$. By employing the interaction representation and integrating the last two expressions with respect to time, it is found that

$$\alpha(t) = \alpha(0) + \frac{e}{i\hbar m}\sum_{m,n}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\bar{e}_j[p_j^{mn}-ik_\ell(p_j q_\ell)^{mn}] \times$$

$$\int_0^t dt'\, e^{i(\omega_{mn}+\omega)t'}\beta_m^\dagger(t')\beta_n(t') +$$

$$\frac{e^2}{i\hbar m}\sum_{\vec{k}',\lambda',m,n}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\beta_m^\dagger(0)\beta_n(0)\bar{e}_j \times$$

$$\left[e_j'\alpha'(0)(1+ik_\ell'q_\ell^{mn}-ik_\ell q_\ell^{mn})\frac{e^{i(\omega_{mn}+\omega-\omega')t}-1}{i(\omega_{mn}+\omega-\omega')} + \right.$$

$$\left.\bar{e}_j'\alpha'^\dagger(0)(1-ik_\ell'q_\ell^{mn}-ik_\ell q_\ell^{mn})\frac{e^{i(\omega_{mn}+\omega+\omega')t}-1}{i(\omega_{mn}+\omega+\omega')}\right] , \quad (2.3.5)$$

and

$$\beta_n^{(1)}(t) = \frac{e}{i\hbar m}\sum_{\vec{k},\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\beta_m(0)\left[e_j\alpha(0)[p_j^{nm}+ik_\ell(p_j q_\ell)^{nm}]\frac{e^{-i(\omega_{mn}+\omega)t}-1}{-i(\omega_{mn}+\omega)}\right.$$

$$\left. + \bar{e}_j\alpha^\dagger(0)[p_j^{nm}-ik_\ell(p_j q_\ell)^{nm}]\frac{e^{-i(\omega_{mn}-\omega)t}-1}{-i(\omega_{mn}-\omega)}\right] . \quad (2.3.6)$$

It is now shown how the various multipole moments to this order of

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approximation may be extracted from the spatial variation of the vector potential [37]. For the mnth matrix element,

$$(p_i q_j)^{mn} = \frac{1}{2}\left\{ [(p_i q_j)^{mn} + (q_i p_j)^{mn}] + [(p_i q_j)^{mn} - (q_i p_j)^{mn}] \right\} . \qquad (2.3.7)$$

Using the fundamental commutator relationship between position and momentum,

$$[\vec{q}, H_{MOL}] = \frac{i\hbar}{m} \vec{p} \qquad (2.3.8)$$

results in

$$p_i^{mn} = \frac{im}{\hbar} E_{mn} q_i^{mn} , \qquad (2.3.9)$$

so that the first term within curly brackets of (2.3.7) becomes

$$\sum_p \left[p_i^{mp} q_j^{pn} + q_i^{mp} p_j^{pn} \right] = \sum_p \left(\frac{im}{\hbar} \right) \left[E_{mp} q_i^{mp} q_j^{pn} + E_{pn} q_i^{mp} q_j^{pn} \right] = \frac{im}{\hbar} E_{mn} (q_i q_j)^{mn} . \qquad (2.3.10)$$

The second term of (2.3.7) can be written as

$$\left[q_j p_i - q_i p_j - i\hbar \delta_{ij} \right]^{mn} = - \varepsilon_{ij\ell} (\vec{q} \times \vec{p})_\ell^{mn} - i\hbar \delta_{ij} \delta_{mn} . \qquad (2.3.11)$$

Adding the last two expressions results in (2.3.7) becoming

$$(p_i q_j)^{mn} = \frac{1}{2}\left\{ \frac{im}{\hbar} E_{mn} (q_i q_j)^{mn} - \varepsilon_{ij\ell} (\vec{q} \times \vec{p})_\ell^{mn} - i\hbar \delta_{ij} \delta_{mn} \right\} . \qquad (2.3.12)$$

The above together with (2.3.9) can be converted to an identity

explicitly involving multipole moments advantageous for future use

$$\frac{-e}{m}e_i[p_i \mp ik_j(p_iq_j)]^{mn} = \frac{i}{\hbar}e_iE_{mn}\mu_i^{mn} \mp ikb_im_i^{mn} \pm \frac{1}{\hbar}e_ik_jE_{mn}Q_{ij}^{mn} \qquad (2.3.13)$$

where $\vec{\mu}$, $\vec{m}$ and $\vec{\vec{Q}}$ have the usual definitions of the electric dipole, magnetic dipole and electric quadrupole moments, and the orthogonality of $\vec{e}$, $\vec{b}$ and $\hat{k}_j$ has been used.

Before going on to derive the magnetic field, the total electric field in the neighbourhood of a molecule is obtained. Its transverse component is proportional to the canonical field momentum in the minimal-coupling approach, and is given by the mode expansion

$$e_i^{\perp}(\vec{r},t) = i\sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}[e_i\alpha(t)e^{i\vec{k}\cdot\vec{r}-i\omega t} - \bar{e}_i\alpha^{\dagger}(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}]. \qquad (2.3.14)$$

To evaluate the transverse electric field in series of powers of the transition moments up to and including the electric quadrupole moment, the operator equations (2.3.5) and (2.3.6) together with the relation (2.3.13) are used. The first order field, linear in the transition moments, is obtained after substituting the first order term of the operator equation $\alpha^{(1)}(t)$. This is given by the first term of (2.3.5), that part linear in the electric charge. Inserting (2.3.13) into the first part of (2.3.5),

$$\alpha^{(1)}(t) = \frac{i}{\hbar}\sum_{m,n}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\beta_m^{\dagger}(0)\beta_n(0) \times$$

$$\left[\frac{i}{\hbar}\bar{e}_iE_{mn}\mu_i^{mn} - ik\bar{b}_im_i^{mn} + \frac{1}{\hbar}\bar{e}_ik_jE_{mn}Q_{ij}^{mn}\right]\frac{e^{i(\omega_{mn}+\omega)t}-1}{i(\omega_{mn}+\omega)}. \qquad (2.3.15)$$

Substituting the above into (2.3.14), the first order transverse

electric field is

$$e_i^{\perp(1)}(\vec{r},t) = \frac{i}{2\varepsilon_0 V} \sum_{\substack{\vec{k},\lambda \\ m;n}} \left\{ \beta_m^\dagger(0)\beta_n(0)e_i e^{i\vec{k}\cdot\vec{r}} \times \right.$$

$$\left. \left[\frac{i}{\hbar}\bar{e}_j E_{mn}\mu_j^{mn} - ik\bar{b}_j m_j^{mn} + \frac{1}{\hbar}\bar{e}_j k_\ell E_{mn}Q_{j\ell}^{mn}\right]\left(\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{\omega_{mn}+\omega}\right) + \text{H.C.}\right\}.$$

$$(2.3.16)$$

After performing the polarisation sum and angular integration, the electric dipole dependent contribution is found to be

$$e_i^{\perp(1)}(\vec{\mu};\vec{r},t) = -\sum_{m,n} \frac{1}{4\pi\varepsilon_0}\beta_m^\dagger(0)\beta_n(0)k_{mn}\mu_j^{mn} \times$$

$$\frac{1}{2\pi i}\int_0^\infty dk k^2 [F_{ij}(kr)-\bar{F}_{ij}(kr)]\frac{e^{-ik_{nm}ct}-e^{-ikct}}{k-k_{nm}} + \text{H.C.} \quad (2.3.17)$$

It is convenient when working in the minimal-coupling formalism to use the definitions of the tensor fields $F_{ij}(kr)$, $G_{ij}(kr)$ etc., since the occurrence of additional poles are then easily visible. Evaluating the k-integral for $r < ct$ gives

$$e_i^{\perp(1)}(\vec{\mu};\vec{r},t) = \frac{-1}{4\pi\varepsilon_0} \sum_{m,n} \beta_m^\dagger(0)\beta_n(0)\mu_j^{mn}k_{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{2\pi ir} \times$$

$$\int_{-\infty}^{\infty} dk \frac{(e^{ikr}-e^{-ikr})(e^{-ik_{nm}ct}-e^{-ikct})}{k(k-k_{nm})}$$

$$= \frac{1}{4\pi\varepsilon_0} \sum_{m,n} \beta_m^\dagger(0)\beta_n(0)\mu_j^{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{-ik_{nm}ct}}{r}(e^{ik_{nm}r}-1). \quad (2.3.18)$$

The longitudinal electric field correct up to the electric quadrupole moment is given by

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$$\varepsilon_0 e''_i(\vec{r},t) = -p''_i(\vec{r},t) = p^\perp_i(\vec{r},t) = \sum_{m,n} (\mu^{mn}_j - Q^{mn}_{jk}\nabla_k)\beta^\dagger_m(t)\beta_n(t)\delta^\perp_{ij}(\vec{r})e^{-i\omega_{nm}t} .$$

(2.3.19)

Noting that for $r \neq 0$,

$$\delta^\perp_{ij}(\vec{r}) = \frac{-1}{4\pi r^3}(\delta_{ij}-3\hat{r}_i\hat{r}_j)$$

(2.3.20)

it follows from (2.3.19) that the first order electric dipole dependent contribution is

$$\frac{-1}{4\pi}\sum_{m,n}\beta^\dagger_m(0)\beta_n(0)\mu^{mn}_j e^{-i\omega_{nm}t}(\delta_{ij}-3\hat{r}_i\hat{r}_j)/r^3 .$$

(2.3.21)

By adding (2.3.21) to the transverse electric field (2.3.18), the *total* electric field to this order of approximation is found to be [31]

$$
e^{\text{Tot}(1)}_i(\vec{\mu};\vec{r},t) = \frac{1}{4\pi\varepsilon_0}\sum_{m,n}\beta^\dagger_m(0)\beta_n(0)\mu^{mn}_j(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{ik_{nm}(r-ct)}}{r}
$$
$$
= \frac{1}{\varepsilon_0}d^{\perp(1)}_i(\vec{\mu};\vec{r},t)
$$

(2.3.22)

which is fully retarded. Returning to (2.3.16) and evaluating the magnetic dipole contribution to the first order transverse electric field, after performing the sum over polarisations and angular averages,

$$
e^{\perp(1)}_i(\vec{m};\vec{r},t) = \frac{-1}{4\pi\varepsilon_0 c}\sum_{m,n}\beta^\dagger_m(0)\beta_n(0)m^{mn}_j(i\varepsilon_{ijk}\nabla_k)\frac{1}{2\pi i r} \times
$$
$$
\int_{-\infty}^{\infty}dk\,\frac{(e^{ikr}-e^{-ikr})(e^{-ik_{nm}ct}-e^{-ikct})}{k-k_{nm}}
$$
$$
= \frac{-1}{4\pi\varepsilon_0 c}\sum_{m,n}\beta^\dagger_m(0)\beta_n(0)m^{mn}_j(ik_{nm}\varepsilon_{ijk}\nabla_k)\frac{e^{ik_{nm}(r-ct)}}{r}
$$

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$$= \frac{-1}{4\pi\epsilon_0 c} \sum_{m,n} \beta_m^\dagger(0)\beta_n(0)m_j^{mn}k_{nm}^3 \epsilon_{\ell j}(k_{nm}r)e^{ik_{nm}(r-ct)} = e_{\ell}^{\text{TOT}(1)}(\vec{m}) = \frac{1}{\epsilon_0}d_{\ell}^{\perp(1)}(\vec{m})$$

$$(2.3.23)$$

which is entirely retarded. Physically a magnetic dipole has no static electric field and hence $\vec{e}'' = 0$. Algebraically this is due to the absence of the pole occurring at $k = 0$ in the integrand above.

The electric quadrupole dependent part is evaluated in a manner similar to that used for the electric dipole dependent term, and its contribution is found to be

$$e_{\ell}^{\perp(1)}(\vec{Q};\vec{r},t) = -\sum_{m,n}\frac{1}{4\pi\epsilon_0}\beta_m^\dagger(0)\beta_n(0)Q_{j\ell}^{mn}k_{nm}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_\ell \frac{1}{2\pi i r} \times$$

$$\int_{-\infty}^{\infty}dk \frac{(e^{ikr}-e^{-ikr})(e^{-ik_{nm}ct}-e^{-ikct})}{k(k-k_{nm})}$$

$$= \frac{-1}{4\pi\epsilon_0}\sum_{m,n}\beta_m^\dagger(0)\beta_n(0)Q_{j\ell}^{mn}k_{nm}^4 h_{ij\ell}(k_{nm}r)e^{ik_{nm}(r-ct)} +$$

$$\frac{1}{4\pi\epsilon_0}\sum_{m,n}\beta_m^\dagger(0)\beta_n(0)Q_{j\ell}^{mn}e^{-ik_{nm}ct}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_\ell \frac{1}{r}. \qquad (2.3.24)$$

From (2.3.19), the first order longitudinal electric field component due to a quadrupole source is

$$\frac{-1}{4\pi\epsilon_0}\sum_{m,n}\beta_m^\dagger(0)\beta_n(0)Q_{j\ell}^{mn}e^{-i\omega_{nm}t}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_\ell \frac{1}{r} \qquad (2.3.25)$$

so that the total quadrupole dependent first order electric field is

$$e_{\ell}^{\text{TOT}(1)}(\vec{Q};\vec{r},t) = \frac{-1}{4\pi\epsilon_0}\sum_{m,n}\beta_m^\dagger(0)\beta_n(0)Q_{j\ell}^{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_\ell \frac{e^{ik_{nm}(r-ct)}}{r}$$

$$= \frac{1}{\epsilon_0}d_{\ell}^{\perp(1)}(\vec{Q};\vec{r},t). \qquad (2.3.26)$$

This completes the derivation of the first order total electric field in the proximity of a molecule in terms of the source moments $\vec{\mu}$, $\vec{m}$ and $\vec{Q}$ in the minimal-coupling formalism. The transverse component of $\vec{e}(\vec{r})$ was obtained directly from the mode expansion for the canonical momentum while the longitudinal part was found from the electric polarisation field. The addition of these two contributions, giving the retarded total electric field, is found to be equal to the transverse displacement field operator of the multipolar formalism. The first order contribution to the electric field was derived using the first term of (2.3.5), that part linear in the electric charge.

To determine the second order electric field, quadratic in the multipole moments, both the terms linear and quadratic in the electric charge are needed. From (2.3.5)

$$
\alpha^{(2)}(t) = \frac{e}{i\hbar m} \sum_{m,p} \left(\frac{\hbar}{2\epsilon_0 ckV}\right)^{1/2} \bar{e}_j [p_j^{mp} - ik_\ell (p_j q_\ell)^{mp}] \times
$$

$$
\int_0^t dt' \, e^{i(\omega_{mp}+\omega)t'} [\beta_m^{+(0)}(t')\beta_p^{(1)}(t') + \beta_m^{+(1)}(t')\beta_p^{(0)}(t')]
$$

$$
+ \frac{e^2}{i\hbar m} \sum_{\substack{\vec{k}',\lambda' \\ m;p}} \left(\frac{\hbar}{2\epsilon_0 ckV}\right)^{1/2} \left(\frac{\hbar}{2\epsilon_0 ck'V}\right)^{1/2} \beta_m^+(0)\beta_p(0)\bar{e}_j \times
$$

$$
\left[e'_j \alpha'(0)(1-ik_\ell q_\ell^{mp}+ik'_\ell q_\ell^{mp})\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{i(\omega_{mp}+\omega-\omega')} + \right.
$$

$$
\left. \bar{e}'_j \alpha'^+(0)(1-ik_\ell q_\ell^{mp}-ik'_\ell q_\ell^{mp})\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{i(\omega_{mp}+\omega+\omega')} \right]. \quad (2.3.27)
$$

After substituting (2.3.6) and its Hermitian-conjugate into the first term of (2.3.27), that part linear in e, which comes from the "$\vec{p}.\vec{a}$" term

of the interaction Hamiltonian, (2.3.27) becomes after carrying out the t-integral,

$$\alpha^{(2)}(t) = \left(\frac{e}{i\hbar m}\right)^2 \sum_{\vec{k}',\lambda',m,n,p} \left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} \left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2} \beta_m^\dagger(0)\beta_p(0)\bar{e}_j$$

$$\left[e'_\ell \alpha'(0)\left\{ [p_\ell^{mn} p_j^{np}+ik'_m(p_\ell q_m)^{mn} p_j^{np}-ik_\ell p_\ell^{mn}(p_j q_\ell)^{np}] \times \right. \right.$$

$$\left[\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{mp}+\omega-\omega')(\omega_{mn}-\omega')}\right) - \left(\frac{e^{i(\omega_{np}+\omega)t}-1}{(\omega_{np}+\omega)(\omega_{mn}-\omega')}\right)\right] +$$

$$[p_j^{mn} p_\ell^{np}-ik_\ell(p_j q_\ell)^{mn} p_\ell^{np}+ik'_m p_j^{mn}(p_\ell q_m)^{np}] \times$$

$$\left. \left[\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{mp}+\omega-\omega')(\omega_{pn}+\omega')}\right) - \left(\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{mn}+\omega)(\omega_{pn}+\omega')}\right)\right]\right\} +$$

$$\bar{e}'_\ell \alpha'^\dagger(0)\left\{ [p_\ell^{mn} p_j^{np}-ik'_m(p_\ell q_m)^{mn} p_j^{np}-ik_\ell p_\ell^{mn}(p_j q_\ell)^{np}] \times \right.$$

$$\left[\left(\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{mp}+\omega+\omega')(\omega_{mn}+\omega')}\right) - \left(\frac{e^{i(\omega_{np}+\omega)t}-1}{(\omega_{np}+\omega)(\omega_{mn}+\omega')}\right)\right] +$$

$$[p_j^{mn} p_\ell^{np}-ik_\ell(p_j q_\ell)^{mn} p_\ell^{np}-ik'_m p_j^{mn}(p_\ell q_m)^{np}] \times$$

$$\left. \left[\left(\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{mp}+\omega+\omega')(\omega_{pn}-\omega')}\right) - \left(\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{mn}+\omega)(\omega_{pn}-\omega')}\right)\right]\right\} +$$

$$\hbar m\delta_{j\ell}\left\{ e'_\ell \alpha'(0)(1-ik_\ell q_\ell^{mp}+ik'_\ell q_\ell^{mp})\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{mp}+\omega-\omega')} + \right.$$

$$\left. \left. \bar{e}'_\ell \alpha'^\dagger(0)(1-ik_\ell q_\ell^{mp}-ik'_\ell q_\ell^{mp})\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{mp}+\omega+\omega')}\right\}\right] \qquad (2.3.28)$$

with $\alpha^{(2)\dagger}(t)$ given by the Hermitian-conjugate term of (2.3.28). To evaluate the second order transverse electric field, (2.3.28) is inserted into the mode expansion (2.3.14). The leading contribution, the quadratic electric dipole dependent transverse electric field is obtained by retaining the $(p_i q_j)^{mp}$ and constant terms of the molecular part of (2.3.28), and with the aid of (2.3.9). There are a whole host of identities and associated sum rules which enable minimal-coupling matrix elements to be written explicitly in terms of molecular multipole moments [38]. One such identity is

$$\frac{-e^2\hbar}{m}\delta_{j\ell} = \sum_{\substack{p\\n}} (\omega_{mn}\mu_j^{mn}\mu_\ell^{np} - \omega_{np}\mu_\ell^{mn}\mu_j^{np})\,\delta_{mp} \ . \tag{2.3.29}$$

Others will be used when needed. Thus

$$e_i^{\perp(2)}(\vec{\mu\mu};\vec{r},t) = \frac{i}{\hbar^2}\sum_{\substack{\vec{k}',\lambda',\vec{k},\lambda\\m,n;p}}\left(\frac{\hbar}{2\varepsilon_0 V}\right)\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\beta_m^\dagger(0)\beta_p(0)\left[e_i\bar{e}_j e^{i\vec{k}\cdot\vec{r}}\times\right.$$

$$\left\{\left[e_\ell'\bar{\alpha}'(0)\left[\mu_\ell^{mn}\mu_j^{np}\omega_{mn}\omega_{np}\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{mn}-\omega')} - \frac{e^{i\omega_{np}t}-e^{-i\omega t}}{(\omega_{np}+\omega)(\omega_{mn}-\omega')}\right)\right.\right.\right.$$

$$\left. + \mu_j^{mn}\mu_\ell^{np}\omega_{mn}\omega_{np}\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{pn}+\omega')} - \frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{(\omega_{mn}+\omega)(\omega_{pn}+\omega')}\right)\right.$$

$$\left.\left.\left.\left. + \delta_{mp}(\omega_{mn}\mu_j^{mn}\mu_\ell^{np} - \omega_{np}\mu_\ell^{mn}\mu_j^{np})\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')}\right)\right]\right\}\right] + \text{H.C.}\right. \tag{2.3.30}$$

After carrying out the polarisation sum and angular average, the above becomes

$$\frac{i}{4\pi\varepsilon_0\hbar}\sum_{\vec{k}',\lambda',m,n,p}\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\beta_m^\dagger(0)\beta_p(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{2\pi ir}\,e_\ell'\bar{\alpha}'(0)\times$$

$$\int_{-\infty}^\infty\frac{dk}{k}(e^{ikr}-e^{-ikr})\left[\mu_\ell^{mn}\mu_j^{np}k_{mn}k_{np}\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')(k_{mn}-k')} - \frac{e^{ik_{np}ct}-e^{-ikct}}{(k_{np}+k)(k_{mn}-k')}\right)\right.$$

$$\left. + \mu_j^{mn}\mu_\ell^{np}k_{mn}k_{np}\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')(k_{pn}+k')} - \frac{e^{ik_{mn}ct}-e^{-ikct}}{(k_{mn}+k)(k_{pn}+k')}\right)\right.$$

$$\left.\left. + \delta_{mp}(k_{mn}\mu_j^{mn}\mu_\ell^{np}-k_{np}\mu_\ell^{mn}\mu_j^{np})\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')}\right)\right]\right]$$

$$\tag{2.3.31}$$

which when integrated gives, for $r < ct$,

$$e_i^{\perp(2)}(\vec{\mu\mu};\vec{r},t) = \frac{i}{4\pi\varepsilon_0\hbar}\sum_{\vec{k},\lambda,m,n,p}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\beta_m^\dagger(0)\beta_p(0)e_\ell\bar{\alpha}(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r}$$

$$\left\{\mu_\ell^{mn}\mu_j^{np}k_{mn}k_{np}\left[\frac{e^{-i(k_{mp}-k)(r-ct)}-e^{i(k_{mp}-k)ct}}{(k_{mn}-k)(k-k_{mp})} + \frac{e^{-ik_{np}(r-ct)}-e^{ik_{np}ct}}{k_{np}(k_{mn}-k)}\right] + \right.$$

$$\mu_j^{mn}\mu_\ell^{np}k_{mn}k_{np}\left[\frac{e^{-i(k_{mp}-k)(r-ct)}-e^{i(k_{mp}-k)ct}}{(k_{pn}+k)(k-k_{mp})} + \frac{e^{-ik_{mn}(r-ct)}-e^{ik_{mn}ct}}{k_{mn}(k_{pn}+k)}\right] +$$

$$\delta_{mp}(k_{mn}\mu_j^{mn}\mu_\ell^{np}-k_{np}\mu_\ell^{mn}\mu_j^{np})\left[\frac{e^{-i(k_{mp}-k)(r-ct)}-e^{i(k_{mp}-k)ct}}{(k-k_{mp})}\right]\Big\} + \text{H.C.} \qquad (2.3.32)$$

The diagonal term from (2.3.32), needed for later applications, can be written as

$$e_i^{\perp(2)}(\vec{\mu\mu};\vec{r},t) = \frac{i}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\m;n}}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}e_\ell\alpha(0)\beta_m^+(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r}\times$$

$$\left[\left\{\frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)}+\frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}(k_{mn}/k)[e^{-ikct}-e^{ik_{mn}ct}+e^{-ik_{mn}(r-ct)}]\right.$$

$$\left.+\frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}(k_{mn}/k)[-e^{-ikct}+e^{-ik_{mn}ct}-e^{ik_{mn}(r-ct)}]\right]$$

$$+ \text{H.C.} \qquad (2.3.33)$$

It may be noted that the term with the factor $e^{ik(r-ct)}$ has the same form as that of $\varepsilon_0^{-1}d_i^{\perp(2)}(\vec{r},t)$ (2.2.46), calculated using the multipolar formalism. To obtain the second order electric dipole dependent *total* electric field, the electric dipole dependent polarisation field to second order must be added to the above. The latter is extracted from the second order term of (2.3.19), which is

$$p_i^{\perp(2)}(\vec{r},t) = \sum_{m,p}(\mu_j^{mp}-Q_{j\ell}^{mp}\nabla_\ell)\delta_{ij}^\perp(\vec{r})e^{-i\omega_{pm}t}[\beta_m^{+(1)}(t)\beta_p^{(0)}(t)+\beta_m^{(0)}(t)\beta_p^{+(1)}(t)]$$

$$= \frac{-e}{i\hbar m}\sum_{\vec{k},\lambda,m,n,p}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\delta_{ij}^\perp(\vec{r})\beta_m^+(0)\beta_p(0)\times$$

$$\left[\left\{\frac{1}{e_\ell}\alpha^+(0)[p_\ell^{mn}-ik_m(p_\ell q_m)^{mn}]\frac{e^{i(\omega_{mp}+\omega)t}-e^{-i\omega_{pn}t}}{i(\omega_{mn}+\omega)}\right.\right. +$$

$$\left.e_\ell\alpha(0)[p_\ell^{mn}+ik_m(p_\ell q_m)^{mn}]\frac{e^{i(\omega_{mp}-\omega)t}-e^{-i\omega_{pn}t}}{i(\omega_{mn}-\omega)}\right\}(\mu_j^{np}-Q_{j\ell}^{np}\nabla_\ell) +$$

$$(\mu_j^{mn}-Q_{jk}^{mn}\nabla_k)\left\{e_\ell\alpha(0)[p_\ell^{np}+ik_m(p_\ell q_m)^{np}]\frac{e^{i(\omega_{mp}-\omega)t}-e^{-i\omega_{nm}t}}{i(\omega_{pn}+\omega)} + \right.$$

$$\left.\bar{e}_\ell\alpha^\dagger(0)[p_\ell^{np}-ik_m(p_\ell q_m)^{np}]\frac{e^{i(\omega_{mp}+\omega)t}-e^{-i\omega_{nm}t}}{i(\omega_{pn}-\omega)}\right\}\right] \qquad (2.3.34)$$

on using (2.3.6). Making use of the relation (2.3.13) and putting $m = p$, (2.3.34) becomes

$$p_i^{\perp(2)}(\vec{r},t) = \frac{i}{4\pi}\sum_{\vec{k},\lambda,m,n}\left(\frac{\hbar c}{2\varepsilon_0 kV}\right)^{1/2}\alpha(0)\beta_m^\dagger(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times$$

$$\left[\left(e_\ell k_{nm}\mu_\ell^{mn}\mu_j^{nm}-e_\ell k_{nm}\mu_\ell^{mn}Q_{j\ell}^{nm}\nabla_\ell+ie_\ell k_\ell k_{nm}Q_{\ell\ell}^{mn}\mu_j^{nm}-\frac{1}{c}kb_\ell m_\ell^{mn}\mu_j^{nm}\right)\frac{(e^{-ikct}-e^{ik_{nm}ct})}{(E_{mn}-\hbar\omega)} + \right.$$

$$\left.\left(e_\ell k_{mn}\mu_j^{mn}\mu_\ell^{nm}-e_\ell k_{mn}Q_{j\ell}^{mn}\mu_\ell^{nm}\nabla_\ell+ie_\ell k_\ell k_{mn}\mu_j^{mn}Q_{\ell\ell}^{nm}-\frac{1}{c}kb_\ell\mu_j^{mn}m_\ell^{nm}\right)\frac{(e^{-ikct}-e^{ik_{mn}ct})}{(E_{mn}+\hbar\omega)}\right]$$

$$+ \text{ H.C.} \qquad (2.3.35)$$

from which the electric dipole contribution is found to be

$$p_i^{\perp(2)}(\vec{\mu\mu};\vec{r},t) = \frac{i}{4\pi}\sum_{\vec{k},\lambda,m,n}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left[e_\ell\alpha(0)\beta_m^\dagger(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times\right.$$

$$\left\{\frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}(k_{nm}/k)[e^{-ikct}-e^{ik_{mn}ct}] + \frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}(k_{mn}/k)[e^{-ikct}-e^{-ik_{mn}ct}]\right\}\right] + \text{ H.C.}$$

$$(2.3.36)$$

so that the second order electric dipole total electric field is

$$e_i^{TOT(2)}(\vec{\mu\mu};\vec{r},t) = e_i^{\perp(2)}(\vec{\mu\mu};\vec{r},t) + \varepsilon_0^{-1}p_i^{\perp(2)}(\vec{\mu\mu};\vec{r},t)$$

$$= \frac{i}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda,m,n}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}e_\ell\alpha(0)\beta_m^\dagger(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times$$

$$\left[\left\{\frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} + \frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}(k_{mn}/k)e^{ik_{nm}(r-ct)}\right.$$

$$\left. + \frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}(k_{nm}/k)e^{ik_{mn}(r-ct)}\right] + \text{ H.C.} \qquad (2.3.37)$$

which is fully retarded and is applicable for r < ct. It is useful to demonstrate that $\vec{e}^{\,TOT(2)}(\vec{r},t)$ vanishes for r > ct, thus showing the causal nature of $\vec{e}^{\,TOT(2)}(\vec{r},t)$. Recalling that $\vec{e}^{\perp(2)}(\vec{r},t)$ has static contributions, by returning to (2.3.31) and evaluating the integral subject to r > ct, these are found to be

$$\frac{i}{4\pi\varepsilon_0\hbar} \sum_{\vec{k},\lambda,m,n,p} \left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} e_{\ell}\alpha(0)\beta_m^+(0)\beta_p(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times$$

$$\left\{\mu_\ell^{mn}\mu_j^{np}k_{mn}k_{np}\left[\frac{1-e^{i(k_{mp}-k)ct}}{(k_{mn}-k)(k-k_{mp})} + \frac{1-e^{ik_{np}ct}}{k_{np}(k_{mn}-k)}\right]\right.$$

$$+ \mu_j^{mn}\mu_\ell^{np}k_{mn}k_{np}\left[\frac{1-e^{i(k_{mp}-k)ct}}{(k_{pn}+k)(k-k_{mp})} + \frac{1-e^{ik_{mn}ct}}{k_{mn}(k_{pn}+k)}\right]$$

$$\left. + \delta_{mp}(k_{mn}\mu_j^{mn}\mu_\ell^{np}-k_{np}\mu_\ell^{mn}\mu_j^{np})\left[\frac{1-e^{i(k_{mp}-k)ct}}{k-k_{mp}}\right]\right\} + H.C. \qquad (2.3.38)$$

which after simplifying, becomes

$$\frac{i}{4\pi\varepsilon_0\hbar} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} e_{\ell}\alpha(0)\beta_m^+(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times$$

$$\left\{\frac{\mu_\ell^{mn}\mu_j^{nm}}{k_{mn}-k} k_{mn}[e^{-ikct}-e^{ik_{nm}ct}] + \frac{\mu_j^{mn}\mu_\ell^{nm}}{k_{mn}+k} k_{mn}[e^{ik_{mn}ct}-e^{-ikct}]\right\} + H.C.$$

$$(2.3.39)$$

Adding (2.3.39) to the electric dipole dependent transverse polarisation field (2.3.36) results in

$$e_i^{\perp(2)}(\vec{\mu}\vec{\mu};\vec{r},t) + \varepsilon_0^{-1}p_i^{\perp(2)}(\vec{\mu}\vec{\mu};\vec{r},t) = \varepsilon_0^{-1}d_i^{\perp(2)}(\vec{\mu}\vec{\mu};\vec{r},t) = 0 , \qquad (2.3.40)$$

so that the total electric field obtained is strictly causal, vanishing for t < r/c.

For the higher multipole contributions to the transverse electric field, the remaining terms of (2.3.28) are substituted into the mode

expansion for $e^{\perp}_i(\vec{r},t)$ (2.3.14) after the conversion of the molecular part to transition moments, making use of the relations (2.3.12) and (2.3.13) and the identity [38]

$$\frac{ie^2}{m}e_i\hat{k}_\ell q^{mp}_\ell = \frac{ic}{\hbar}e_j\hat{k}_\ell \sum_{n}\left(k_{np}\mu^{mn}_i Q^{np}_{j\ell}-k_{mn}Q^{mn}_{j\ell}\mu^{np}_i\right)+\frac{1}{\hbar}b_j\sum_{n}\left(\mu^{mn}_i m^{np}_j-m^{mn}_j\mu^{np}_i\right). \quad (2.3.41)$$

Thus the complete transverse electric field bilinear in the moments is

$$e^{\perp(2)}_i(\vec{r},t) = \frac{i}{\hbar}\sum_{\substack{\vec{k}',\lambda' \\ \vec{k},\lambda}}\sum_{m,n,p}\left(\frac{1}{2\epsilon_0 V}\right)\left(\frac{\hbar}{2\epsilon_0 ck'V}\right)^{1/2}e_\ell\alpha'(0)\beta^+_m(0)\beta_p(0)\times$$

$$\left[e_i e^{i\vec{k}\cdot\vec{r}}\left\{\left[\mu^{mn}_\ell\mu^{np}_j\omega_{mn}\omega_{np}\bar{e}_j-ik'_\ell\bar{e}_j\left(\left(\frac{i}{\hbar}\right)^2 E_{mn}E_{np}Q^{mn}_{\ell\ell}\mu^{np}_j-\frac{i}{\hbar}\epsilon_{\ell\ell i}E_{np}m^{mn}_i\mu^{np}_j-\right.\right.\right.$$

$$\left.\frac{e}{2m}\delta_{\ell\ell}\delta_{mn}E_{np}\mu^{np}_j\right)+i\left(\frac{i}{\hbar}\right)^2\bar{e}_jk_\ell E_{mn}E_{np}\mu^{mn}_\ell Q^{np}_{j\ell}+i\left(\frac{i}{\hbar}\right)kb_j E_{mn}\mu^{mn}_\ell m^{np}_j\right]\times$$

$$\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{mn}-\omega')}-\frac{e^{i\omega_{np}t}-e^{-i\omega t}}{(\omega_{np}+\omega)(\omega_{mn}-\omega')}\right)$$

$$+\left[\mu^{mn}_j\mu^{np}_\ell\omega_{mn}\omega_{np}\bar{e}_j-ik'_\ell\bar{e}_j\left(\left(\frac{i}{\hbar}\right)^2 E_{mn}E_{np}\mu^{mn}_j Q^{np}_{\ell\ell}-\frac{i}{\hbar}\epsilon_{\ell\ell i}E_{mn}\mu^{mn}_j m^{np}_\ell-\right.\right.$$

$$\left.\frac{e}{2m}\delta_{\ell\ell}\delta_{pn}E_{mn}\mu^{mn}_j\right)+i\left(\frac{i}{\hbar}\right)^2\bar{e}_jk_\ell E_{mn}E_{np}Q^{mn}_{j\ell}\mu^{np}_\ell+i\left(\frac{i}{\hbar}\right)kb_j E_{np}m^{mn}_j\mu^{np}_\ell\right]\times$$

$$\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{pn}+\omega')}-\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{(\omega_{mn}+\omega)(\omega_{pn}+\omega')}\right)+$$

$$\left[\left(\frac{\hbar e^2}{im}\bar{e}_j\delta_{j\ell}k'_m q^{mp}_m+\delta_{mp}\bar{e}_j(\omega_{mn}\mu^{mn}_j\mu^{np}_\ell-\omega_{np}\mu^{mn}_\ell\mu^{np}_j)\right.\right.$$

$$\left.+k\left\{ic\bar{e}_j\hat{k}_\ell(k_{np}\mu^{mn}_\ell Q^{np}_{j\ell}-k_{mn}Q^{mn}_{j\ell}\mu^{np}_\ell)+\bar{b}_j(\mu^{mn}_\ell m^{np}_j-m^{mn}_j\mu^{np}_\ell)\right\}\right)\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')}\right)\right]\right]\right\}$$

$$+ \text{H.C.} \qquad (2.3.42)$$

Collecting together terms of the type $\bar{e}_i\bar{e}_j e^{i\vec{k}\cdot\vec{r}}$ and performing the polarisation sum, angular average and the k-integral subject to $r < ct$ with the imposition of the diagonal condition $m = p$, (2.3.42) gives

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$$\frac{-1}{4\pi\varepsilon_0 \hbar c} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \alpha(0)\beta_m^+(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times$$

$$\left\{\left(e_\ell k_{\it k}\left[\mu_j^{mn}Q_{{\it k}\ell}^{nm}\left(\frac{k_{nm}^2}{k^2(k_{nm}-k)} - \frac{k_{nm}}{k^2}\right)+Q_{{\it k}\ell}^{mn}\mu_j^{nm}\left(\frac{k_{nm}^2}{k^2(k_{nm}+k)} - \frac{k_{nm}}{k^2}\right)\right]\left(e^{ik(r-ct)}-e^{-ikct}\right)\right.\right.$$

$$\left.+\frac{\mu_j^{mn}Q_{{\it k}\ell}^{nm}}{k_{nm}-k}\left(\frac{k_{mn}}{k}\right)[e^{ik_{nm}(r-ct)}-e^{-ik_{nm}ct}]+\frac{Q_{{\it k}\ell}^{mn}\mu_j^{nm}}{k_{nm}+k}\left(\frac{k_{nm}}{k}\right)[e^{-ik_{nm}(r-ct)}-e^{ik_{nm}ct}]\right]\right) -$$

$$\left(\frac{i}{c}b_{\it k}\left[\left\{\mu_j^{mn}m_{\it k}^{nm}\left(\frac{k_{nm}}{k(k_{nm}-k)} - \frac{1}{k}\right)+m_{\it k}^{mn}\mu_j^{nm}\left(\frac{k_{mn}}{k(k_{nm}+k)} + \frac{1}{k}\right)\right\}\left(e^{ik(r-ct)}-e^{-ikct}\right)\right.\right.$$

$$\left.\left.\left.-\frac{\mu_j^{mn}m_{\it k}^{nm}}{k_{nm}-k}[e^{ik_{nm}(r-ct)}-e^{-ik_{nm}ct}] - \frac{m_{\it k}^{mn}\mu_j^{nm}}{k_{nm}+k}[e^{-ik_{nm}(r-ct)}-e^{ik_{nm}ct}]\right]\right)\right\} + \text{H.C.}$$

$$(2.3.43)$$

The terms with the factor $e_i \bar{b}_j e^{i\vec{k}\cdot\vec{r}}$ in (2.3.42) after the polarisation sum and k-integration, give

$$\frac{-1}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} e_{\it k}\alpha(0)\beta_m^+(0)\beta_m(0)(\varepsilon_{ij\ell}\nabla_\ell\frac{1}{r}) \times$$

$$\left[\left\{\frac{\mu_{\it k}^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}+\frac{m_j^{mn}\mu_{\it k}^{nm}}{E_{nm}+\hbar\omega}\right\}ke^{ik(r-ct)}- \frac{\mu_{\it k}^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}(k_{nm}^2/k)e^{ik_{nm}(r-ct)}\right.$$

$$\left.- \frac{m_j^{mn}\mu_{\it k}^{nm}}{E_{nm}+\hbar\omega}(k_{nm}^2/k)e^{ik_{mn}(r-ct)}\right] + \text{H.C.} \quad (2.3.44)$$

while the contribution from those containing $e_i e_j k e^{i\vec{k}\cdot\vec{r}}$ is found to be

$$\frac{-i}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} e_{\it k}\alpha(0)\beta_m^+(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_{\it k}\frac{1}{r} \times$$

$$\left[\left\{\frac{\mu_{\it k}^{mn}Q_{j{\it k}}^{nm}}{E_{nm}-\hbar\omega}+\frac{Q_{j{\it k}}^{mn}\mu_{\it k}^{nm}}{E_{nm}+\hbar\omega}\right\}(e^{ik(r-ct)}-e^{-ikct}) - \frac{\mu_{\it k}^{mn}Q_{j{\it k}}^{nm}}{E_{nm}-\hbar\omega}(k_{nm}/k)(e^{ik_{nm}(r-ct)}-e^{-ik_{nm}ct})\right.$$

$$\left.- \frac{Q_{j{\it k}}^{mn}\mu_{\it k}^{nm}}{E_{nm}+\hbar\omega}(k_{mn}/k)(e^{ik_{mn}(r-ct)}-e^{ik_{nm}ct})\right]$$

$$+ \text{H.C.} \quad (2.3.45)$$

The total electric field in the proximity of a molecule correct to second order in the sources is obtained by adding the last three expressions to the polarisation field quadratic in the moments (2.3.35), resulting in the individual quadratic fields

$$
e_i^{TOT(2)}(\vec{\mu m};\vec{r},t) = \frac{i}{4\pi\varepsilon_0 c} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2} b_\ell \alpha(0)\beta_m^\dagger(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times
$$

$$
\left[\left\{\frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega} + \frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega}e^{ik_{nm}(r-ct)}\right.
$$

$$
\left. - \frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}e^{ik_{mn}(r-ct)}\right] +
$$

$$
\frac{i}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} e_\ell \alpha(0)\beta_m^\dagger(0)\beta_m(0)(ik\varepsilon_{ij\ell}\nabla_\ell\frac{1}{r}) \times
$$

$$
\left[\left\{\frac{\mu_\ell^{mn}m_j^{nm}}{E_{nm}-\hbar\omega} + \frac{m_j^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_\ell^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}\right.
$$

$$
\left. - \frac{m_j^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\right] + H.C. \qquad (2.3.46)
$$

$$
e_i^{TOT(2)}(\vec{\mu Q};\vec{r},t) = \frac{-1}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2} e_\ell k_\ell \alpha(0)\beta_m^\dagger(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times
$$

$$
\left[\left\{\frac{\mu_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{\ell\ell}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}\right.
$$

$$
\left. - \frac{Q_{\ell\ell}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\right]
$$

$$
\frac{-i}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2} e_\ell \alpha(0)\beta_m^\dagger(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_\ell\frac{1}{r} \times
$$

$$
\left[\left\{\frac{\mu_\ell^{mn}Q_{jk}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{jk}^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_\ell^{mn}Q_{jk}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}\right.
$$

$$
\left. - \frac{Q_{jk}^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\right] + H.C. \qquad (2.3.47)
$$

with the quadratic electric dipole contribution given earlier in

(2.3.37). As for the electric dipole case, the instantaneous

contributions occurring in $\vec{e}^{\perp}$, arising when the integral is evaluated

for r > ct, when added to the transverse polarisation field, results in

the total electric field in the neighbourhood of the source vanishing,

as demanded by causality.

Finally the magnetic field is determined in the minimal-coupling

formalism. The free field operator independent of the sources is the

same in both frameworks, obtained by inserting $\alpha(t) = \alpha(0)$ into the mode

expansion for $\vec{b}(\vec{r},t)$ (2.2.52). The higher order contributions are

obtained using the minimal-coupling equations of motion derived earlier

in this Section when used in the evaluation of the transverse electric

field.

Substituting the equation of motion for $\alpha(t)$ to first order

(2.3.15) into the mode expansion for $\vec{b}(\vec{r},t)$, the minimal-coupling

magnetic field linear in the sources is

$$b_i^{(1)}(\vec{r},t) = \frac{i}{\hbar} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar}{2\varepsilon_0 cV}\right)\left\{\beta_m^+(0)\beta_n(0)b_i e^{i\vec{k}\cdot\vec{r}} \times\right.$$

$$\left[\frac{i}{\hbar}\bar{e}_j E_{mn}\mu_j^{mn} - ik\bar{b}_j m_j^{mn} + \frac{1}{\hbar}\bar{e}_j k_\ell E_{mn}Q_{j\ell}^{mn}\right]\left(\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{(\omega_{mn}+\omega)}\right) + \left. H.C.\right\} .$$

(2.3.48)

Evaluating in the usual manner results in

$$b_i^{(1)}(\vec{r},t) = \frac{1}{4\pi\varepsilon_0 c}\sum_{m,n}\beta_m^+(0)\beta_n(0)\left[\mu_j^{mn}k_{nm}^3 g_{ij}(k_{nm}r)+\frac{1}{c}m_j^{mn}k_{nm}^3 f_{ij}(k_{nm}r) -\right.$$

$$\left. iQ_{j\ell}^{mn}k_{nm}^4 j_{ij\ell}(k_{nm}r)\right]e^{ik_{nm}(r-ct)}, \qquad r < ct$$

$$= 0 , \qquad r > ct. \qquad (2.3.49)$$

As expected, the magnetic field is causal, confirmed by the absence of

the pole at k = 0. On comparing the above with the analogous result obtained within the multipolar framework (2.2.55), the two first order magnetic fields are seen to be identical. This is despite the fact that the equations of motion (2.2.17) and (2.3.15) are different in both approaches.

For the second order contribution to the magnetic field, $\alpha^{(2)}(t)$ given by (2.3.28) is substituted into the mode expansion for $\vec{b}(\vec{r},t)$, with the molecular part converted to multipole moments using the identities given earlier in this Section. Thus

$$b_i^{(2)}(\vec{r},t) = \frac{i}{\hbar c}\sum_{\vec{k},\lambda,m,n,p}\sum_{\vec{k}',\lambda'}\left(\frac{1}{2\varepsilon_0 V}\right)\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}e'_\ell\alpha'(0)\beta_m^\dagger(0)\beta_p(0)\times$$

$$\left[b_i e^{i\vec{k}\cdot\vec{r}}\left\{\left[\mu_\ell^{mn}\mu_j^{np}\omega_{mn}\omega_{np}\bar{e}_j - ik'_\ell\bar{e}_j\left(\left(\frac{i}{\hbar}\right)^2 E_{mn}E_{np}Q_{\ell\ell}^{mn}\mu_j^{np} - \frac{i}{\hbar}\varepsilon_{\ell k l}E_{np}m_\ell^{mn}\mu_j^{np}-\right.\right.\right.$$

$$\left.\frac{e}{2m}\delta_{k\ell}\delta_{mn}E_{np}\mu_j^{np}\right) + i\left(\frac{i}{\hbar}\right)^2\bar{e}_j k_k E_{mn}E_{np}\mu_\ell^{mn}Q_{jk}^{np}+i\left(\frac{i}{\hbar}\right)k\bar{b}_j E_{mn}\mu_\ell^{mn}m_j^{np}\right]\times$$

$$\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{mn}-\omega')} - \frac{e^{i\omega_{np}t}-e^{-i\omega t}}{(\omega_{np}+\omega)(\omega_{mn}-\omega')}\right) +$$

$$\left[\mu_j^{mn}\mu_\ell^{np}\omega_{mn}\omega_{np}\bar{e}_j - ik'_\ell\bar{e}_j\left(\left(\frac{i}{\hbar}\right)^2 E_{mn}E_{np}\mu_j^{mn}Q_{\ell\ell}^{np}- \frac{i}{\hbar}\varepsilon_{\ell k l}E_{mn}\mu_j^{mn}m_\ell^{np}- \frac{e}{2m}\delta_{k\ell}\delta_{np}E_{mn}\mu_j^{mn}\right)\right.$$

$$\left.+ i\left(\frac{i}{\hbar}\right)^2\bar{e}_j k_k E_{mn}E_{np}Q_{jk}^{mn}\mu_\ell^{np}+i\left(\frac{i}{\hbar}\right)k\bar{b}_j E_{np}m_j^{mn}\mu_\ell^{np}\right]\times$$

$$\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{pn}+\omega')} - \frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{(\omega_{mn}+\omega)(\omega_{pn}+\omega')}\right) +$$

$$\left[\bar{e}_j\delta_{mp}(\omega_{mn}\mu_j^{mn}\mu_\ell^{np}-\omega_{np}\mu_\ell^{mn}\mu_j^{np}) + \frac{e^2\hbar}{im}\bar{e}_j\delta_{j\ell}k'_m q_m^{mp} +\right.$$

$$\left.ic\bar{e}_j k_k(k_{np}\mu_\ell^{mn}Q_{jk}^{np}-k_{mn}Q_{jk}^{mn}\mu_\ell^{np})+k\bar{b}_j(\mu_\ell^{mn}m_j^{np}-m_j^{mn}\mu_\ell^{np})\right]\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')}\right)\right\}\right]$$

$$+ \text{ H.C.} \qquad (2.3.50)$$

The contribution arising from terms with the factor $b_i\bar{e}_j e^{i\vec{k}\cdot\vec{r}}$ after performing the polarisation sum and angular integral, is given by

$$\frac{i}{4\pi\varepsilon_0 \hbar c} \sum_{\vec{k}',\lambda',m,n,p} \left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2} e_{\ell}'\alpha'(0)\beta_m^{\dagger}(0)\beta_p(0)(i\varepsilon_{ijs}\nabla_s \frac{1}{r}) \times$$

$$\frac{1}{2\pi i}\int_{-\infty}^{\infty} dk(e^{ikr}-e^{-ikr}) \left\{\left[\mu_\ell^{mn}\mu_j^{np}k_{mn}k_{np}-ik_{\ell}'\left(-k_{mn}k_{np}Q_{\ell\ell j}^{mn}\mu_j^{np}-\frac{i}{c}\varepsilon_{\ell\ell i}k_{np}m_\ell^{mn}\mu_j^{np}\right)\right] \times\right.$$

$$\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')(k_{mn}-k')} - \frac{e^{ik_{np}ct}-e^{-ikct}}{(k_{np}+k)(k_{mn}-k')}\right) +$$

$$\left[\mu_j^{mn}\mu_\ell^{nm}k_{mn}k_{np}-ik_{\ell}'\left(-k_{mn}k_{np}\mu_j^{mn}Q_{\ell\ell}^{nm}-\frac{i}{c}\varepsilon_{\ell\ell i}k_{mn}\mu_j^{mn}m_\ell^{nm}\right)\right] \times$$

$$\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')(k_{pn}+k')} - \frac{e^{ik_{mn}ct}-e^{-ikct}}{(k_{mn}+k)(k_{pn}+k')}\right) +$$

$$\left.\left[\delta_{mp}(k_{mn}\mu_j^{mn}\mu_\ell^{np}-k_{np}\mu_\ell^{mn}\mu_j^{np}) + \frac{e^2\hbar}{imc}\delta_{j\ell}k_m'q_m^{mp}\right]\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')}\right)\right\} + H.C.$$

$$(2.3.51)$$

After evaluating the k-integral subject to r < ct and with m = p, the quadratic electric dipole contribution is found to be

$$\frac{i}{4\pi\varepsilon_0 \hbar c} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2} e_{\ell}\alpha(0)(i\varepsilon_{ij\ell}\nabla_\ell\frac{1}{r})\beta_m^{\dagger}(0)\beta_m(0) \times$$

$$\left\{\mu_\ell^{mn}\mu_j^{nm}(-)k_{mn}^2\left[\frac{e^{ik(r-ct)}}{k_{mn}-k} - \frac{e^{ik_{mn}(r-ct)}}{k_{mn}-k} - \frac{e^{ik(r-ct)}}{k_{mn}}\right] +\right.$$

$$\left.\mu_j^{mn}\mu_\ell^{nm}(-)k_{mn}^2\left[\frac{e^{ik(r-ct)}}{k_{mn}+k} - \frac{e^{ik_{nm}(r-ct)}}{k_{mn}+k} - \frac{e^{ik(r-ct)}}{k_{mn}}\right]\right\} + H.C. \qquad (2.3.52)$$

The molecular terms with the exponential factor $e^{ik(r-ct)}$ has the same form as the corresponding term evaluated in the multipolar framework (2.2.60). This results in the electric dipole dependent magnetic field in the minimal-coupling framework

$$b_i^{(2)}(\vec{\mu}\vec{\mu};\vec{r},t) = \frac{i}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} e_\ell \alpha(0)(ik\varepsilon_{ij\ell}\nabla_\ell \frac{1}{r})\beta_m^+(0)\beta_m(0) \times$$

$$\left[\left\{\frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega} + \frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_j^{mn}\mu_\ell^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{nm}(r-ct)}\right.$$

$$\left. - \frac{\mu_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{mn}(r-ct)}\right] + H.C. \qquad (2.3.53)$$

Returning to (2.3.51) and evaluating the remaining terms results in the magnetic dipole and electric quadrupole dependent contributions

$$b_i^{(2)}(\vec{\mu}m;\vec{r},t) = \frac{i}{4\pi\varepsilon_0 c} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} b_\ell \alpha(0)(ik\varepsilon_{ij\ell}\nabla_\ell \frac{1}{r})\beta_m^+(0)\beta_m(0) \times$$

$$\left[\left\{\frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega} + \frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_j^{mn}m_\ell^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}\right.$$

$$\left. - \frac{m_\ell^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\right] + H.C. \qquad (2.3.54)$$

$$b_i^{(2)}(\vec{\mu}Q;\vec{r},t) = \frac{-1}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} e_\ell k_\ell \alpha(0)(ik\varepsilon_{ij\ell}\nabla_\ell \frac{1}{r})\beta_m^+(0)\beta_m(0) \times$$

$$\left[\left\{\frac{\mu_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{\ell\ell}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_j^{mn}Q_{\ell\ell}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{nm}(r-ct)}\right.$$

$$\left. - \frac{Q_{\ell\ell}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{mn}(r-ct)}\right] + H.C. \qquad (2.3.55)$$

Returning to (2.3.50) and collecting terms of the type $b_i \bar{b}_j e^{i\vec{k}\cdot\vec{r}}$, and evaluating in the familiar way results in the remaining $\vec{\mu}m$ contributions

$$b_i^{(2)}(\vec{\mu}m;\vec{r},t) = \frac{i}{4\pi\varepsilon_0 c} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} e_\ell \alpha(0)\beta_m^+(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r} \times$$

$$\left[\left\{\frac{\mu_\ell^{mn}m_j^{nm}}{E_{nm}-\hbar\omega} + \frac{m_j^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_\ell^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{nm}(r-ct)}\right.$$

$$\left. - \frac{m_j^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{mn}(r-ct)}\right] + H.C. \qquad (2.3.56)$$

Returning to (2.3.50) and extracting terms of the type $b_\ell \bar{e}_{j_k \ell} e^{i\vec{k}\cdot\vec{r}}$ and

evaluating in the familiar way results in the remaining $\vec{\mu}\vec{Q}$ dependent

field being

$$
b_\ell^{(2)}(\vec{\mu}\vec{Q};\vec{r},t) = \frac{1}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda,m,n} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} e_\ell \alpha(0)\beta_m^\dagger(0)\beta_m(0)(k\varepsilon_{ij\flat}\nabla_\flat\nabla_\ell \frac{1}{r}) \times
$$

$$
\left[\left\{\frac{\mu_\ell^{mn}Q_{j\ell}^{nm}}{E_{nm}-\hbar\omega} + \frac{Q_{j\ell}^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\right\}e^{ik(r-ct)} - \frac{\mu_\ell^{mn}Q_{j\ell}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{nm}(r-ct)}\right.
$$

$$
\left. - \frac{Q_{j\ell}^{mn}\mu_\ell^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{mn}(r-ct)}\right] + \text{H.C.} \qquad (2.3.57)
$$

This completes the formal derivation in this Chapter of the quantum

electrodynamical Maxwell fields in the proximity of a molecule using the

multipolar and minimal-coupling Hamiltonians in the Heisenberg picture.

Specifically, the time dependent electric displacement and magnetic

field operators correct up to second order in the electric quadrupole

moment, including all interaction terms of a comparable order, have been

derived using the multipolar version of the theory. The causal

electromagnetic source fields are functions of the photon and electron

creation and annihilation operators. Since the equations of motion

describing the dynamical system in minimal-coupling are different to

those occurring in the multipolar framework, in the former approach the

transverse electric field operator, which is the canonical field

momentum in minimal-coupling, was determined as opposed to the

displacement vector field operator. The transverse electric field in

both first and second order was found to contain non-retarded

contributions, arising from the occurrence of additional poles at k = 0.

However, the total electric field, after adding the longitudinal part of

the electric field, which was evaluated from the electric polarisation

field, to the transverse component was shown to be fully retarded. The

magnetic field operator to second order was also evaluated and compared in both frameworks.

The zeroth order fields in both formalisms act in the photon space only, simply being the free field operator independent of the source. The first order transverse electric displacement and total electric field operators were shown to be identical as were the minimal- and multipolar-coupling magnetic fields. These operators act solely in the electron space, leading to changes of molecular state, and correspond to the classical radiation field emitted by an excited multipole source undergoing real transitions. Unlike the first order minimal-coupling Maxwell fields, the second order operators, when compared to their multipolar counterparts, are seen not to be identically equivalent on inspection, although similarities do exist. Despite differences between the second order multipolar- and minimal-coupling radiation field operators, when the latter are applied to the calculation of a physical process or quantity for which energy is conserved, the resulting matrix element is identical to that obtained using the multipolar formalism. In both frameworks, the second order Maxwell fields operate in the totality of electron and photon field spaces, changing the state of the electron, and the photon number by unity.

These Maxwell fields are now employed in the following Chapter to evaluate the energy density in a radiation field and the rate of flow of electromagnetic energy from a molecule in an excited electronic state. The equivalence of the matrix element obtained for these processes using the electric dipole approximated multipolar- and minimal-coupling radiation fields is demonstrated. The multipolar Maxwell fields are then used in the fourth Chapter to calculate the energy of interaction between two polarisable bodies in both the ground and electronically excited states using a generalisation of molecular response theory.

As mentioned in the text, the geometric tensors defined by (2.2.28)-(2.2.31) are continually used in all the applications considered in the rest of this work and their complete, explicit forms are now given. From (2.2.28)

$$
\begin{aligned}
F_{ij}(kr) &= \frac{1}{k^3}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{ikr}}{r} \\
&= \left[-\frac{\alpha_{ij}}{kr} + \beta_{ij}\left(\frac{-i}{k^2r^2} + \frac{1}{k^3r^3}\right)\right]e^{ikr} = f_{ij}(kr)e^{ikr}.
\end{aligned}
\tag{2.A.1}
$$

On inserting $k = iu$,

$$
F_{ij}(iur) = \frac{i}{u^3}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{-ur}}{r} = f_{ij}(iur)e^{-ur}.
\tag{2.A.2}
$$

The following useful relations are easily deduced

$$
f_{ij}(kr) = -\bar{f}_{ij}(-kr)
\tag{2.A.3}
$$

$$
f_{ij}(-kr) = -\bar{f}_{ij}(kr)
\tag{2.A.4}
$$

and

$$
f_{ij}(-iur) = -\bar{f}_{ij}(-iur) = \bar{f}_{ij}(iur) = -f_{ij}(iur)
\tag{2.A.5}
$$

$$
f_{ij}(iur) = -\bar{f}_{ij}(iur) = \bar{f}_{ij}(-iur).
\tag{2.A.6}
$$

From (2.2.29)

$$G_{ij}(kr) = \frac{i}{k^2}\varepsilon_{ij\ell}\nabla_\ell\frac{e^{ikr}}{r} = -\varepsilon_{ij\ell}\hat{r}_\ell\left[\frac{1}{kr} + \frac{i}{k^2r^2}\right]e^{ikr} = g_{ij}(kr)e^{ikr} \qquad (2.A.7)$$

$$G_{ij}(iur) = \frac{1}{iu^2}\varepsilon_{ij\ell}\nabla_\ell\frac{e^{-ur}}{r} = i\varepsilon_{ij\ell}\hat{r}_\ell\left[\frac{1}{ur} + \frac{1}{u^2r^2}\right]e^{-ur} = g_{ij}(iur)e^{-ur} \qquad (2.A.8)$$

and

$$g_{ij}(kr) = -\overline{g}_{ij}(-kr) \qquad (2.A.9)$$

$$g_{ij}(-kr) = -\overline{g}_{ij}(kr) \qquad (2.A.10)$$

$$g_{ij}(iur) = -\overline{g}_{ij}(iur) = \overline{g}_{ij}(-iur) = -g_{ij}(-iur). \qquad (2.A.11)$$

From (2.2.30)

$$H_{ij\ell}(kr) = \frac{1}{k}\nabla_\ell F_{ij}(kr) = \frac{1}{k^4}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\nabla_\ell\frac{e^{ikr}}{r}$$

$$= \left[\frac{i\alpha_{ij}\hat{r}_\ell}{kr} - \left(\frac{(2\delta_{ij}\hat{r}_\ell + \delta_{j\ell}\hat{r}_i + \delta_{i\ell}\hat{r}_\ell) - 6\hat{r}_i\hat{r}_j\hat{r}_\ell}{k^2r^2}\right) + \right.$$

$$\left. \left(3(\delta_{ij}\hat{r}_\ell + \delta_{j\ell}\hat{r}_i + \delta_{i\ell}\hat{r}_j) - 15\hat{r}_i\hat{r}_j\hat{r}_\ell\right)\left(\frac{-i}{k^3r^3} + \frac{1}{k^4r^4}\right)\right]e^{ikr} = h_{ij\ell}(kr)e^{ikr}$$

$$(2.A.12)$$

$$H_{ij\ell}(iur) = \frac{1}{iu}\nabla_\ell F_{ij}(iur) = \frac{1}{u^4}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\nabla_\ell\frac{e^{-ur}}{r} = h_{ij\ell}(iur)e^{-ur}$$

$$(2.A.13)$$

with

$$h_{ij\ell}(kr) = \overline{h}_{ij\ell}(-kr) \quad ; \quad \overline{h}_{ij\ell}(kr) = h_{ij\ell}(-kr) \qquad (2.A.14)$$

$$h_{ij\ell}(iur) = \overline{h}_{ij\ell}(iur) \quad ; \quad h_{ij\ell}(-iur) = \overline{h}_{ij\ell}(-iur). \qquad (2.A.15)$$

From (2.2.31)

$$J_{ij\ell}(kr) = \frac{i}{k}\nabla_\ell G_{ij}(kr) = \frac{-1}{k^3}\epsilon_{ijk}\nabla_k\nabla_\ell\frac{e^{ikr}}{r}$$

$$= \epsilon_{ijk}\left[\frac{\hat{r}_k\hat{r}_\ell}{kr} - \beta_{k\ell}\left(\frac{i}{k^2r^2} - \frac{1}{k^3r^3}\right)\right]e^{ikr} = j_{ij\ell}(kr)e^{ikr} \qquad (2.A.16)$$

$$J_{ij\ell}(iur) = \frac{1}{u}\nabla_\ell G_{ij}(iur) = \frac{-i}{u^3}\epsilon_{ijk}\nabla_k\nabla_\ell\frac{e^{-ur}}{r} = j_{ij\ell}(iur)e^{-ur} \qquad (2.A.17)$$

with

$$j_{ij\ell}(kr) = -\bar{j}_{ij\ell}(-kr) \quad ; \quad \bar{j}_{ij\ell}(kr) = -j_{ij\ell}(-kr) \qquad (2.A.18)$$

$$j_{ij\ell}(iur) = -j_{ij\ell}(-iur) = \bar{j}_{ij\ell}(-iur) = -\bar{j}_{ij\ell}(iur). \qquad (2.A.19)$$

In addition one further tensor is defined as

$$L_{ij k\ell}(kr) = \frac{1}{k}\nabla_\ell H_{ijk}(kr) = \frac{1}{k^5}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_k\nabla_\ell\frac{e^{ikr}}{r} = l_{ijk\ell}(kr)e^{ikr} =$$

$$\left[\frac{-\alpha_{ij}\hat{r}_k\hat{r}_\ell}{kr} + \frac{i\delta_{ij}\delta_{k\ell}}{k^2r^2} - \frac{4i\delta_{ij}\hat{r}_k\hat{r}_\ell}{k^2r^2} + \frac{10i\hat{r}_i\hat{r}_j\hat{r}_k\hat{r}_\ell}{k^2r^2} - \frac{(2\delta_{ij}\delta_{k\ell}+\delta_{ik}\delta_{j\ell}+\delta_{jk}\delta_{i\ell})}{k^3r^3}\right.$$

$$+ (\delta_{ik}\hat{r}_j\hat{r}_\ell+\delta_{i\ell}\hat{r}_j\hat{r}_k+\delta_{jk}\hat{r}_i\hat{r}_\ell+\delta_{j\ell}\hat{r}_i\hat{r}_k+\delta_{k\ell}\hat{r}_i\hat{r}_j)\left(\frac{-i}{k^2r^2} + \frac{6}{k^3r^3}\right) + \frac{9\delta_{ij}\hat{r}_k\hat{r}_\ell}{k^3r^3} +$$

$$(\delta_{ij}\delta_{k\ell}+\delta_{ik}\delta_{j\ell}+\delta_{jk}\delta_{i\ell})\left(\frac{-3i}{k^4r^4} + \frac{3}{k^5r^5}\right) + \hat{r}_i\hat{r}_j\hat{r}_k\hat{r}_\ell\left(-\frac{45}{k^3r^3} - \frac{105i}{k^4r^4} + \frac{105}{k^5r^5}\right) +$$

$$\left.(\delta_{ij}\hat{r}_k\hat{r}_\ell+\delta_{ik}\hat{r}_j\hat{r}_\ell+\delta_{i\ell}\hat{r}_j\hat{r}_k+\delta_{jk}\hat{r}_i\hat{r}_\ell+\delta_{j\ell}\hat{r}_i\hat{r}_k+\delta_{k\ell}\hat{r}_i\hat{r}_j)\left(\frac{15i}{k^4r^4} - \frac{15}{k^5r^5}\right)\right]e^{ikr}$$

$$(2.A.20)$$

$$L_{ijk\ell}(iur) = \frac{1}{iu}\nabla_\ell H_{ijk}(iur) = \frac{-i}{u^5}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_k\nabla_\ell\frac{e^{-ur}}{r} = l_{ijk\ell}(iur)e^{-ur}$$

$$(2.A.21)$$

with

$$l_{ijk\ell}(kr) = -\bar{l}_{ijk\ell}(-kr) \quad ; \quad l_{ijk\ell}(-kr) = -\bar{l}_{ijk\ell}(kr) \qquad (2.A.22)$$

$$l_{ijk\ell}(iur) = -\bar{l}_{ijk\ell}(-iur) = \bar{l}_{ijk\ell}(iur) = -l_{ijk\ell}(-iur). \qquad (2.A.23)$$

CHAPTER 3

ENERGY DENSITIES AND POYNTING VECTOR

3.1 INTRODUCTION

In classical electromagnetic theory, oscillating charge and current sources give rise to radiation fields which obey Maxwell's equations. A multipolar expansion of the charge distribution produces electric and magnetic fields propagating from the source multipole moments corresponding to dipole, quadrupole and higher multipole electromagnetic radiation.

It has long been known that excited atoms and molecules emit wavefields as in the electromagnetic theory, emitted by charges vibrating with wavelengths subject to the Bohr frequency condition. In Chapter 2 the quantum electrodynamical analogue of the classical Maxwell field of an oscillating multipole moment was obtained by considering atoms and molecules to be composed of constituent charges and currents which are taken to be the sources of electromagnetic radiation. The Maxwell fields in the proximity of a molecule were derived in both the multipolar and minimal-coupling frameworks in the Heisenberg picture.

In this Chapter, the microscopic Maxwell fields are employed in the evaluation of the expectation values of quadratic operators of the electromagnetic field such as the Thompson energy density and the Poynting vector for specified states. The electric and magnetic energy densities are obtained to second order in the transition moments for a molecule in both the ground and excited state using the field operators of Chapter 2 in the multipolar formalism, extending work which was limited to the electric dipole approximation [33]. This is followed by the demonstration of the equivalence of the electric dipole dependent

energy density using the total electric and magnetic Maxwell fields in minimal-coupling. This is despite the minimal- and multipolar-coupling Hamiltonians being different in both cases, leading to different operator equations of motion. The importance of the electromagnetic energy density calculation lies in its relation to the intermolecular pair potential for a polarisable test body placed in the radiation field of the source molecule. For two molecules in their ground states this approach leads to the dispersion force [33]. When the source molecule is in an excited state the intermolecular energy shift has an additional unmodulated term including a part that has an inverse square dependence on distance corresponding to real photon emission.

The rate of flow of electromagnetic energy, or Poynting's vector, is also determined in this Chapter. Poynting's vector is a direct consequence of the more important Poynting's theorem of classical electromagnetic theory, which states that the divergence of the flux of energy (electromagnetic energy), plus the rate at which the energy density increases with time, equals the rate at which energy is produced [39]. This has the form of an equation of continuity. The vector representing the flux of energy, Poynting's vector $\vec{s} = \frac{1}{2}\varepsilon_0 c^2 (\vec{e} \times \vec{b})$, is interpreted as the amount of energy crossing unit area perpendicular to the vector, per unit time. This energy flow is calculated for sources correct up to and including the electric quadrupole moment using the multipolar framework Maxwell fields of the previous Chapter, while the equivalence of the matrix element for the electric dipole case is demonstrated using the minimal-coupling radiation fields. The relation between the quantum mechanical rate of spontaneous emission by an excited system and the classical rate of energy loss by radiation from an oscillating multipole is also investigated. The importance of the calculation of the Poynting vector appears in the study of

intermolecular energy transfer processes [40]. The simplest such interaction being the much examined resonance coupling between two molecules, one of which is in an excited state. The field picture enables the transfer of excitation between the two molecules, explored over all separation distances beyond electron overlap, to be viewed as spontaneous emission by the excited molecule followed by absorption by the other.

Before going on to calculate the energy density and the Poynting vector associated with the quantum electrodynamical Maxwell field, the electric displacement and magnetic fields obtained in Chapter 2 are written in a form which facilitates their application to the calculations to be performed in this Chapter, and in the evaluation of the interaction energy between two neutral polarisable molecules in Chapter 4. As matrix elements involving quadratic operators of the radiation field are being determined, it is necessary to include the second order source fields which are quadratic in the transition moments. Contributions arise from the product of the first order fields, and from the interference of the vacuum field with the second order field. In the latter contribution, only that part of the quadratic field that is diagonal in the electron space is required since $\vec{d}^{(0)}$ operates entirely in the photon space and cannot change the state of the molecule. By taking the diagonal matrix element for a state $|p\rangle$ of the molecule, the second order Maxwell fields then operate solely in the photon space. This is done for the individual second order electric displacement and magnetic source fields derived in Chapter 2, and are now given below along with the definitions of the appropriate tensor fields. The benefit of writing the fields in the following fashion will become apparent when calculations are carried out.

$$\langle p|d_i^{(2)}(\vec{\mu}\vec{\mu})|p\rangle = \frac{i}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V\epsilon_0}\right)^{1/2}[e_\ell\alpha(0)e^{-i\omega t}\mathscr{A}_{\ell i}-\bar{e}_\ell\alpha^+(0)e^{i\omega t}\bar{\mathscr{A}}_{\ell i}] \qquad (3.1.1)$$

$$\langle p|d_i^{(2)}(\vec{\mu}\vec{m})|p\rangle = \frac{i}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2cV\epsilon_0}\right)^{1/2}[\alpha(0)e^{-i\omega t}(b_\ell\mathscr{B}_{\ell i}+e_\ell\mathscr{C}_{\ell i})$$
$$-\alpha^+(0)e^{i\omega t}(\bar{b}_\ell\bar{\mathscr{B}}_{\ell i}+\bar{e}_\ell\bar{\mathscr{C}}_{\ell i})] \qquad (3.1.2)$$

$$\langle p|d_i^{(2)}(\vec{m}\vec{m})|p\rangle = \frac{-i}{4\pi c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2cV\epsilon_0}\right)^{1/2}[b_\ell\alpha(0)e^{-i\omega t}\mathscr{D}_{\ell i}-\bar{b}_\ell\alpha^+(0)e^{i\omega t}\bar{\mathscr{D}}_{\ell i}]$$
$$(3.1.3)$$

$$\langle p|d_i^{(2)}(\vec{\mu}\vec{Q})|p\rangle = \frac{1}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V\epsilon_0}\right)^{1/2}[\alpha(0)e^{-i\omega t}(e_\ell k_\ell\mathscr{C}_{\ell\ell i}+ie_j\mathscr{F}_{ji})$$
$$-\alpha^+(0)e^{i\omega t}(\bar{e}_\ell k_\ell\bar{\mathscr{C}}_{\ell\ell i}+i\bar{e}_j\bar{\mathscr{F}}_{ji})] \qquad (3.1.4)$$

$$\langle p|d_i^{(2)}(\vec{m}\vec{Q})|p\rangle = \frac{1}{4\pi c}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V\epsilon_0}\right)^{1/2}[\alpha(0)e^{-i\omega t}(e_\ell k_\ell\mathscr{C}_{\ell\ell i}+ib_j\mathscr{H}_{ji})$$
$$-\alpha^+(0)e^{i\omega t}(\bar{e}_\ell k_\ell\bar{\mathscr{C}}_{\ell\ell i}+i\bar{b}_j\bar{\mathscr{H}}_{ji})] \qquad (3.1.5)$$

$$\langle p|d_i^{(2)}(\vec{Q}\vec{Q})|p\rangle = \frac{1}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V\epsilon_0}\right)^{1/2}[e_m k_\ell\alpha(0)e^{-i\omega t}\mathscr{J}_{\ell mi}-\bar{e}_m k_\ell\alpha^+(0)e^{i\omega t}\bar{\mathscr{J}}_{\ell mi}]$$
$$(3.1.6)$$

$$\langle p|b_i^{(2)}(\vec{\mu}\vec{\mu})|p\rangle = \frac{i}{4\pi\epsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2Vc\epsilon_0}\right)^{1/2}[e_\ell\alpha(0)e^{-i\omega t}\mathscr{J}_{\ell i}-\bar{e}_\ell\alpha^+(0)e^{i\omega t}\bar{\mathscr{J}}_{\ell i}]$$
$$(3.1.7)$$

$$\langle p|b_i^{(2)}(\vec{\mu}\vec{m})|p\rangle = \frac{i}{4\pi\epsilon_0 c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2cV\epsilon_0}\right)^{1/2}[\alpha(0)e^{-i\omega t}(b_\ell\mathscr{K}_{\ell i}+e_\ell\mathscr{L}_{\ell i})$$
$$-\alpha^+(0)e^{i\omega t}(\bar{b}_\ell\bar{\mathscr{K}}_{\ell i}+\bar{e}_\ell\bar{\mathscr{L}}_{\ell i})] \qquad (3.1.8)$$

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$$\langle p|b_i^{(2)}(\vec{\text{mm}})|p\rangle = \frac{i}{4\pi\varepsilon_0 c^2}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2Vc\varepsilon_0}\right)^{1/2}[b_\ell\alpha(0)e^{-i\omega t}\mathcal{M}_{\ell i}-\bar{b}_\ell\alpha^+(0)e^{i\omega t}\bar{\mathcal{M}}_{\ell i}]$$

(3.1.9)

$$\langle p|b_i^{(2)}(\vec{\mu Q})|p\rangle = \frac{1}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2cV\varepsilon_0}\right)^{1/2}[\alpha(0)e^{-i\omega t}(e_m k_\ell \mathcal{N}_{\ell im}+e_\ell\mathcal{P}_{\ell i})$$
$$-\alpha^+(0)e^{i\omega t}(\bar{e}_m k_\ell \bar{\mathcal{N}}_{\ell im}+\bar{e}_\ell\bar{\mathcal{P}}_{\ell i})]$$

(3.1.10)

$$\langle p|b_i^{(2)}(\vec{\text{m}Q})|p\rangle = \frac{1}{4\pi\varepsilon_0 c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2cV\varepsilon_0}\right)^{1/2}[\alpha(0)e^{-i\omega t}(e_m k_\ell \mathcal{Q}_{\ell mi}+b_\ell\mathcal{R}_{\ell i})$$
$$-\alpha^+(0)e^{i\omega t}(\bar{e}_m k_\ell \bar{\mathcal{Q}}_{\ell mi}+\bar{b}_\ell\bar{\mathcal{R}}_{\ell i})] \quad (3.1.11)$$

$$\langle p|b_i^{(2)}(\vec{\text{QQ}})|p\rangle = \frac{i}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2Vc\varepsilon_0}\right)^{1/2}[e_m k_\ell\alpha(0)e^{-i\omega t}\mathcal{S}_{\ell mi}-\bar{e}_m k_\ell\alpha^+(0)e^{i\omega t}\bar{\mathcal{S}}_{\ell mi}]$$

(3.1.12)

In the above the $(\vec{k},\lambda)$ dependence of the photon variables has been omitted with the tensor fields defined as

$$\mathcal{A}_{\ell i} = \sum_n \frac{\mu_j^{pn}\mu_\ell^{np}}{E_{np}-\hbar\omega}k^3 F_{ij}(kr) - \sum_n \frac{\mu_j^{pn}\mu_\ell^{np}}{E_{np}-\hbar\omega}k_{np}^3 F_{ij}(k_{np}r)e^{i(k_{pn}+k)ct} +$$
$$\sum_n \frac{\mu_\ell^{pn}\mu_j^{np}}{E_{np}+\hbar\omega}k^3 F_{ij}(kr) - \sum_n \frac{\mu_\ell^{pn}\mu_j^{np}}{E_{np}+\hbar\omega}k_{pn}^3 F_{ij}(k_{pn}r)e^{-i(k_{pn}-k)ct} \quad (3.1.13)$$

$$\mathcal{B}_{\ell i} = \sum_n \frac{\mu_j^{pn}m_\ell^{np}}{E_{np}-\hbar\omega}k^3 F_{ij}(kr) - \sum_n \frac{\mu_j^{pn}m_\ell^{np}}{E_{np}-\hbar\omega}k_{np}^3 F_{ij}(k_{np}r)e^{i(k_{pn}+k)ct} +$$
$$\sum_n \frac{m_\ell^{pn}\mu_j^{np}}{E_{np}+\hbar\omega}k^3 F_{ij}(kr) - \sum_n \frac{m_\ell^{pn}\mu_j^{np}}{E_{np}+\hbar\omega}k_{pn}^3 F_{ij}(k_{pn}r)e^{-i(k_{pn}-k)ct} \quad (3.1.14)$$

$$\mathcal{C}_{k i} = -\sum_{n} \frac{m_j^{pn} \mu_k^{np}}{E_{np} - \hbar\omega} k^3 G_{ij}(kr) + \sum_{n} \frac{m_j^{pn} \mu_k^{np}}{E_{np} - \hbar\omega} k_{np}^3 G_{ij}(k_{np} r) e^{i(k_{pn}+k)ct}$$

$$- \sum_{n} \frac{\mu_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k^3 G_{ij}(kr) + \sum_{n} \frac{\mu_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 G_{ij}(k_{pn} r) e^{-i(k_{pn}-k)ct} \qquad (3.1.15)$$

$$\mathcal{D}_{k i} = \sum_{n} \frac{m_j^{pn} m_k^{np}}{E_{np} - \hbar\omega} k^3 G_{ij}(kr) - \sum_{n} \frac{m_j^{pn} m_k^{np}}{E_{np} - \hbar\omega} k_{np}^3 G_{ij}(k_{np} r) e^{i(k_{pn}+k)ct} +$$

$$\sum_{n} \frac{m_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k^3 G_{ij}(kr) - \sum_{n} \frac{m_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 G_{ij}(k_{pn} r) e^{-i(k_{pn}-k)ct} \qquad (3.1.16)$$

$$\mathcal{E}_{k\ell i} = -\sum_{n} \frac{\mu_j^{pn} Q_{k\ell}^{np}}{E_{np} - \hbar\omega} k^3 F_{ij}(kr) + \sum_{n} \frac{\mu_j^{pn} Q_{k\ell}^{np}}{E_{np} - \hbar\omega} k_{np}^3 F_{ij}(k_{np} r) e^{i(k_{pn}+k)ct} -$$

$$\sum_{n} \frac{Q_{k\ell}^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k^3 F_{ij}(kr) + \sum_{n} \frac{Q_{k\ell}^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 F_{ij}(k_{pn} r) e^{-i(k_{pn}-k)ct} \qquad (3.1.17)$$

$$\mathcal{F}_{j i} = -\sum_{n} \frac{Q_{k\ell}^{pn} \mu_j^{np}}{E_{np} - \hbar\omega} k^4 H_{i\ell k}(kr) + \sum_{n} \frac{Q_{k\ell}^{pn} \mu_j^{np}}{E_{np} - \hbar\omega} k_{np}^4 H_{i\ell k}(k_{np} r) e^{i(k_{pn}+k)ct} -$$

$$\sum_{n} \frac{\mu_j^{pn} Q_{k\ell}^{np}}{E_{np} + \hbar\omega} k^4 H_{i\ell k}(kr) + \sum_{n} \frac{\mu_j^{pn} Q_{k\ell}^{np}}{E_{np} + \hbar\omega} k_{pn}^4 H_{i\ell k}(k_{pn} r) e^{-i(k_{pn}-k)ct} \qquad (3.1.18)$$

$$\mathcal{G}_{k\ell i} = \sum_{n} \frac{m_j^{pn} Q_{k\ell}^{np}}{E_{np} - \hbar\omega} k^3 G_{ij}(kr) - \sum_{n} \frac{m_j^{pn} Q_{k\ell}^{np}}{E_{np} - \hbar\omega} k_{np}^3 G_{ij}(k_{np} r) e^{i(k_{pn}+k)ct} +$$

$$\sum_{n} \frac{Q_{k\ell}^{pn} m_j^{np}}{E_{np} + \hbar\omega} k^3 G_{ij}(kr) - \sum_{n} \frac{Q_{k\ell}^{pn} m_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 G_{ij}(k_{pn} r) e^{-i(k_{pn}-k)ct} \qquad (3.1.19)$$

$$\mathcal{H}_{j i} = -\sum_{n} \frac{Q_{k\ell}^{pn} m_j^{np}}{E_{np} - \hbar\omega} k^4 H_{i\ell k}(kr) + \sum_{n} \frac{Q_{k\ell}^{pn} m_j^{np}}{E_{np} - \hbar\omega} k_{np}^4 H_{i\ell k}(k_{np} r) e^{i(k_{pn}+k)ct} -$$

$$\sum_{n} \frac{m_j^{pn} Q_{k\ell}^{np}}{E_{np} + \hbar\omega} k^4 H_{i\ell k}(kr) + \sum_{n} \frac{m_j^{pn} Q_{k\ell}^{np}}{E_{np} + \hbar\omega} k_{pn}^4 H_{i\ell k}(k_{pn} r) e^{-i(k_{pn}-k)ct} \qquad (3.1.20)$$

$$\mathcal{J}_{\ell m i} = \sum_n \frac{Q_{jk}^{pn} Q_{\ell m}^{np}}{E_{np} - \hbar\omega} k^4 H_{ikj}(kr) - \sum_n \frac{Q_{jk}^{pn} Q_{\ell m}^{np}}{E_{np} - \hbar\omega} k_{np}^4 H_{ikj}(k_{np}r) e^{i(k_{pn}+k)ct} +$$

$$\sum_n \frac{Q_{\ell m}^{pn} Q_{jk}^{np}}{E_{np} + \hbar\omega} k^4 H_{ikj}(kr) - \sum_n \frac{Q_{\ell m}^{pn} Q_{jk}^{np}}{E_{np} + \hbar\omega} k_{pn}^4 H_{ikj}(k_{pn}r) e^{-i(k_{pn}-k)ct} \qquad (3.1.21)$$

$$\mathcal{J}_{k i} = \sum_n \frac{\mu_j^{pn} \mu_k^{np}}{E_{np} - \hbar\omega} k^3 G_{ij}(kr) - \sum_n \frac{\mu_j^{pn} \mu_k^{np}}{E_{np} - \hbar\omega} k_{np}^3 G_{ij}(k_{np}r) e^{i(k_{pn}+k)ct} +$$

$$\sum_n \frac{\mu_k^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k^3 G_{ij}(kr) - \sum_n \frac{\mu_k^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 G_{ij}(k_{pn}r) e^{-i(k_{pn}-k)ct} \qquad (3.1.22)$$

$$\mathcal{K}_{k i} = \sum_n \frac{\mu_j^{pn} m_k^{np}}{E_{np} - \hbar\omega} k^3 G_{ij}(kr) - \sum_n \frac{\mu_j^{pn} m_k^{np}}{E_{np} - \hbar\omega} k_{np}^3 G_{ij}(k_{np}r) e^{i(k_{pn}+k)ct} +$$

$$\sum_n \frac{m_k^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k^3 G_{ij}(kr) - \sum_n \frac{m_k^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 G_{ij}(k_{pn}r) e^{-i(k_{pn}-k)ct} \qquad (3.1.23)$$

$$\mathcal{L}_{k i} = \sum_n \frac{m_j^{pn} \mu_k^{np}}{E_{np} - \hbar\omega} k^3 F_{ij}(kr) - \sum_n \frac{m_j^{pn} \mu_k^{np}}{E_{np} - \hbar\omega} k_{np}^3 F_{ij}(k_{np}r) e^{i(k_{pn}+k)ct} +$$

$$\sum_n \frac{\mu_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k^3 F_{ij}(kr) - \sum_n \frac{\mu_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 F_{ij}(k_{pn}r) e^{-i(k_{pn}-k)ct} \qquad (3.1.24)$$

$$\mathcal{M}_{k i} = \sum_n \frac{m_j^{pn} m_k^{np}}{E_{np} - \hbar\omega} k^3 F_{ij}(kr) - \sum_n \frac{m_j^{pn} m_k^{np}}{E_{np} - \hbar\omega} k_{np}^3 F_{ij}(k_{np}r) e^{i(k_{pn}+k)ct} +$$

$$\sum_n \frac{m_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k^3 F_{ij}(kr) - \sum_n \frac{m_k^{pn} m_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 F_{ij}(k_{pn}r) e^{-i(k_{pn}-k)ct} \qquad (3.1.25)$$

$$\mathcal{N}_{\ell i m} = -\sum_n \frac{\mu_j^{pn} Q_{\ell m}^{np}}{E_{np} - \hbar\omega} k^3 G_{ij}(kr) + \sum_n \frac{\mu_j^{pn} Q_{\ell m}^{np}}{E_{np} - \hbar\omega} k_{np}^3 G_{ij}(k_{np}r) e^{i(k_{pn}+k)ct} -$$

$$\sum_n \frac{Q_{\ell m}^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k^3 G_{ij}(kr) + \sum_n \frac{Q_{\ell m}^{pn} \mu_j^{np}}{E_{np} + \hbar\omega} k_{pn}^3 G_{ij}(k_{pn}r) e^{-i(k_{pn}-k)ct} \qquad (3.1.26)$$

$$\mathscr{P}_{\ell i} = \sum_{n} \frac{Q_{j\ell}^{pn}\mu_{\ell}^{np}}{E_{np}-\hbar\omega} k^4 J_{\ell ij}(kr) - \sum_{n} \frac{Q_{j\ell}^{pn}\mu_{\ell}^{np}}{E_{np}-\hbar\omega} k_{np}^4 J_{\ell ij}(k_{np}r)e^{i(k_{pn}+k)ct} +$$

$$\sum_{n} \frac{\mu_{\ell}^{pn}Q_{j\ell}^{np}}{E_{np}+\hbar\omega} k^4 J_{\ell ij}(kr) - \sum_{n} \frac{\mu_{\ell}^{pn}Q_{j\ell}^{np}}{E_{np}+\hbar\omega} k_{pn}^4 J_{\ell ij}(k_{pn}r)e^{-i(k_{pn}-k)ct} \qquad (3.1.27)$$

$$Q_{\ell mi} = -\sum_{n} \frac{m_{j}^{pn}Q_{\ell m}^{np}}{E_{np}-\hbar\omega} k^3 F_{ij}(kr) + \sum_{n} \frac{m_{j}^{pn}Q_{\ell m}^{np}}{E_{np}-\hbar\omega} k_{np}^3 F_{ij}(k_{np}r)e^{i(k_{pn}+k)ct} -$$

$$\sum_{n} \frac{Q_{\ell m}^{pn}m_{j}^{np}}{E_{np}+\hbar\omega} k^3 F_{ij}(kr) + \sum_{n} \frac{Q_{\ell m}^{pn}m_{j}^{np}}{E_{np}+\hbar\omega} k_{pn}^3 F_{ij}(k_{pn}r)e^{-i(k_{pn}-k)ct} \qquad (3.1.28)$$

$$\mathscr{R}_{\ell i} = \sum_{n} \frac{Q_{j\ell}^{pn}m_{\ell}^{np}}{E_{np}-\hbar\omega} k^4 J_{\ell ij}(kr) - \sum_{n} \frac{Q_{j\ell}^{pn}m_{\ell}^{np}}{E_{np}-\hbar\omega} k_{np}^4 J_{\ell ij}(k_{np}r)e^{i(k_{pn}+k)ct} +$$

$$\sum_{n} \frac{m_{\ell}^{pn}Q_{j\ell}^{np}}{E_{np}+\hbar\omega} k^4 J_{\ell ij}(kr) - \sum_{n} \frac{m_{\ell}^{pn}Q_{j\ell}^{np}}{E_{np}+\hbar\omega} k_{pn}^4 J_{\ell ij}(k_{pn}r)e^{-i(k_{pn}-k)ct} \qquad (3.1.29)$$

$$\mathscr{P}_{\ell mi} = \sum_{n} \frac{Q_{j\ell}^{pn}Q_{\ell m}^{np}}{E_{np}-\hbar\omega} k^4 J_{\ell ij}(kr) - \sum_{n} \frac{Q_{j\ell}^{pn}Q_{\ell m}^{np}}{E_{np}-\hbar\omega} k_{np}^4 J_{\ell ij}(k_{np}r)e^{i(k_{pn}+k)ct} +$$

$$\sum_{n} \frac{Q_{\ell m}^{pn}Q_{j\ell}^{np}}{E_{np}+\hbar\omega} k^4 J_{\ell ij}(kr) - \sum_{n} \frac{Q_{\ell m}^{pn}Q_{j\ell}^{np}}{E_{np}+\hbar\omega} k_{pn}^4 J_{\ell ij}(k_{pn}r)e^{-i(k_{pn}-k)ct} \qquad (3.1.30)$$

3.2 ENERGY DENSITY USING MULTIPOLAR MAXWELL FIELDS

3.2.1 Electric Energy Density

The energy density associated with the electric displacement vector field is

$$\frac{1}{2\varepsilon_0}[\vec{d}^{\perp}(\vec{r},t)]^2 = \frac{1}{2\varepsilon_0}[\vec{d}^{(0)}(\vec{r},t)+\vec{d}^{(1)}(\vec{r},t)+\vec{d}^{(2)}(\vec{r},t)+\ldots]^2$$

$$= \frac{1}{2\varepsilon_0}[d_i^{(0)}d_i^{(0)}+d_i^{(1)}d_i^{(0)}+d_i^{(0)}d_i^{(1)}+d_i^{(1)}d_i^{(1)}+d_i^{(0)}d_i^{(2)}+d_i^{(2)}d_i^{(0)}+\ldots]$$

$$(3.2.1)$$

using the expansion of the field in successive powers of the transition moments correct up to second order in the sources. The important contributions to the energy density arise from the last three terms of (3.2.1). It is clear that the first term of (3.2.1) cannot contribute as the free field is independent of all sources. The second and third terms do not contribute to the expectation value for a state since they lead to a change in the photon number. The first contribution to be retained and used in calculations is the fourth term of (3.2.1), the product of the first order fields. The last two terms correspond to the interference of the vacuum field and second order field. The expectation value of the electric energy density for the molecular state $|p\rangle$ and the radiation field in the vacuum state, is

$$\frac{1}{2\varepsilon_0}\langle 0;p|(d_i^{(1)}d_i^{(1)}+d_i^{(0)}d_i^{(2)}+d_i^{(2)}d_i^{(0)})|p;0\rangle. \qquad (3.2.2)$$

3.2.1(a) *Electric Dipole Contribution*

The leading source-dependent term of the electric energy density is that arising from the electric dipole dependent displacement field. This particular example has been dealt with by Power and Thirunamachandran [33] and is given in complete detail here as a preliminary to the calculation of higher order terms. The contribution from the product of the first order field is now evaluated using (2.2.34). Recalling that the field linear in the sources operates entirely in the electron Fock space, the contribution from the electric dipole dependent displacement field to the electric energy density is

$$\frac{1}{2\varepsilon_0}\sum_n \langle p|d_i^{(1)}(\vec{\mu})|n\rangle\langle n|d_i^{(1)}(\vec{\mu})|p\rangle = \frac{1}{32\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6\bar{f}_{ij}(k_{pn}r)f_{ik}(k_{pn}r).$$

$$(3.2.3)$$

For the contribution from the zeroth and second order fields, use is now made of the diagonal matrix elements of the quadratic fields given in Section 3.1. Using (3.1.1), the last two terms of (3.2.2) are

$$
\frac{1}{2\varepsilon_0} \sum_{\vec{k},\lambda} [\langle 0;p|d_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|d_i^{(2)}|p;0\rangle +
$$

$$
\langle 0;p|d_i^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|d_i^{(0)}|p;0\rangle]
$$

$$
= \frac{1}{8\pi\varepsilon_0} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right) [e_i e^{i\vec{k}\cdot\vec{r}}\overline{e_\ell}\,\overline{\mathscr{A}}_{\ell i} + e_\ell\mathscr{A}_{\ell i}\overline{e}_i e^{-i\vec{k}\cdot\vec{r}}]. \qquad (3.2.4)
$$

The first term of (3.2.4), after the polarisation sum and angular average using (2.2.19) and (2.2.24), is

$$
\frac{\hbar c}{32\pi^2\varepsilon_0} \frac{1}{2\pi i} \int_0^\infty dk\, k^3 [F_{i\ell}(kr)-\overline{F}_{i\ell}(kr)]\,\overline{\mathscr{A}}_{\ell i}. \qquad (3.2.5)
$$

Using the definition (3.1.13) for the tensor field $\mathscr{A}_{\ell i}$ and collecting terms with the same denominator, (3.2.5) can be written

$$
\frac{1}{32\pi^2\varepsilon_0} \sum_{n} \mu_j^{pn}\mu_\ell^{np} \frac{PV}{2\pi i} \int_0^\infty dk\, k^3 \times
$$

$$
\left\{ \frac{[F_{i\ell}(kr)-\overline{F}_{i\ell}(kr)][k^3\overline{F}_{ij}(kr)-k_{np}^3\,\overline{F}_{ij}(k_{np}r)e^{-i(k_{pn}+k)ct}]}{(k_{np}-k)} \right. +
$$

$$
\left. \frac{[F_{i\ell}(kr)-\overline{F}_{i\ell}(kr)][k^3\overline{F}_{ij}(kr)-k_{pn}^3\,\overline{F}_{ij}(k_{pn}r)e^{i(k_{pn}-k)ct}]}{(k_{np}+k)} \right\}
$$

$$
= \frac{-1}{32\pi^2\varepsilon_0} \sum_{n} \mu_j^{pn}\mu_\ell^{np} \frac{PV}{2\pi i} \int_0^\infty \frac{dk\,k^3}{k-k_{np}} \left[-k^3\overline{f}_{i\ell}(kr)\overline{f}_{ij}(kr)e^{-2ikr} \right.
$$

$$
-k_{np}^3 f_{i\ell}(kr)\overline{f}_{ij}(k_{np}r)e^{ik(r-ct)}e^{ik_{pn}(r-ct)}
$$

$$
\left. +k_{np}^3 \overline{f}_{i\ell}(kr)\overline{f}_{ij}(k_{np}r)e^{-ik(r+ct)}e^{ik_{pn}(r-ct)} \right]
$$

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$$+ \frac{1}{32\pi^2\varepsilon_0} \sum_{\tilde{n}} \mu_j^{pn}\mu_\ell^{np} \frac{PV}{2\pi i} \int_0^\infty \frac{dkk^3}{k-k_{pn}} \left[-k^3\bar{f}_{i\ell}(kr)\bar{f}_{ij}(kr)e^{-2ikr} \right.$$

$$-k_{pn}^3 f_{i\ell}(kr)\bar{f}_{ij}(k_{pn}r)e^{ik(r-ct)}e^{-ik_{pn}(r-ct)}$$

$$\left. +k_{pn}^3 \bar{f}_{i\ell}(kr)\bar{f}_{ij}(k_{pn}r)e^{-ik(r+ct)}e^{-ik_{pn}(r-ct)}\right]$$

$$(3.2.6)$$

where use has been made of the j,ℓ-index symmetry to eliminate the term without an exponential dependence. Expression (3.2.6) contains both time-independent and time-dependent terms. The abbreviation PV denotes the Cauchy principal value, which is taken since exact resonances are excluded in the k-integral when making the continuum approximation to the mode sum. The evaluation of the integral depends on the sign of k_{pn} and is carried out by transforming the integral from one along the real axis to one along the imaginary axis in the complex plane. For a state for which $E_p > E_n$, after making the substitution $k = -iu$, the time-independent part of (3.2.6) is

$$\frac{1}{64\pi^2\varepsilon_0} \sum_{\tilde{n}} \mu_j^{pn}\mu_\ell^{np}k_{pn}^6 \bar{f}_{ij}(k_{pn}r)f_{i\ell}(k_{pn}r)$$

$$+ \frac{1}{64\pi^3\varepsilon_0} \sum_{\tilde{n}} \mu_j^{pn}\mu_\ell^{np} \int_0^\infty \frac{duu^6 e^{-2ur}}{u^2 + k_{pn}^2} 2k_{pn}f_{ij}(iur)f_{i\ell}(iur). \qquad (3.2.7)$$

The time-dependent part is given by

$$\frac{1}{64\pi^3\varepsilon_0} \sum_{\tilde{n}} \mu_j^{pn}\mu_\ell^{np}(-k_{pn}^3) \int_0^\infty duu^3 \times$$

$$\left[\bar{f}_{ij}(k_{np}r)e^{ik_{pn}(r-ct)}f_{i\ell}(-iur)\frac{e^{-uc(t-r/c)}}{u + ik_{pn}} \right.$$

$$\left. -\bar{f}_{ij}(k_{np}r)e^{ik_{pn}(r-ct)}\bar{f}_{i\ell}(-iur)\frac{e^{-uc(t+r/c)}}{u + ik_{pn}} \right.$$

$$+\bar{f}_{ij}(k_{pn}r)e^{ik_{np}(r-ct)}f_{il}(-iur)\frac{e^{-uc(t-r/c)}}{u-ik_{pn}}$$

$$-\bar{f}_{ij}(k_{pn}r)e^{ik_{np}(r-ct)}\bar{f}_{il}(-iur)\frac{e^{-uc(t+r/c)}}{u-ik_{pn}}\Bigg].$$

$$(3.2.8)$$

The time-dependent terms tend to zero for t $\gg$ r/c as the integrals have exponentially decreasing values for large t. In addition, the average of (3.2.8) over a finite time interval tends to zero because of the modulation factors $e^{\pm ik_{pn}ct}$. These oscillatory terms are ignored henceforth. Returning to (3.2.6) and evaluating the integral for the case k_{np} > 0, the pole contribution is

$$\frac{-1}{64\pi^2\epsilon_0} \sum_n \mu_j^{pn}\mu_l^{np}k_{pn}^6 \bar{f}_{il}(k_{pn}r)f_{ij}(k_{pn}r) .$$

$$(3.2.9)$$

The u-integral part is identical to that obtained in the second term of (3.2.7). Use has been made of the relations (2.A.3)-(2.A.6) given in the Appendix to Chapter 2 regarding the geometrical tensors.

It is important to note that the first term of (3.2.7) has the same sign as the corresponding term arising from the first order fields (3.2.3). However, for those states n with E_n > E_p, the pole contribution has opposite sign as indicated by (3.2.9), and cancels with the corresponding term of (3.2.3). The reinforcing and cancelling of pole contributions from the zeroth and second order fields with terms from the product of the first order fields is a striking characteristic throughout the calculations carried out in this Chapter. This is a direct consequence of the inclusion of the second order fields; its importance was first shown by Power and Thirunamachandran [31,33] concerning the relation between the spontaneous emission rate and

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Poynting vector energy flow. These authors showed that the Poynting energy flow from the quantum first order fields was equal to one half of the spontaneous power. Inclusion of the second order fields doubled the flow, demonstrating that the spontaneous rate and the Poynting vector flow are equal when quantum fields to second order are used.

The second term of (3.2.4) is simply the complex conjugate of the first so that the total contribution to the electric energy density due to an electric dipole source is

$$
\frac{1}{16\pi^2\varepsilon_0} \sum_{\substack{n \\ E_p > E_n}} \mu_j^{pn}\mu_k^{np}k_{pn}^6 \overline{f}_{ik}(k_{pn}r)f_{ij}(k_{pn}r)
$$

$$
+ \frac{1}{32\pi^3\varepsilon_0} \sum_{\substack{n \\ ALL\ E_n}} \mu_j^{pn}\mu_k^{np} \int_0^\infty \frac{duu^6 e^{-2ur}}{u^2 + k_{pn}^2} 2k_{pn}f_{ij}(iur)f_{ik}(iur). \qquad (3.2.10)
$$

This general expression is applicable to transitions from the initial state $|p\rangle$ with summation carried out over a complete set of intermediate states $|n\rangle$. The two terms given in (3.2.10), whose properties are markedly different, are now examined in detail.

When the initial state is the ground state, only the second term of (3.2.10) remains, which is

$$
\frac{\hbar c}{32\pi^3\varepsilon_0} \int_0^\infty duu^6 e^{-2ur}\alpha_{jk}(iu)\left[\frac{\alpha_{jk}}{u^2 r^2} + \frac{2\alpha_{jk}}{u^3 r^3} + \frac{2\alpha_{jk}+\gamma_{jk}}{u^4 r^4} + \frac{2\gamma_{jk}}{u^5 r^5} + \frac{\gamma_{jk}}{u^6 r^6}\right]
$$

$$
(3.2.11)
$$

with

$$
\alpha_{jk}(iu) = \sum_n \frac{2k_{no}\mu_j^{on}\mu_k^{no}}{\hbar c(k_{no}^2 + u^2)}, \qquad (3.2.12)
$$

the ground state dynamic polarisability expressed in terms of imaginary

frequencies, with the dyadics defined as

$$\alpha_{ij} = (\delta_{ij} - \hat{r}_i \hat{r}_j) \quad ; \quad \gamma_{ij} = (\delta_{ij} + 3\hat{r}_i \hat{r}_j).$$
(3.2.13)

The expression (3.2.11) applies for fixed molecular orientation. To deal

with species in a fluid phase a rotational average is required. By

following the standard procedure [41], (3.2.11) becomes

$$\frac{\hbar c}{16\pi^3 \epsilon_0} \int_0^\infty du\, u^6 e^{-2ur} \alpha(iu) \left[\frac{1}{u^2 r^2} + \frac{2}{u^3 r^3} + \frac{5}{u^4 r^4} + \frac{6}{u^5 r^5} + \frac{3}{u^6 r^6} \right].$$
(3.2.14)

It is instructive to examine the asymptotic behaviour of (3.2.14) in the

limits of large and small distances r. In the far-zone limit r is much

larger than the wavelength of the molecular transition. After performing

the u-integral [42], the far-zone asymptote is found to be

$$\frac{23\hbar c \alpha(0)}{64\pi^3 \epsilon_0 r^7},$$
(3.2.15)

where $\alpha(0)$ is the static polarisability of the source. In the near-zone

r is much smaller than characteristic transition wavelengths, resulting

in kr $\ll$ 1. Retaining the leading term after setting the exponential

factor to unity, the near-zone limit is found to be

$$\frac{1}{16\pi^2 \epsilon_0 r^6} \sum_{n} |\vec{\mu}^{0n}|^2,$$
(3.2.16)

which is in fact the electric energy density of a static electric dipole

source.

Returning now to the general result (3.2.10), the first term is the additional contribution arising from real photon emission by a molecule in an excited state. After expanding the geometrical tensors and rotational averaging, this term is found to be

$$\frac{1}{16\pi^2\varepsilon_0} \sum_{\substack{n \\ E_p > E_n}} \mu_j^{pn}\mu_\ell^{np} k_{pn}^6 \left[\alpha_{j\ell}\left(\frac{1}{k_{pn}^2 r^2} - \frac{2}{k_{pn}^4 r^4}\right) + \gamma_{j\ell}\left(\frac{1}{k_{pn}^4 r^4} + \frac{1}{k_{pn}^6 r^6}\right)\right]$$

$$= \frac{1}{24\pi^2\varepsilon_0} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}|^2 k_{pn}^6 \left[\frac{1}{k_{pn}^2 r^2} + \frac{1}{k_{pn}^4 r^4} + \frac{3}{k_{pn}^6 r^6}\right]. \qquad (3.2.17)$$

This term falls of as r^{-2} for large r, being associated with real photon emission. The energy in a large spherical shell of unit thickness is

$$\frac{1}{6\pi\varepsilon_0} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}|^2 k_{pn}^4 \qquad (3.2.18)$$

and is independent of the radius of the shell. The r^{-2} term of (3.2.17) obviously dominates the far-zone density since the second term of (3.2.10) was shown to produce an r^{-7} dependence. Both terms of (3.2.10) however, exhibit an r^{-6} dependence for small r, with the contribution from the first term of (3.2.10), found from (3.2.17), given by

$$\frac{1}{8\pi^2\varepsilon_0 r^6} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}|^2, \qquad (3.2.19)$$

while the contribution from the second term of (3.2.10) is

$$\frac{-1}{16\pi^2\varepsilon_0 r^6} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}|^2 + \frac{1}{16\pi^2\varepsilon_0 r^6} \sum_{\substack{n \\ E_p < E_n}} |\vec{\mu}^{pn}|^2. \qquad (3.2.20)$$

A direct manifestation of the electromagnetic energy density determined above is the intermolecular interaction energy of a test polarisable body placed in the radiation fields of the source. The response of a polarisable test molecule in the ground state, with static electric dipole polarisability $\alpha_{TEST}(0)$ to the far-zone limit of the electric energy density (3.2.15) is

$$\frac{-1}{2\varepsilon_0^2}\,\alpha_{TEST}(0)\vec{d}^{\perp 2} = \frac{-23\hbar c}{64\pi^3\varepsilon_0^2 r^7}\,\alpha_{TEST}(0)\alpha(0)\ , \tag{3.2.21}$$

which is the familiar Casimir dispersion energy at large separation distances [43]. The far-zone response of a polarisable test body to the energy density of an excited source using (3.2.18) is found to be

$$\frac{-1}{24\pi^2\varepsilon_0^2 r^2}\ \sum_{\substack{n \\ E_p > E_n}}|\vec{\mu}^{pn}|^2\alpha_{TEST}(0)k_{pn}^4\ , \tag{3.2.22}$$

while the near-zone shift from (3.2.19) and (3.2.20) is

$$\frac{-1}{16\pi^2\varepsilon_0^2 r^6}\ \sum_{\substack{n \\ ALL\ E_n}}|\vec{\mu}^{pn}|^2\alpha_{TEST}(0) \tag{3.2.23}$$

and is recognisable as a London type dispersion potential, also obtainable using electrostatic coupling. This particular aspect of the calculation of intermolecular potentials is examined in greater detail in the following Chapter where a generalised version of response theory is used to obtain the energy of interaction between molecules in both ground and electronically excited states directly.

This completes the evaluation of the electric energy density due to an electric dipole source, correct to second order in the transition moments. The next contribution to the energy density to be considered is that arising from a mixed electric dipole-magnetic dipole source. The electric and magnetic energy densities from this source, along with molecules with mixed electric dipole-quadrupole and mixed magnetic dipole-electric quadrupole moments are found to vanish on orientational averaging and are not considered any further. The next non-zero contribution to the electric energy density arises from a pure magnetic dipole source, whose method of calculation, along with the pure electric quadrupole source and the remaining magnetic energy densities, follows that outlined above for the electric dipole case.

3.2.1(b) *Magnetic Dipole Contribution*

The electric energy density due to a magnetic dipole source is the expectation value of

$$\frac{1}{2\varepsilon_0}[\vec{d}^{\perp}(\vec{r},t;\overrightarrow{mm})]^2 \simeq \frac{1}{2\varepsilon_0}[\vec{d}^{(1)}(\vec{m}).\vec{d}^{(1)}(\vec{m})+\vec{d}^{(2)}(\overrightarrow{mm}).\vec{d}^{(0)}+\vec{d}^{(0)}.\vec{d}^{(2)}(\overrightarrow{mm})].$$

$$(3.2.24)$$

The contribution from the product of the first order magnetic dipole dependent electric displacement field is found using (2.2.34) to be

$$\frac{1}{2\varepsilon_0}\sum_{n}\langle p|d_i^{(1)}(\vec{m})|n\rangle\langle n|d_i^{(1)}(\vec{m})|p\rangle = \frac{1}{32\pi^2\varepsilon_0 c^2}\sum_{n} m_j^{pn} m_\ell^{np} k_{pn}^6 \bar{g}_{ij}(k_{pn}r)g_{i\ell}(k_{pn}r)$$

$$(3.2.25)$$

while the contribution from the product of the zeroth and second order fields using (3.1.3) is

$$\frac{1}{2\epsilon_0} \sum_{\vec{k},\lambda} [<0;p|d_{\ell}^{(2)}|p;\vec{k},\lambda><\vec{k},\lambda;p|d_{\ell}^{(0)}|p;0> +$$

$$<0;p|d_{\ell}^{(0)}|p;\vec{k},\lambda><\vec{k},\lambda;p|d_{\ell}^{(2)}|p;0>]$$

$$= \frac{-1}{8\pi\epsilon_0 c} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) [b_{\ell}\mathscr{D}_{\ell i}\bar{e}_{\ell} e^{-i\vec{k}\cdot\vec{r}} + e_{\ell} e^{i\vec{k}\cdot\vec{r}}\bar{b}_{\ell}\bar{\mathscr{D}}_{\ell i}]. \qquad (3.2.26)$$

Evaluating the terms above using the polarisation sum (2.2.19), the angular integration (2.2.25) and making use of the definition of the tensor field $\mathscr{D}_{\ell i}$ given by (3.1.16), and noting the respective adding and cancelling of the pole terms when $k_{pn} > 0$ and $k_{pn} < 0$ with (3.2.25), the total electric energy density due to a magnetic dipole source is

$$\frac{1}{16\pi^2\epsilon_0 c^2} \sum_{\substack{n \\ E_p > E_n}} m_j^{pn} m_{\ell}^{np} k_{pn}^6 \bar{g}_{ij}(k_{pn}r)g_{i\ell}(k_{pn}r)$$

$$+ \frac{1}{32\pi^3\epsilon_0 c^2} \sum_{\substack{n \\ ALL\ E_n}} m_j^{pn} m_{\ell}^{np} \int_0^{\infty} \frac{du\, u^6 e^{-2ur}}{u^2 + k_{np}^2} 2k_{np} g_{ij}(iur)g_{i\ell}(iur) \qquad (3.2.27)$$

which is the oriented result. For a randomly oriented molecule the first term of (3.2.27), the contribution from real photon emission due to the source being in an excited state, is

$$\frac{1}{16\pi^2\epsilon_0 c^2} \sum_{\substack{n \\ E_n < E_p}} m_j^{pn} m_{\ell}^{np} k_{pn}^6 \epsilon_{ijs}\epsilon_{i\ell t}\hat{r}_s\hat{r}_t \left[\frac{1}{k_{pn}^2 r^2} + \frac{1}{k_{pn}^4 r^4}\right]$$

$$= \frac{1}{24\pi^2\epsilon_0 c^2} \sum_{\substack{n \\ E_p > E_n}} |\vec{m}^{pn}|^2 k_{pn}^6 \left[\frac{1}{k_{pn}^2 r^2} + \frac{1}{k_{pn}^4 r^4}\right]. \qquad (3.2.28)$$

The far-zone limit of the energy density in a large spherical shell is

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$$\frac{1}{6\pi\varepsilon_0 c^2} \sum_{\substack{n \\ E_p > E_n}} |\vec{m}^{pn}|^2 k_{pn}^4 \qquad (3.2.29)$$

and is independent of the radius of the shell, while the near-zone behaviour shows an r^{-4} dependence on distance. Examining the second term of (3.2.27), the u-integral is

$$\frac{-1}{32\pi^3\varepsilon_0 c^2} \sum_n m_j^{pn} m_k^{np} \varepsilon_{iks}\varepsilon_{ijl} \hat{r}_s \hat{r}_l \int_0^\infty \frac{duu^6 e^{-2ur}}{u^2 + k_{np}^2} 2k_{np}\left[\frac{1}{u^2 r^2} + \frac{2}{u^3 r^3} + \frac{1}{u^4 r^4}\right]$$

$$= \frac{-\hbar}{16\pi^3\varepsilon_0 c} \int_0^\infty duu^6 e^{-2ur}\chi(iu)\left[\frac{1}{u^2 r^2} + \frac{2}{u^3 r^3} + \frac{1}{u^4 r^4}\right] \qquad (3.2.30)$$

where

$$\chi(iu) = \frac{2}{3} \sum_n \frac{k_{np}|\vec{m}^{pn}|^2}{\hbar c(k_{np}^2 + u^2)} \qquad (3.2.31)$$

is the isotropic magnetic susceptibility of the molecule in excited state $|p\rangle$. The far-zone limit of (3.2.30) after evaluating the u-integral is

$$\frac{-7\hbar\chi(0)}{64\pi^3\varepsilon_0 cr^7} \qquad (3.2.32)$$

where $\chi(0)$ is the $u = 0$ limit of (3.2.31), corresponding to the static excited susceptibility. When the initial state is the ground state only upward transitions are possible and the first term of (3.2.27) does not contribute. The u-integral term is seen to give (3.2.32) but $\chi(0)$ now being the ground state static magnetic susceptibility. The response of a polarisable test body to the far-zone limit (3.2.32) then gives the dispersion interaction between an electric dipole polarisable molecule

and a magnetic dipole source as

$$\frac{-1}{2\varepsilon_0^2}\,\alpha_{TEST}(0)\vec{d}^{\perp 2} = \frac{7\hbar}{64\pi^3\varepsilon_0^2 cr^7}\,\alpha_{TEST}(0)\chi(0) \tag{3.2.33}$$

which is repulsive, while for an excited source the interaction varies as r^{-2} as in

$$\frac{-1}{24\pi^2\varepsilon_0^2 c^2 r^2}\sum_{\substack{\bar{n}\\E_p>E_n}}|\vec{m}^{pn}|^2\alpha_{TEST}(0)k_{pn}^4 \ , \tag{3.2.34}$$

on making use of (3.2.28).

3.2.1(c) *Electric Quadrupole Contribution*

The final contribution to the electric energy density to be considered is that arising from an electric quadrupole source. This is evaluated from

$$\frac{1}{2\varepsilon_0}[\vec{d}^{\perp}(\vec{r},t;\overset{\leftrightarrow}{\vec{Q}\vec{Q}})]^2 \simeq \frac{1}{2\varepsilon_0}[\vec{d}^{(1)}(\vec{Q}).\vec{d}^{(1)}(\vec{Q})+\vec{d}^{(2)}(\overset{\leftrightarrow}{\vec{Q}\vec{Q}}).\vec{d}^{(0)}+\vec{d}^{(0)}.\vec{d}^{(2)}(\overset{\leftrightarrow}{\vec{Q}\vec{Q}})].$$

$$\tag{3.2.35}$$

Using the electric quadrupole dependent part of the displacement field linear in the sources (2.2.34), the contribution from the product of the first order fields is

$$\frac{1}{2\varepsilon_0}\sum_{\bar{n}}\langle p|d_i^{(1)}(\vec{Q})|n\rangle\langle n|d_i^{(1)}(\vec{Q})|p\rangle = \frac{1}{32\pi^2\varepsilon_0}\sum_{\bar{n}}Q_{jk}^{pn}Q_{\ell m}^{np}k_{pn}^8\,\bar{h}_{ikj}(k_{pn}r)h_{im\ell}(k_{pn}r). \tag{3.2.36}$$

The contribution to the energy density from the interference of the

vacuum and second order fields is determined using (3.1.6),

$$\frac{1}{2\varepsilon_0} \sum_{\vec{k},\lambda} [\langle 0;p|d_i^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|d_i^{(0)}|p;0\rangle +$$

$$\langle 0;p|d_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|d_i^{(2)}|p;0\rangle]$$

$$= \frac{-ic}{8\pi\varepsilon_0} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) [e_\ell k_m \mathcal{T}_{\ell m i}\bar{e}_i e^{-i\vec{k}\cdot\vec{r}} + e_i e^{i\vec{k}\cdot\vec{r}}\bar{e}_\ell k_m \mathcal{T}_{\ell m i}]. \qquad (3.2.37)$$

Evaluating the two terms above after the polarisation sum, using the angular integral (2.2.26) and the tensor field definition (3.1.21), the total electric energy density due to an oriented electric quadrupole source is

$$\frac{1}{16\pi^2\varepsilon_0} \sum_{\substack{\bar{n} \\ E_p > E_n}} Q_{jk}^{pn}Q_{\ell m}^{np}k_{pn}^8 \bar{h}_{ikj}(k_{pn}r)h_{im\ell}(k_{pn}r)$$

$$+ \frac{1}{32\pi^3\varepsilon_0} \sum_{\substack{\bar{n} \\ ALL\ E_n}} Q_{jk}^{pn}Q_{\ell m}^{np}\int_0^\infty \frac{duu^8 e^{-2ur}}{u^2 + k_{np}^2} 2k_{np}h_{ikj}(iur)h_{im\ell}(iur). \qquad (3.2.38)$$

For a molecule in the ground state only the second term of (3.2.38) survives, which after multiplying the geometrical tensors, whose explicit form are given in an Appendix at the end of this Chapter, can be written as

$$\frac{\hbar c}{32\pi^3\varepsilon_0} \int_0^\infty duu^8 e^{-2ur}\theta_{jk\ell m}(iu) \left[\frac{A_{jk\ell m}}{u^2 r^2} + \frac{B_{jk\ell m}}{u^3 r^3} + \frac{C_{jk\ell m}}{u^4 r^4} + \frac{D_{jk\ell m}}{u^5 r^5} + \frac{E_{jk\ell m}}{u^6 r^6} + \frac{F_{jk\ell m}}{u^7 r^7} + \frac{G_{jk\ell m}}{u^8 r^8}\right]$$

$$(3.2.39)$$

where $\theta_{jk\ell m}(iu)$ is the quadrupole polarisability expressed in terms of imaginary frequencies. To obtain the isotropic energy density a rotational average is taken. Utilising the fact that the quadrupole

moment tensor is traceless, the average entails the product of

$\frac{1}{30}(-2\delta_{jk}\delta_{\ell m}+3\delta_{j\ell}\delta_{km}+3\delta_{jm}\delta_{k\ell})$ with each of $A_{jk\ell m}$ to $G_{jk\ell m}$; (3.2.39) then becomes

$$\frac{1}{960\pi^3\varepsilon_0}\sum_{\bar{n}}Q^{0n}_{\lambda\mu}Q^{n0}_{\lambda\mu}\int_0^{\infty}\frac{duu^8e^{-2ur}}{u^2+k^2_{n0}}\,2k_{n0}\left[\frac{6}{u^2r^2}+\frac{36}{u^3r^3}+\frac{162}{u^4r^4}+\frac{504}{u^5r^5}+\frac{972}{u^6r^6}+\frac{1080}{u^7r^7}+\frac{540}{u^8r^8}\right].$$

(3.2.40)

The far-zone result is obtained by retaining all such terms and taking $u^2+k^2_{n0}=k^2_{n0}$ while the near-zone limit requires the retention of only the $G_{jk\ell m}$ part. After the usual approximations the u-integrals can be evaluated to give the asymptotic values

$$\frac{1593\hbar c}{1280\pi^3\varepsilon_0 r^9}\,\theta_{\lambda\mu\lambda\mu}(0)$$

(3.2.41)

for the far-zone and

$$\frac{9}{16\pi^2\varepsilon_0 r^8}\sum_{\bar{n}}Q^{0n}_{\lambda\mu}Q^{n0}_{\lambda\mu}$$

(3.2.42)

for the near-zone. For an excited state $|p\rangle$ both terms in (3.2.38) contribute to the energy density. Taking into account that the quadrupole polarisability for an excited state includes both positive and negative contributions, the structure of the second term is unaltered. After expanding the tensors which are given in the Appendix under (3.A.2), the first term of (3.2.38) after orientational averaging becomes

$$\frac{1}{80\pi^2\varepsilon_0}\sum_{\substack{n\\E_p>E_n}}Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np}k_{pn}^8\left[\frac{1}{k_{pn}^2r^2}+\frac{3}{k_{pn}^4r^4}+\frac{18}{k_{pn}^6r^6}+\frac{90}{k_{pn}^8r^8}\right] \qquad (3.2.43)$$

so that the near- and far-zone asymptotic behaviour are respectively given by

$$\frac{9}{8\pi^2\varepsilon_0 r^8}\sum_{\substack{n\\E_p>E_n}}Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np}\ , \qquad (3.2.44)$$

$$\frac{1}{80\pi^2\varepsilon_0 r^2}\sum_{\substack{n\\E_p>E_n}}Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np}k_{pn}^6\ . \qquad (3.2.45)$$

The far-zone quadrupole dependent electric energy density (3.2.41) leads directly to the intermolecular energy of interaction in the presence of a test electric dipole polarisable molecule

$$\frac{-1593\hbar c}{1280\pi^3\varepsilon_0^2 r^9}\ \alpha_{TEST}(0)\theta_{\lambda\mu\lambda\mu}(0)\ . \qquad (3.2.46)$$

With the source in an excited state, the near- and far-zone energy shifts using (3.2.43) are respectively found to be

$$\frac{-9}{8\pi^2\varepsilon_0^2 r^8}\sum_{\substack{n\\E_p>E_n}}\alpha_{TEST}(0)Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np}\ , \qquad (3.2.47)$$

$$\frac{-1}{80\pi^2\varepsilon_0^2 r^2}\sum_{\substack{n\\E_p>E_n}}\alpha_{TEST}(0)Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np}k_{pn}^6\ . \qquad (3.2.48)$$

This completes the evaluation of the electric energy density for

electric dipole, magnetic dipole and electric quadrupole sources.

3.2.2 Magnetic Energy Density

The magnetic energy density associated with these sources is now calculated.

3.2.2(a) *Electric Dipole Contribution*

The magnetic energy density correct to second order in the electric dipole moments is computed from

$$\frac{1}{2}\epsilon_0 c^2 [\vec{b}(\vec{r},t;\vec{\mu\mu})]^2 \simeq \frac{1}{2}\epsilon_0 c^2 [\vec{b}^{(1)}(\vec{\mu}).\vec{b}^{(1)}(\vec{\mu})+\vec{b}^{(0)}.\vec{b}^{(2)}(\vec{\mu\mu})+\vec{b}^{(2)}(\vec{\mu\mu}).\vec{b}^{(0)}].$$

$$(3.2.49)$$

Using the magnetic field linear in the electric dipole moment (2.2.55), the first term of (3.2.49) is

$$\frac{1}{2}\epsilon_0 c^2 \sum_n \langle p|b_i^{(1)}(\vec{\mu})|n\rangle\langle n|b_i^{(1)}(\vec{\mu})|p\rangle = \frac{1}{32\pi^2\epsilon_0}\sum_n \mu_j^{pn}\mu_\ell^{np}k_{pn}^6 \bar{g}_{ij}(k_{pn}r)g_{i\ell}(k_{pn}r).$$

$$(3.2.50)$$

Using the diagonal matrix element for the second order magnetic field of an electric dipole source (3.1.7), the contribution from the zeroth order and quadratic fields is

$$\frac{1}{2}\epsilon_0 c^2 \sum_{\vec{k},\lambda} [\langle 0;p|b_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(2)}|p;0\rangle +$$

$$\langle 0;p|b_i^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(0)}|p;0\rangle]$$

$$= \frac{c}{8\pi\epsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)[b_i e^{i\vec{k}.\vec{r}}e_\ell\bar{g}_{\ell i}+e_\ell g_{\ell i}\bar{b}_i e^{-i\vec{k}.\vec{r}}].$$

$$(3.2.51)$$

Evaluating the above in the usual way, making use of (3.1.22), the total

contribution to the magnetic energy density from an electric dipole source is

$$\frac{1}{16\pi^2\varepsilon_0} \sum_{\substack{n \\ E_n < E_p}} \mu_j^{pn}\mu_k^{np} k_{pn}^6 \bar{g}_{ij}(k_{pn}r) g_{ik}(k_{pn}r)$$

$$\frac{-1}{32\pi^3\varepsilon_0} \sum_{\substack{n \\ ALL\ E_n}} \mu_j^{pn}\mu_k^{np} \int_0^\infty \frac{du\, u^6 e^{-2ur}}{u^2 + k_{pn}^2}\, 2k_{pn} g_{ij}(iur) g_{ik}(iur) \qquad (3.2.52)$$

which as expected, is similar to the result obtained for the electric energy density of a magnetic dipole source (3.2.27) since the magnetic field of an electric dipole is the negative of the electric field of a magnetic dipole with $\vec{m}$ replaced by $\vec{\mu}$. Thus the magnetic energy density for the ground state is

$$\frac{\hbar c}{32\pi^3\varepsilon_0} \int_0^\infty du\, u^6 e^{-2ur} \alpha_{jk}(iu) g_{ij}(iur) g_{ik}(iur), \qquad (3.2.53)$$

which for an isotropic molecule reduces to [33]

$$\frac{-\hbar c}{16\pi^3\varepsilon_0} \int_0^\infty du\, u^6 e^{-2ur} \alpha(iu) \left[\frac{1}{u^2 r^2} + \frac{2}{u^3 r^3} + \frac{1}{u^4 r^4} \right], \qquad (3.2.54)$$

and which in the far-zone gives the asymptotic value

$$\frac{-7\hbar c \alpha(0)}{64\pi^3\varepsilon_0 r^7}. \qquad (3.2.55)$$

After expanding the tensors in the first part of (3.2.52) and rotationally averaging, the additional contribution to the energy density due to downward transitions is

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$$\frac{1}{24\pi^2\epsilon_0} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}|^2 k_{pn}^6 \left[\frac{1}{k_{pn}^2 r^2} + \frac{1}{k_{pn}^4 r^4}\right] \qquad (3.2.56)$$

exhibiting r^{-2} and r^{-4} far- and near-zone behaviour respectively. Analogous to the calculation in (3.2.33) of the asymptotic intermolecular energy between an electric dipole polarisable molecule and a magnetic dipole polarisable molecule, the interchange of source and test bodies leads to the intermolecular energy of repulsion

$$\frac{-1}{2\epsilon_0 c^2} \chi_{TEST}(0)\vec{b}^2 = \frac{7\hbar}{64\pi^3\epsilon_0^2 cr^7} \chi_{TEST}(0)\alpha(0) \qquad (3.2.57)$$

in agreement with (3.2.33). For a source in an electronic excited state, the near- and far-zone interaction energies are found using (3.2.56) to be

$$\frac{-1}{48\pi^2\epsilon_0^2 c^2 r^4} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}|^2 \chi_{TEST}(0) k_{pn}^2 \ , \qquad (3.2.58)$$

$$\frac{-1}{24\pi^2\epsilon_0^2 c^2 r^2} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}|^2 \chi_{TEST}(0) k_{pn}^4 \ . \qquad (3.2.59)$$

3.2.2(b) Magnetic Dipole Contribution

Since the magnetic field of a magnetic dipole has the same functional form as the displacement field of an electric dipole, the expressions for the magnetic energy density from a magnetic dipole source are similar to those of the electric energy density from an electric dipole source found earlier. To second order in the moments,

$$\frac{1}{2}\varepsilon_0 c^2 |\vec{b}(\vec{r},t;\vec{mm})|^2 \simeq \frac{1}{2}\varepsilon_0 c^2 [\vec{b}^{(1)}(\vec{m})\cdot\vec{b}^{(1)}(\vec{m})+\vec{b}^{(2)}(\vec{mm})\cdot\vec{b}^{(0)}+\vec{b}^{(0)}\cdot\vec{b}^{(2)}(\vec{mm})].$$

$$(3.2.60)$$

Evaluating the first term using the $\vec{m}$-dependent part of $\vec{b}^{(1)}(\vec{r},t)$ given by (2.2.55),

$$\frac{1}{2}\varepsilon_0 c^2 \sum_n \langle p|b_i^{(1)}(\vec{m})|n\rangle\langle n|b_i^{(1)}(\vec{m})|p\rangle = \frac{1}{32\pi^2\varepsilon_0 c^2}\sum_n m_j^{pn} m_k^{np} k_{pn}^6 \, \overline{f}_{ij}(k_{pn}r)f_{ik}(k_{pn}r)$$

$$(3.2.61)$$

while the contribution from the product of the free field and the quadratic field (3.1.9) is

$$\frac{1}{2}\varepsilon_0 c^2 \sum_{\vec{k},\lambda} [\langle 0;p|b_i^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(0)}|p;0\rangle +$$

$$\langle 0;p|b_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(2)}|p;0\rangle]$$

$$= \frac{1}{8\pi\varepsilon_0 c}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)[b_\ell \mathcal{M}_{\ell i}\overline{b}_i e^{-i\vec{k}\cdot\vec{r}} + b_i e^{i\vec{k}\cdot\vec{r}}\overline{b}_\ell \overline{\mathcal{M}}_{\ell i}].$$

$$(3.2.62)$$

Adding the contribution from (3.2.61) to (3.2.62), the total magnetic energy density from an oriented magnetic dipole source is given by the expression

$$\frac{1}{16\pi^2\varepsilon_0 c^2}\sum_{\substack{n \\ E_p>E_n}} m_j^{pn} m_k^{np} k_{pn}^6 \, f_{ik}(k_{pn}r)\overline{f}_{ij}(k_{pn}r)$$

$$+ \frac{1}{32\pi^3\varepsilon_0 c^2}\sum_{\substack{n \\ \text{ALL } E_n}} m_j^{pn} m_k^{np}\int_0^\infty \frac{duu^6 e^{-2ur}}{u^2 + k_{pn}^2} 2k_{pn} f_{ij}(iur)f_{ik}(iur).$$

$$(3.2.63)$$

The u-integral term, applicable to both upward and downward transitions, becomes after averaging

$$\frac{\hbar}{16\pi^3\varepsilon_0 c} \int_0^\infty du u^6 e^{-2ur}\chi(iu)\left[\frac{1}{u^2 r^2} + \frac{2}{u^3 r^3} + \frac{5}{u^4 r^4} + \frac{6}{u^5 r^5} + \frac{3}{u^6 r^6}\right] \qquad (3.2.64)$$

giving the asymptotic limits

$$\frac{23\hbar\chi(0)}{64\pi^3\varepsilon_0 c r^7} \qquad (3.2.65)$$

for the far-zone, and

$$\frac{1}{16\pi^2\varepsilon_0^2 c^2 r^6} \sum_{\bar{n}} |\vec{m}^{pn}|^2 \qquad (3.2.66)$$

for the near-zone. The additional contribution from downward transitions, the first term of (3.2.63), after orientational averaging, is found to be

$$\frac{1}{24\pi^2\varepsilon_0^2 c^2} \sum_{\substack{\bar{n} \\ E_p > E_n}} |\vec{m}^{pn}|^2 k_{pn}^6 \left[\frac{1}{k_{pn}^2 r^2} + \frac{1}{k_{pn}^4 r^4} + \frac{3}{k_{pn}^6 r^6}\right] \qquad (3.2.67)$$

with the overall far-zone density dominated by

$$\frac{1}{24\pi^2\varepsilon_0^2 c^2 r^2} \sum_{\substack{\bar{n} \\ E_p > E_n}} |\vec{m}^{pn}|^2 k_{pn}^4 \qquad (3.2.68)$$

while the near-zone behaviour, like that from the u-integral term, has an r^{-6} dependence.

3.2.2(c) *Electric Quadrupole Contribution*

The final contribution to the magnetic energy density to be determined is that arising from the electric quadrupole source. This is evaluated from

$$\frac{1}{2}\varepsilon_0 c^2 [\vec{b}(\vec{r},t;\vec{\vec{Q}})]^2 \simeq \frac{1}{2}\varepsilon_0 c^2 [\vec{b}^{(1)}(\vec{Q}).\vec{b}^{(1)}(\vec{Q})+\vec{b}^{(2)}(\vec{\vec{Q}}).\vec{b}^{(0)}+\vec{b}^{(0)}.\vec{b}^{(2)}(\vec{\vec{Q}})].$$

$$(3.2.69)$$

Using the quadrupole-dependent part of the magnetic field linear in the sources (2.2.55), the first term of (3.2.69) is

$$\frac{1}{2}\varepsilon_0 c^2 \sum_{n}\langle p|b_i^{(1)}(\vec{Q})|n\rangle\langle n|b_i^{(1)}(\vec{Q})|p\rangle = \frac{1}{32\pi^2\varepsilon_0}\sum_{n} Q_{jk}^{pn}Q_{\ell m}^{np}k_{pn}^8 \bar{j}_{ijk}(k_{pn}r)j_{i\ell m}(k_{pn}r)$$

$$(3.2.70)$$

while the contribution from the interference of the source independent field with the quadratic field (3.1.12) is obtained from

$$\frac{1}{2}\varepsilon_0 c^2 \sum_{\vec{k},\lambda} [\langle 0;p|b_i^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(0)}|p;0\rangle +$$

$$\langle 0;p|b_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(2)}|p;0\rangle]$$

$$= \frac{c}{8\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)[e_\ell k_m^{\mathscr{P}}\ell_{mi}\bar{b}_i e^{-i\vec{k}.\vec{r}}+b_i e^{i\vec{k}.\vec{r}}e_\ell k_m^{\mathscr{P}}\ell_{mi}].$$

$$(3.2.71)$$

Evaluating the above in the usual manner, making use of (3.1.30), the total magnetic energy density from an electric quadrupole source is

$$\frac{1}{16\pi^2\varepsilon_0}\sum_{n} Q_{jk}^{pn}Q_{\ell m}^{np}k_{pn}^8 \bar{j}_{ijk}(k_{pn}r)j_{i\ell m}(k_{pn}r) + $$
$$E_n < E_p$$

$$\frac{1}{32\pi^3\varepsilon_0} \sum_{\substack{n \\ \text{ALL } E_n}} Q_{jk}^{pn}Q_{\ell m}^{np} \int_0^{r} \frac{du\,u^8\,e^{-2ur}}{u^2 + k_{np}^2}\, 2k_{np}\, j_{ijk}(iur)\,j_{i\ell m}(iur) . \qquad (3.2.72)$$

After multiplying the geometric tensors in the first term above, which is given by (3.A.6) in the Appendix, the pole contribution on rotational averaging is

$$\frac{1}{80\pi^2\varepsilon_0} \sum_{\substack{n \\ E_p > E_n}} Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np} k_{pn}^8 \left[\frac{1}{k_{pn}^2 r^2} + \frac{3}{k_{pn}^4 r^4} + \frac{9}{k_{pn}^6 r^6}\right] \qquad (3.2.73)$$

with the near-zone limit

$$\frac{9}{80\pi^2\varepsilon_0 r^6} \sum_{\substack{n \\ E_p > E_n}} Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np} k_{pn}^2 \qquad (3.2.74)$$

and the far-zone asymptote

$$\frac{1}{80\pi^2\varepsilon_0 r^2} \sum_{\substack{n \\ E_p > E_n}} Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np} k_{pn}^6 \qquad (3.2.75)$$

with the energy density in a spherical shell at large r being

$$\frac{1}{20\pi\varepsilon_0} \sum_{\substack{n \\ E_p > E_n}} Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np} k_{pn}^6 . \qquad (3.2.76)$$

The u-integral part of (3.2.72), after expanding the geometric tensors, which is given by (3.A.8) in the Appendix, and orientational averaging, becomes

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$$\frac{1}{160\pi^3\varepsilon_0} \sum_n Q^{pn}_{\lambda\mu} Q^{np}_{\lambda\mu} \int_0^\infty \frac{du\, u^8 e^{-2ur}}{u^2 + k_{np}^2} \, 2k_{np}\left[\frac{1}{u^2 r^2} + \frac{6}{u^3 r^3} + \frac{15}{u^4 r^4} + \frac{18}{u^5 r^5} + \frac{9}{u^6 r^6}\right] \, .$$

$$(3.2.77)$$

After the usual approximations, the far-zone limit is

$$\frac{297\hbar c}{1280\pi^3\varepsilon_0 r^9} \, \theta_{\lambda\mu\lambda\mu}(0) . \qquad\qquad (3.2.78)$$

This completes the evaluation of the electric and magnetic Thompson energy densities correct to second order in the electric dipole, magnetic dipole and electric quadrupole transition moments in the neighbourhood of a molecule using the multipolar Hamiltonian. Each resulting expression for the energy density is composed of two terms; a u-integral term and one applicable only to downward transitions from the initial state. For a molecule in an excited state, the overall far-zone behaviour is dominated by this latter contribution, exhibiting an r^{-2} distance dependence in all cases, corresponding to real photon emission. For a molecule in its ground state, the u-integral term is the sole contribution to the energy density. The energy density is directly observable as an intermolecular energy shift when a test polarisable body is placed in the fields of the source.

In the following Section, the electric and magnetic energy densities due to an electric dipole source are evaluated in the minimal-coupling formalism in the Heisenberg picture. The densities calculated using the total electric field and the magnetic field are shown to be equivalent to those obtained using the multipolar framework.

3.3 ENERGY DENSITY USING MINIMAL-COUPLING MAXWELL FIELDS

In this Section the total electric field and the magnetic field in the proximity of a molecule obtained in the last Chapter in the minimal-coupling approach are used to calculate the energy densities due to an electric dipole source. They are shown to be identical to those derived within the multipolar framework.

Considering terms second order in the sources, the expectation value of the electric energy density for the electromagnetic field in the state where no photons are present, with the molecule in a state $|p\rangle$, is

$$\frac{1}{2}\varepsilon_0 \langle 0;p| e_i^{TOT(1)} e_i^{TOT(1)} + e_i^{(0)} e_i^{TOT(2)} + e_i^{TOT(2)} e_i^{(0)} |p;0\rangle. \qquad (3.3.1)$$

The first term of (3.3.1), the contribution from the product of the first order total electric field of an electric dipole source is exactly the same as the corresponding term in the multipolar calculation (3.2.3), namely

$$\frac{1}{32\pi^2\varepsilon_0} \sum_n \mu_j^{pn}\mu_\ell^{np} k_{pn}^6 \bar{f}_{ij}(k_{pn}r) f_{i\ell}(k_{pn}r) , \qquad (3.3.2)$$

since the first order transverse displacement field was shown in the second Chapter (see (2.3.22)) to be ε_0 times the total electric field. It was also pointed out then, that the second order minimal-coupling Maxwell field operators were not equivalent to their multipolar counterparts. That the minimal-coupling fields quadratic in the sources result in identical expectation values will now be demonstrated explicitly. By taking the diagonal matrix element for the electron state of the second order total electric field due to an electric dipole

source (2.3.37) in complete analogy with that carried out in Section 3.1 for the multipolar fields, results in an operator acting solely in the photon space

$$\langle p|e_i^{TOT(2)}(\vec{r},t;\vec{\mu}\vec{\mu})|p\rangle = \frac{i}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V\varepsilon_0}\right)^{1/2}[e_{\ell}\alpha(0)e^{-i\omega t}A_{\ell i}-\bar{e}_{\ell}\alpha^+(0)e^{i\omega t}\bar{A}_{\ell i}] \tag{3.3.3}$$

with

$$A_{\ell i} = \sum_{n}\frac{\mu_j^{pn}\mu_{\ell}^{np}}{E_{np}-\hbar\omega}\left[k^3F_{ij}(kr) - \frac{k_{np}^4}{k}F_{ij}(k_{np}r)e^{i(k_{pn}+k)ct}\right]$$

$$+ \sum_{n}\frac{\mu_{\ell}^{pn}\mu_j^{np}}{E_{np}+\hbar\omega}\left[k^3F_{ij}(kr) - \frac{k_{pn}^4}{k}F_{ij}(k_{pn}r)e^{-i(k_{pn}-k)ct}\right], \tag{3.3.4}$$

in contrast to $\mathcal{A}_{\ell i}$ (3.1.13) in the multipolar case. Using the mode expansion for the zeroth order electric field and (3.3.3), the last two terms of (3.3.1) are

$$\frac{1}{2}\varepsilon_0\sum_{\vec{k},\lambda}[\langle 0;p|e_i^{TOT(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|e_i^{(0)}|p;0\rangle +$$

$$\langle 0;p|e_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|e_i^{TOT(2)}|p;0\rangle]$$

$$= \frac{1}{8\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V}\right)[e_{\ell}A_{\ell i}\bar{e}_i e^{-i\vec{k}.\vec{r}}+e_i e^{i\vec{k}.\vec{r}}\bar{e}_{\ell}\bar{A}_{\ell i}]. \tag{3.3.5}$$

After performing the polarisation sum and angular integral, the first term of (3.3.5), using (3.3.4) becomes

$$\frac{1}{32\pi^2\varepsilon_0}\frac{\hbar c}{2\pi i}\int_0^{\infty}dkk^3[F_{i\ell}(kr)-\bar{F}_{i\ell}(kr)]A_{\ell i}$$

$$= \frac{-1}{32\pi^2\varepsilon_0}\sum_{n}\mu_j^{pn}\mu_{\ell}^{np}\frac{PV}{2\pi i}\int_0^{\infty}\frac{dkk^3}{k-k_{np}}\left[k^3f_{i\ell}(kr)f_{ij}(kr)e^{2ikr}\right.$$

$$-(k_{np}^4/k)f_{i\ell}(kr)f_{ij}(k_{np}r)e^{ik(r+ct)}e^{ik_{np}(r-ct)}$$

$$+(k_{np}^4/k)\bar{f}_{i\ell}(kr)f_{ij}(k_{np}r)e^{-ik(r-ct)}e^{ik_{np}(r-ct)}\Big]$$

$$+\ \frac{1}{32\pi^2\epsilon_0}\ \sum_{\bar{n}}\ \mu_j^{pn}\mu_\ell^{np}\ \frac{PV}{2\pi i}\ \int_0^\infty\frac{dk\,k^3}{k-k_{pn}}\ \Big[k^3f_{i\ell}(kr)f_{ij}(kr)e^{2ikr}$$

$$-(k_{pn}^4/k)f_{i\ell}(kr)f_{ij}(k_{pn}r)e^{ik(r+ct)}e^{ik_{pn}(r-ct)}$$

$$+(k_{pn}^4/k)\bar{f}_{i\ell}(kr)f_{ij}(k_{pn}r)e^{-ik(r-ct)}e^{ik_{pn}(r-ct)}\Big].$$

$$(3.3.6)$$

Evaluating the integral for downward transitions from p, with $k_{pn} > 0$,

$$\frac{1}{64\pi^2\epsilon_0}\ \sum_{\bar{n}}\ \mu_j^{pn}\mu_\ell^{np}k_{pn}^6\,\bar{f}_{i\ell}(k_{pn}r)f_{ij}(k_{pn}r)$$

$$+\ \frac{1}{64\pi^3\epsilon_0}\ \sum_{\bar{n}}\ \mu_j^{pn}\mu_\ell^{np}\ \int_0^\infty\frac{du\,u^6e^{-2ur}}{u^2+k_{pn}^2}\ 2k_{pn}f_{ij}(iur)f_{i\ell}(iur).\qquad(3.3.7)$$

For $k_{pn} < 0$, the u-integral term remains unchanged while the pole contribution changes sign,

$$\frac{-1}{64\pi^2\epsilon_0}\ \sum_{\bar{n}}\ \mu_j^{pn}\mu_\ell^{np}k_{pn}^6f_{i\ell}(k_{pn}r)\bar{f}_{ij}(k_{pn}r).\qquad(3.3.8)$$

The second term of (3.3.5) is simply the complex conjugate of the first so that the total electric energy density in electric dipole approximation in the minimal-coupling approach, after adding the contribution from the product of the first order fields (3.3.2) is

$$\frac{1}{16\pi^2\epsilon_0}\ \sum_{\substack{\bar{n}\\E_p>E_n}}\ \mu_j^{pn}\mu_\ell^{np}k_{pn}^6\,\bar{f}_{i\ell}(k_{pn}r)f_{ij}(k_{pn}r)\ +$$

$$\frac{1}{32\pi^3\epsilon_0}\ \sum_{\substack{\bar{n}\\ALL\ E_n}}\ \mu_j^{pn}\mu_\ell^{np}\ \int_0^\infty\frac{du\,u^6e^{-2ur}}{u^2+k_{pn}^2}\ 2k_{pn}f_{ij}(iur)f_{i\ell}(iur),\qquad(3.3.9)$$

in agreement with expression (3.2.10) obtained using the electric displacement field of the multipolar framework.

The magnetic energy density in minimal-coupling is determined from

$$\frac{1}{2}\varepsilon_0 c^2 \langle 0;p | \vec{b}^{(1)}.\vec{b}^{(1)} + \vec{b}^{(2)}.\vec{b}^{(0)} + \vec{b}^{(0)}.\vec{b}^{(2)} | p;0 \rangle . \tag{3.3.10}$$

The contribution from the product of the first order electric dipole dependent magnetic field is easily seen to be

$$\frac{1}{32\pi^2\varepsilon_0} \sum_n \mu_j^{pn} \mu_\ell^{np} k_{pn}^6 \bar{g}_{ij}(k_{pn}r) g_{i\ell}(k_{pn}r) \tag{3.3.11}$$

as the minimal-coupling magnetic field linear in the sources (2.3.49) was shown to be identically equal to its multipolar analogue (2.2.55). For the evaluation of the remaining two terms of (3.3.10), the diagonal matrix element over the molecular space is required for the magnetic field quadratic in the electric dipole moments. From (2.3.53),

$$\langle p | b_i^{(2)}(\vec{r},t;\vec{\mu}\vec{\mu}) | p \rangle = \frac{i}{4\pi\varepsilon_0} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} [e_\ell \alpha(0)e^{-i\omega t}B_{\ell i} - \bar{e}_\ell \alpha^+(0)e^{i\omega t}\bar{B}_{\ell i}] \tag{3.3.12}$$

where

$$B_{\ell i} = \sum_n \frac{\mu_j^{pn}\mu_\ell^{np}}{E_{np}-\hbar\omega} \left[k^3 G_{ij}(kr) - \frac{k_{np}^4}{k}G_{ij}(k_{np}r)e^{i(k_{pn}+k)ct}\right]$$

$$+ \sum_n \frac{\mu_\ell^{pn}\mu_j^{np}}{E_{np}+\hbar\omega} \left[k^3 G_{ij}(kr) - \frac{k_{pn}^4}{k}G_{ij}(k_{pn}r)e^{-i(k_{pn}-k)ct}\right], \tag{3.3.13}$$

in contrast to $\mathcal{G}_{\ell i}$ of (3.1.22). Using the mode expansion for the free field and (3.3.12), the contribution to the magnetic energy density arising from the interference of the vacuum and quadratic fields is

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$$\frac{1}{2}\epsilon_0 c^2 \sum_{\vec{k},\lambda} [\langle 0;p|b_i^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(0)}|p;0\rangle +$$

$$\langle 0;p|b_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(2)}|p;0\rangle]$$

$$= \frac{c}{8\pi\epsilon_0} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) [e_\ell B_{\ell i}\bar{b}_i e^{-i\vec{k}\cdot\vec{r}} + b_i e^{i\vec{k}\cdot\vec{r}}e_\ell\bar{B}_{\ell i}]. \tag{3.3.14}$$

Performing the polarisation sum and angular average and using (3.3.13), the first term of (3.3.14) is

$$\frac{-\hbar c}{32\pi^2\epsilon_0} \frac{1}{2\pi i} \int_0^\infty dk k^3 [G_{i\ell}(kr)+\bar{G}_{i\ell}(kr)]B_{\ell i}$$

$$= \frac{1}{32\pi^2\epsilon_0} \sum_n \mu_j^{pn}\mu_\ell^{np} \frac{PV}{2\pi i} \int_0^\infty \frac{dk k^3}{k-k_{np}} \left[k^3 g_{i\ell}(kr)g_{ij}(kr)e^{2ikr}\right.$$

$$-(k_{np}^4/k)g_{i\ell}(kr)g_{ij}(k_{np}r)e^{ik(r+ct)}e^{ik_{np}(r-ct)}$$

$$\left.-(k_{np}^4/k)\bar{g}_{i\ell}(kr)g_{ij}(k_{np}r)e^{-ik(r-ct)}e^{ik_{np}(r-ct)}\right]$$

$$\frac{-1}{32\pi^2\epsilon_0} \sum_n \mu_j^{pn}\mu_\ell^{np} \frac{PV}{2\pi i} \int_0^\infty \frac{dk k^3}{k-k_{pn}} \left[k^3 g_{i\ell}(kr)g_{ij}(kr)e^{2ikr}\right.$$

$$-(k_{pn}^4/k)g_{i\ell}(kr)g_{ij}(k_{pn}r)e^{ik(r+ct)}e^{ik_{pn}(r-ct)}$$

$$\left.-(k_{pn}^4/k)\bar{g}_{i\ell}(kr)g_{ij}(k_{pn}r)e^{-ik(r-ct)}e^{ik_{pn}(r-ct)}\right]. \tag{3.3.15}$$

Evaluating the integral subject to $k_{pn} < 0$, corresponding to upward transitions from $|p\rangle$,

$$\frac{-1}{64\pi^2\epsilon_0} \sum_n \mu_j^{pn}\mu_\ell^{np}k_{pn}^6 g_{i\ell}(k_{pn}r)\bar{g}_{ij}(k_{pn}r) +$$

$$\frac{\hbar c}{64\pi^3\epsilon_0} \int_0^\infty du u^6 e^{-2ur}\alpha_{j\ell}(iu)g_{ij}(iur)g_{i\ell}(iur) \tag{3.3.16}$$

is obtained, while for $k_{pn} > 0$, the pole term changes sign,

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$$\frac{1}{64\pi^2\varepsilon_0} \sum_{\bar{n}} \mu_j^{pn}\mu_{\ell}^{np}k_{pn}^6\,\bar{g}_{i\ell}(k_{pn}r)g_{ij}(k_{pn}r) \qquad (3.3.17)$$

with the u-integral remaining unaltered. Evaluating the second term of (3.3.14), which is the complex conjugate of the first and adding the part from the fields linear in the sources, the total magnetic energy density is

$$\frac{1}{16\pi^2\varepsilon_0} \sum_{\substack{\bar{n} \\ E_p > E_n}} \mu_j^{pn}\mu_{\ell}^{np}k_{pn}^6\,\bar{g}_{ij}(k_{pn}r)g_{i\ell}(k_{pn}r)$$

$$+ \frac{1}{32\pi^3\varepsilon_0} \sum_{\substack{\bar{n} \\ ALL\ E_n}} \mu_j^{pn}\mu_{\ell}^{np} \int_0^\infty \frac{duu^6e^{-2ur}}{u^2 + k_{np}^2}\ 2k_{np}g_{ij}(iur)g_{i\ell}(iur)\ , \qquad (3.3.18)$$

in agreement with the multipolar result (3.2.52).

Despite the separation of the minimal- and multipolar-coupling Hamiltonians being different in both cases as shown in Chapter 1, leading to different Heisenberg equations of motion for the operators, although the first order fields were seen to be identical in both formalisms, identical matrix elements are obtained for the electromagnetic energy density. This is a direct consequence of the two forms of Hamiltonian being equivalent, thus giving equal matrix elements "on the energy shell".

The remainder of this Chapter is devoted to the calculation of the Poynting vector in both formalisms and its relation to the transition rate for spontaneous emission.

3.4 ENERGY FLUX USING MULTIPOLAR MAXWELL FIELDS

The quantum mechanical Hermitian operator for the Poynting vector $\vec{S}(\vec{r},t)$ is [31,33]

$$\vec{S}(\vec{r},t) = \frac{1}{2}\varepsilon_0 c^2 \left[\vec{e}^{TOT}(\vec{r},t) \times \vec{b}(\vec{r},t) - \vec{b}(\vec{r},t) \times \vec{e}^{TOT}(\vec{r},t) \right]. \qquad (3.4.1)$$

As noted earlier, for a neutral molecule, ε_0 times the total electric field is equal to the transverse displacement vector outside the source, so that in the multipolar formalism molecules couple to the displacement field and not to the electric field as in the minimal-coupling framework. Thus

$$S_i(\vec{r},t) = \frac{c^2}{2} \varepsilon_{ijk} \left[d_j^\perp(\vec{r},t) b_k(\vec{r},t) + b_k(\vec{r},t) d_j^\perp(\vec{r},t) \right]. \qquad (3.4.2)$$

The multipolar electric displacement and magnetic fields in the Heisenberg picture obtained in Section 2.2 therefore provide a suitable basis for the calculation of the energy flux from a molecule in an excited state. The Poynting vector can, of course, still be evaluated in the minimal-coupling version of QED by utilising the total electric and magnetic fields in the neighbourhood of a molecule derived in Section 2.3. This is carried out in the following Section where the equivalence of matrix elements for the process obtained from both methods is demonstrated for the electric dipole case.

The expectation value of the Poynting vector for the radiation field in the vacuum state with the molecule in an excited state $|p\rangle$, after expansion of the field in successive powers of the multipole moments, is

$$\langle 0;p|S_i(\vec{r},t)|p;0\rangle$$

$$= \frac{c^2}{2}\varepsilon_{ijk}\langle 0;p|(d_j^{(0)}+d_j^{(1)}+d_j^{(2)}+\ldots)(b_k^{(0)}+b_k^{(1)}+b_k^{(2)}+\ldots)|p;0\rangle + c.c.$$

$$\simeq \frac{c^2}{2}\varepsilon_{ijk}\langle 0;p|d_j^{(1)}b_k^{(1)}+d_j^{(2)}b_k^{(0)}+d_j^{(0)}b_k^{(2)}|p;0\rangle + c.c. \qquad (3.4.3)$$

concentrating only on terms second order in the transition moments. As for the calculation of the electromagnetic energy density, the individual contribution to the energy flow arising from the pure electric dipole dependent fields, the mixed electric-magnetic dipole dependent fields, pure magnetic dipole dependent fields etc., for all possible permuatations up to and including the electric quadrupole moment, are evaluated.

Beginning with the contribution to the Poynting vector from the electric dipole dependent terms of the electromagnetic field, the first term of (3.4.3) using (2.2.34) and (2.2.55), is

$$\frac{c^2}{2}\varepsilon_{ijk}\langle 0;p|d_j^{(1)}(\vec{\mu})b_k^{(1)}(\vec{\mu})+b_k^{(1)}(\vec{\mu})d_j^{(1)}(\vec{\mu})|p;0\rangle$$

$$= \frac{c^2}{2}\varepsilon_{ijk}\sum_n\left[\langle p|d_j^{(1)}|n\rangle\langle n|b_k^{(1)}|p\rangle + \langle p|b_k^{(1)}|n\rangle\langle n|d_j^{(1)}|p\rangle\right]$$

$$= \frac{c}{32\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_n\mu_\ell^{pn}\mu_m^{np}k_{pn}^6\left[\bar{f}_{j\ell}(k_{pn}r)g_{km}(k_{pn}r)+\bar{g}_{km}(k_{pn}r)f_{j\ell}(k_{pn}r)\right].$$

$$(3.4.4)$$

Using the definitions of the tensor fields $f_{ij}(kr)$ and $g_{ij}(kr)$ as given by (2.A.1) and (2.A.7) from the Appendix to Chapter 2, the terms of (3.4.4) can be simplified to give

$$\frac{c}{16\pi^2\varepsilon_0 r^2}\varepsilon_{ijk}\varepsilon_{kmn}\hat{r}_n\sum_n\mu_\ell^{pn}\mu_m^{np}k_{pn}^4(\delta_{j\ell}-\hat{r}_j\hat{r}_\ell). \qquad (3.4.5)$$

After orientational averaging and contracting the tensors, the contribution to $S_i(\vec{r},t)$ from the product of the first order fields is

$$\frac{c}{24\pi^2\epsilon_0 r^2} \sum_n |\vec{\mu}^{pn}|^2 k_{pn}^4 \hat{r}_i \; . \tag{3.4.6}$$

The contribution to the rate of energy loss out of a sphere at any radius is

$$4\pi r^2 \hat{r}_i \langle S_i(\vec{r},t)\rangle = \frac{c}{6\pi\epsilon_0} \sum_n |\vec{\mu}^{pn}|^2 k_{pn}^4 \tag{3.4.7}$$

with the summation including both upward and downward transitions from $|p\rangle$. The r^{-2} dependence on separation distance in (3.4.6) is consistent with the conservation of energy requirement that the energy flow through a spherical surface be independent of the radius, as seen in (3.4.7).

The contribution to the Poynting vector from the interference of the zeroth order field with the quadratic field, remembering that both these fields are linear in the photon creation and destruction operators, using (3.1.1) and (3.1.7), is

$$\frac{c^2}{2} \epsilon_{ijk} \sum_{\vec{k},\lambda} \left[\langle 0;p|d_j^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(2)}(\overrightarrow{\mu\mu})|p;0\rangle + \right.$$

$$\left. \langle 0;p|d_j^{(2)}(\overrightarrow{\mu\mu})|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle \right] + \text{c.c.}$$

$$= \sum_{\vec{k},\lambda} \frac{\hbar k c^2}{16\pi\epsilon_0 V} \epsilon_{ijk}[e_j e^{i\vec{k}\cdot\vec{r}}\bar{e}_m \mathcal{T}_{mk} + e_m \mathcal{A}_{mj}\bar{b}_k e^{-i\vec{k}\cdot\vec{r}}] + \text{c.c.} \tag{3.4.8}$$

The first term of (3.4.8) and its complex conjugate, after performing the polarisation sum and angular average using (2.2.19) and (2.2.24) respectively, and the definition of the tensor field $\mathcal{T}_{mk}$ (3.1.22), is

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$$\frac{hc^2}{32\pi^2\varepsilon_0}\,\epsilon_{ijk}\,\frac{1}{2\pi i}\int_0^\infty dk\,k^3[F_{jm}(kr)-\bar{F}_{jm}(kr)]\bar{\mathcal{G}}_{mk}+\text{c.c.}$$

$$=\frac{c}{32\pi^2\varepsilon_0}\,\epsilon_{ijk}\sum_n \mu_\ell^{pn}\mu_m^{np}\,\frac{PV}{2\pi i}\int_0^\infty dk\,k^3\times$$

$$\left\{\frac{[F_{jm}(kr)-\bar{F}_{jm}(kr)][k^3\bar{G}_{k\ell}(kr)-k_{np}^3\bar{G}_{k\ell}(k_{np}r)e^{-i(k_{pn}+k)ct}]}{(k_{np}-k)}+\right.$$

$$\left.\frac{[F_{jm}(kr)-\bar{F}_{jm}(kr)][k^3\bar{G}_{k\ell}(kr)-k_{pn}^3\bar{G}_{k\ell}(k_{pn}r)e^{i(k_{pn}-k)ct}]}{(k_{np}+k)}\right\}+\text{c.c.}$$

$$=\frac{-c}{32\pi^2\varepsilon_0}\,\epsilon_{ijk}\sum_n\mu_\ell^{pn}\mu_m^{np}\frac{PV}{2\pi i}\int_0^\infty\frac{dk\,k^3}{k+k_{pn}}\Big[-k^3\bar{f}_{jm}(kr)\bar{g}_{k\ell}(kr)e^{-2ikr}$$

$$-k_{np}^3 f_{jm}(kr)\bar{g}_{k\ell}(k_{np}r)e^{ik(r-ct)}e^{ik_{pn}(r-ct)}$$

$$+k_{np}^3\bar{f}_{jm}(kr)\bar{g}_{k\ell}(k_{np}r)e^{-ik(r+ct)}e^{ik_{pn}(r-ct)}\Big]$$

$$+\frac{c}{32\pi^2\varepsilon_0}\,\epsilon_{ijk}\sum_n\mu_\ell^{pn}\mu_m^{np}\frac{PV}{2\pi i}\int_0^\infty\frac{dk\,k^3}{k-k_{pn}}\Big[-k^3\bar{f}_{jm}(kr)\bar{g}_{k\ell}(kr)e^{-2ikr}$$

$$-k_{pn}^3 f_{jm}(kr)\bar{g}_{k\ell}(k_{pn}r)e^{ik(r-ct)}e^{-ik_{pn}(r-ct)}$$

$$+k_{pn}^3\bar{f}_{jm}(kr)\bar{g}_{k\ell}(k_{pn}r)e^{-ik(r+ct)}e^{-ik_{pn}(r-ct)}\Big]$$

$$+\text{c.c.}\qquad\qquad(3.4.9)$$

where index manipulation has been used to eliminate the terms without an exponential dependence. The k-integration involved in the Poynting vector can be evaluated exactly for the time independent part by extending the integration limits to $(-\infty,\infty)$. This results in the pole contributions

$$\frac{-c}{64\pi^2\epsilon_0} \epsilon_{ijk} \sum_n \mu_\ell^{pn}\mu_m^{np}k_{pn}^6 \bar{f}_{jm}(k_{pn}r)g_{k\ell}(k_{pn}r) \ , \ k_{pn} < 0$$

(3.4.10)

$$\frac{c}{64\pi^2\epsilon_0} \epsilon_{ijk} \sum_n \mu_\ell^{pn}\mu_m^{np}k_{pn}^6 f_{jm}(k_{pn}r)\bar{g}_{k\ell}(k_{pn}r) \ , \ k_{pn} > 0.$$

Such an extension of the limits however, is not possible in the determination of the energy densities occurring earlier. Therefore there are no terms involving a u-integral occurring in (3.4.10). Evaluating the remaining terms of (3.4.8) in a manner identical to that illustrated above, the contribution from the vacuum and second order fields is

$$\frac{c}{32\pi^2\epsilon_0} \epsilon_{ijk} \sum_n (\text{sgn } k_{pn})\mu_\ell^{pn}\mu_m^{np}k_{pn}^6 \left[\bar{f}_{j\ell}(k_{pn}r)g_{km}(k_{pn}r)+\bar{g}_{km}(k_{pn}r)f_{j\ell}(k_{pn}r)\right].$$

(3.4.11)

The total contribution to the Poynting vector from the electric dipole dependent fields [31,33] is given by the sum of (3.4.4) and (3.4.11),

$$\frac{c}{16\pi^2\epsilon_0} \epsilon_{ijk} \sum_n \mu_\ell^{pn}\mu_m^{np}k_{pn}^6 \left[\bar{f}_{j\ell}(k_{pn}r)g_{km}(k_{pn}r)+\bar{g}_{km}(k_{pn}r)f_{j\ell}(k_{pn}r)\right]$$
$$E_p>E_n$$

$$= \frac{c}{3\pi\epsilon_0} \sum_n |\vec{\mu}^{pn}|^2 k_{pn}^4 \ .$$
$$E_p>E_n$$

(3.4.12)

It is seen that the contribution from upward transitions from $|p\rangle$ comes with opposite sign to the term from the product of the fields linear in the moments, resulting in complete cancellation; downward transition contributions however, are identical to (3.4.4) and consequently double in magnitude, as given by (3.4.12). The adding and cancelling of pole contributions from the interference of the second order field with the

vacuum field, with terms arising from the product of the first order fields is, as in the energy density calculations carried out in the previous Sections, a characteristic feature in the calculation of the Poynting vector. The rate of flow of electromagnetic energy from a radiating electric dipole source (3.4.12) can also be calculated from the spontaneous decay rate of a molecule in an excited state. By determining the matrix element for the spontaneous emission of a photon from an excited molecule and using the Fermi golden rule, the transition rate can be used to determine the power loss through a spherical surface by spontaneous emission, leading directly to (3.4.12). The importance of the inclusion of the quadratic field is evident since the Poynting energy flow from the first order fields gives only one half of the spontaneous power rate. Including the second order field doubles the flow, resulting in the equivalence of the spontaneous rate and the Poynting vector flow.

Having calculated the leading contribution to the energy flow, that arising from the electric dipole dependent fields above, the next contribution to be evaluated is from the mixed electric-magnetic dipole dependent radiation field. The method outlined in the first example is followed throughout the rest of this Section.

The contribution from the product of the first order fields to the Poynting vector energy flow from a chiral molecule is, using (2.2.34) and (2.2.55)

$$\frac{c^2}{2} \varepsilon_{ijk} \sum_n \left[\langle p|d_j^{(1)}(\vec{\mu})|n\rangle\langle n|b_k^{(1)}(\vec{m})|p\rangle + \langle p|b_k^{(1)}(\vec{m})|n\rangle\langle n|d_j^{(1)}(\vec{\mu})|p\rangle \right.$$
$$\left. + \langle p|d_j^{(1)}(\vec{m})|n\rangle\langle n|b_k^{(1)}(\vec{\mu})|p\rangle + \langle p|b_k^{(1)}(\vec{\mu})|n\rangle\langle n|d_j^{(1)}(\vec{m})|p\rangle \right]$$

$$= \frac{1}{32\pi^2\varepsilon_0} \varepsilon_{ijk} \sum_{n} \mu_\ell^{pn} m_m^{np} k_{pn}^6 \left[\left(\overline{f}_{j\ell}(k_{pn}r) f_{\ell m}(k_{pn}r) - \overline{f}_{\ell m}(k_{pn}r) f_{j\ell}(k_{pn}r) \right) + \right.$$
$$\left. \left(\overline{g}_{j\ell}(k_{pn}r) g_{\ell m}(k_{pn}r) - \overline{g}_{\ell m}(k_{pn}r) g_{j\ell}(k_{pn}r) \right) \right].$$

$$(3.4.13)$$

The above vanishes for an isotropic chiral source. The contribution from the free and second order fields, evaluated from

$$\frac{c^2}{2} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left[\langle 0;p|d_j^{(0)}|p;\vec{k},\lambda\rangle \langle\vec{k},\lambda;p|b_\ell^{(2)}(\vec{\mu m})|p;0\rangle + \right.$$
$$\left. \langle 0;p|d_j^{(2)}(\vec{\mu m})|p;\vec{k},\lambda\rangle \langle\vec{k},\lambda;p|b_\ell^{(0)}|p;0\rangle \right] + c.c.$$

$$= \frac{1}{8\pi\varepsilon_0} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right) \left[e_j e^{i\vec{k}\cdot\vec{r}} (\overline{b}_\ell \overline{\mathcal{X}}_{\ell k} + \overline{e}_\ell \overline{\mathcal{F}}_{\ell k}) + (b_\ell \mathcal{B}_{\ell j} + e_\ell \mathcal{E}_{\ell j}) \overline{b}_\ell e^{-i\vec{k}\cdot\vec{r}} \right] + c.c.$$

$$= \frac{1}{16\pi^2\varepsilon_0} \varepsilon_{ijk} \sum_{\substack{n \\ E_p > E_n}} \mu_\ell^{pn} m_m^{np} k_{pn}^6 \left[\left(\overline{f}_{j\ell}(k_{pn}r) f_{\ell m}(k_{pn}r) - \overline{f}_{\ell m}(k_{pn}r) f_{j\ell}(k_{pn}r) \right) + \right.$$
$$\left. \left(\overline{g}_{j\ell}(k_{pn}r) g_{\ell m}(k_{pn}r) - \overline{g}_{\ell m}(k_{pn}r) g_{j\ell}(k_{pn}r) \right) \right].$$

$$(3.4.14)$$

also vanishes for an isotropic source.

The next contribution to the Poynting vector comes from the magnetic dipole dependent Maxwell fields. Using the fields linear in the sources (2.2.34) and (2.2.55), the contribution from the product of the first order fields, is

$$\frac{c^2}{2} \varepsilon_{ijk} \sum_{n} \left[\langle p|d_j^{(1)}(\vec{m})|n\rangle \langle n|b_\ell^{(1)}(\vec{m})|p\rangle + \langle p|b_\ell^{(1)}(\vec{m})|n\rangle \langle n|d_j^{(1)}(\vec{m})|p\rangle \right]$$

$$= \frac{-1}{32\pi^2\varepsilon_0 c} \varepsilon_{ijk} \sum_{n} m_\ell^{pn} m_m^{np} k_{pn}^6 \left[\overline{g}_{j\ell}(k_{pn}r) f_{\ell m}(k_{pn}r) + \overline{f}_{\ell m}(k_{pn}r) g_{j\ell}(k_{pn}r) \right]$$

$$(3.4.15)$$

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which becomes, after simplifying the geometric tensors, whose definitions were given in the Appendix to Chapter 2,

$$\frac{-1}{16\pi^2 \varepsilon_0 cr^2} \varepsilon_{ijk}\varepsilon_{j\ell s}\hat{r}_s \sum_n m_\ell^{pn} m_m^{np} k_{pn}^4 \alpha_{\ell m} \tag{3.4.16}$$

which after rotational averaging results in

$$\frac{1}{24\pi^2 \varepsilon_0 cr^2} \sum_n |\vec{m}^{pn}|^2 k_{pn}^4 \hat{r}_i \ . \tag{3.4.17}$$

The contribution from the zeroth and quadratic fields is

$$\frac{c^2}{2} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left[\langle 0;p|d_j^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(2)}|p;0\rangle + \right.$$

$$\left. \langle 0;p|d_j^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle \right] + c.c.$$

$$= \frac{1}{8\pi\varepsilon_0} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) \left[e_j e^{i\vec{k}\cdot\vec{r}} \bar{b}_\ell \bar{m}_{\ell k} - b_\ell \mathcal{D}_{\ell j} \bar{b}_k e^{-i\vec{k}\cdot\vec{r}} \right] + c.c. \tag{3.4.18}$$

where use has been made of the free field (2.2.15), and (3.1.3) and (3.1.9). On evaluating the four terms above, it is found that (3.4.18) becomes

$$\frac{-1}{32\pi^2 \varepsilon_0 c} \varepsilon_{ijk} \sum_n m_\ell^{pn} m_m^{np} k_{pn}^6 (sgnk_{pn}) \left[g_{j\ell}(k_{pn}r)\bar{f}_{km}(k_{pn}r) + \bar{g}_{j\ell}(k_{pn}r)f_{km}(k_{pn}r) \right]. \tag{3.4.19}$$

Comparing (3.4.19) with the contribution from the product of the first order fields (3.4.15), it is seen that when $k_{pn} < 0$, corresponding to upward transitions from $|p\rangle$, the two terms come with opposite sign and cancel on addition. Only downward transitions, for which $k_{pn} > 0$,

contribute to the Poynting energy flow, so that

$$S_i(\vec{r},t) = \frac{-1}{8\pi^2\varepsilon_0 c r^2}\ \varepsilon_{ijk}\varepsilon_{j\ell s}\hat{r}_s\ \sum_{E_p > E_n}\ m_\ell^{pn} m_m^{np} k_{pn}^4 \alpha_{\ell m}\ ,$$ (3.4.20)

from which the energy flow across a spherical surface is calculated as

$$\frac{1}{3\pi\varepsilon_0 c}\ \sum_{E_p > E_n}\ |\vec{m}^{pn}|^2 k_{pn}^4$$ (3.4.21)

which, as expected, is independent of the radius of the shell. The flux (3.4.21) is exactly equal to the power loss from a molecule in an excited state undergoing spontaneous emission.

The rate of flow of electromagnetic energy from an electric dipole-quadrupole source is the next contribution to the Poynting vector to be examined. Using the electric dipole and quadrupole dependent terms of the radiation fields (2.2.34) and (2.2.55), the term from the product of the first order fields is

$$\frac{c^2}{2}\varepsilon_{ijk}\ \sum_n\left[\langle p|d_j^{(1)}(\vec{\mu})|n\rangle\langle n|b_k^{(1)}(\vec{Q})|p\rangle\ +\ \langle p|d_j^{(1)}(\vec{Q})|n\rangle\langle n|b_k^{(1)}(\vec{\mu})|p\rangle\right]\ +\ c.c.$$

$$= \frac{c}{32\pi^2\varepsilon_0}\ \varepsilon_{ijk}\ \sum_n\ \mu_\ell^{pn} Q_{mn}^{np} k_{pn}^7\left[i\left(\bar{j}_{\ell mn}(k_{pn}r)f_{j\ell}(k_{pn}r)-\bar{f}_{j\ell}(k_{pn}r)j_{\ell mn}(k_{pn}r)\right)\ - \right.$$

$$\left.\left(\bar{h}_{jmn}(k_{pn}r)g_{k\ell}(k_{pn}r)+\bar{g}_{k\ell}(k_{pn}r)h_{jmn}(k_{pn}r)\right)\right]$$
(3.4.22)

which after expanding the geometric tensors and averaging, gives zero. The contribution from the source independent field and the quadratic field, determined from

$$\frac{c^2}{2} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left[\langle 0;p|d_j^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(2)}|p;0\rangle + \right.$$

$$\left. \langle 0;p|d_j^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle \right] + c.c.$$

$$= \frac{-ic^2}{8\pi\varepsilon_0} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) \left[e_j e^{i\vec{k}\cdot\vec{r}} (\bar{e}_m k_\ell \mathcal{N}_{\ell km} + \bar{e}_\ell \mathcal{F}_{\ell k}) + (e_m k_\ell \mathcal{E}_{\ell m j} + ie_\ell \mathcal{F}_{\ell j}) \bar{b}_k e^{-i\vec{k}\cdot\vec{r}} \right]$$

$$+ c.c. \qquad (3.4.23)$$

similarly disappears, as expected for dipole-quadrupole coupling.

The next contribution to the Poynting vector, that arising from the magnetic dipole-electric quadrupole interaction term, also vanishes on averaging. The contribution from the product of the first order fields for an oriented source is given by

$$\frac{c^2}{2} \varepsilon_{ijk} \sum_n \left[\langle p|d_j^{(1)}(\vec{m})|n\rangle\langle n|b_k^{(1)}(\vec{Q})|p\rangle + \langle p|d_j^{(1)}(\vec{Q})|n\rangle\langle n|b_k^{(1)}(\vec{m})|p\rangle \right] + c.c.$$

$$= \frac{1}{32\pi^2\varepsilon_0} \varepsilon_{ijk} \sum_n m_\ell^{pn} Q_{mn}^{np} k_{pn}^7 \left[i\left(\bar{g}_{j\ell}(k_{pn}r) j_{\ell mn}(k_{pn}r) + \bar{j}_{\ell mn}(k_{pn}r) g_{j\ell}(k_{pn}r)\right) + \right.$$

$$\left. \left(\bar{h}_{jmn}(k_{pn}r) f_{k\ell}(k_{pn}r) - \bar{f}_{k\ell}(k_{pn}r) h_{jmn}(k_{pn}r)\right) \right],$$

$$(3.4.24)$$

while the contribution from the interference of the vacuum and second order fields is found from

$$\frac{c^2}{2} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left[\langle 0;p|d_j^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(2)}|p;0\rangle + \right.$$

$$\left. \langle 0;p|d_j^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle \right] + c.c.$$

$$= \frac{-ic}{8\pi\varepsilon_0} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) \left[e_j e^{i\vec{k}\cdot\vec{r}} (\bar{e}_m k_\ell \bar{\mathcal{Q}}_{\ell mk} + \bar{b}_\ell \bar{\mathcal{R}}_{\ell k}) + (e_m k_\ell \mathcal{E}_{\ell m j} + ib_\ell \mathcal{H}_{\ell j}) \bar{b}_k e^{-i\vec{k}\cdot\vec{r}} \right]$$

$$+ c.c. \qquad (3.4.25)$$

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on using (3.1.5) and (3.1.11), and is simply twice (3.4.24) for downward

transitions and zero for upward transitions from $|p\rangle$.

The last non-zero contribution to be considered is that arising

from the electric quadrupole coupling term, with the product of the

first order fields giving

$$\frac{c^2}{2}\,\varepsilon_{ijk}\sum_{n}\left[\langle p|d_j^{(1)}(\vec{Q})|n\rangle\langle n|b_k^{(1)}(\vec{Q})|p\rangle + \langle p|b_k^{(1)}(\vec{Q})|n\rangle\langle n|d_j^{(1)}(\vec{Q})|p\rangle\right]$$

$$= \frac{ic}{32\pi^2\varepsilon_0}\,\varepsilon_{ijk}\sum_{n}Q_{\ell m}^{pn}Q_{np}^{np}k_{pn}^8\left(\bar{h}_{j\ell m}(k_{pn}r)j_{knn}(k_{pn}r)-\bar{j}_{knn}(k_{pn}r)h_{j\ell m}(k_{pn}r)\right).$$

$$(3.4.26)$$

Evaluating the geometrical tensor product occurring in parenthesis above

using (2.A.12) and (2.A.16) results in

$$\frac{c}{16\pi^2\varepsilon_0 r^2}\,\varepsilon_{ijk}\varepsilon_{knn}\sum_{n}Q_{\ell m}^{pn}Q_{nn}^{np}k_{pn}^6\alpha_{jm}\hat{r}_\ell\hat{r}_s\hat{r}_n\,. \qquad (3.4.27)$$

Rotational averaging and contracting the tensors results in

$$\frac{c}{80\pi^2\varepsilon_0 r^2}\sum_{n}Q_{\lambda\mu}^{pn}Q_{\lambda\mu}^{np}k_{pn}^6\hat{r}_i\,. \qquad (3.4.28)$$

The contribution from the free field and the second order field is

determined from,

$$\frac{c^2}{2}\,\varepsilon_{ijk}\sum_{\vec{k},\lambda}\left[\langle 0;p|d_j^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(2)}|p;0\rangle +\right.$$

$$\left.\langle 0;p|d_j^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle\right] + c.c.$$

$$= \frac{c^2}{8\pi\varepsilon_0}\,\varepsilon_{ijk}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)\left[e_j e^{i\vec{k}\cdot\vec{r}}\bar{e}_m k_\ell\mathcal{P}_{\ell mk}-ie_m k_\ell\mathcal{P}_{\ell mj}\bar{b}_k e^{-i\vec{k}\cdot\vec{r}}\right] + c.c. \qquad (3.4.29)$$

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Evaluating the four terms above in the now familiar way, the Poynting vector from a quadrupole source is

$$S_i(\vec{r},t) = \frac{ic}{16\pi^2\varepsilon_0} \varepsilon_{ijk} \sum_{\substack{n \\ E_p > E_n}} Q^{pn}_{\ell m} Q^{np}_{n\pi} k^8_{pn} \left[\bar{h}_{j\ell m}(k_{pn}r) j_{kn\pi}(k_{pn}r) \right.$$

$$\left. -\bar{j}_{kn\pi}(k_{pn}r) h_{j\ell m}(k_{pn}r) \right]$$

$$= \frac{c}{40\pi^2\varepsilon_0 r^2} \sum_{\substack{n \\ E_p > E_n}} Q^{pn}_{\lambda\mu} Q^{np}_{\lambda\mu} k^6_{pn} \hat{r}_i \; , \qquad\qquad (3.4.30)$$

with only downward transitions contributing to the flow. The energy flux through a spherical surface is then

$$\frac{c}{10\pi\varepsilon_0} \sum_{\substack{n \\ E_p > E_n}} Q^{pn}_{\lambda\mu} Q^{np}_{\lambda\mu} k^6_{pn} \; , \qquad\qquad (3.4.31)$$

and is independent of the radius of the shell and is in agreement with the conventional calculation of the spontaneous power across a spherical surface using the Fermi rule transition rate for spontaneous emission.

The final contribution to the Poynting vector to be examined under the approximations considered is that arising from the diamagnetic coupling term. The electric displacement and magnetic fields due to the diamagnetic interaction were obtained at the end of Section 2.2. Recalling that both these fields are quadratic in the electric charge, there are no first order diamagnetic correction terms. Thus

$$S_i^{DIA} = \frac{c^2}{2} \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left[\langle 0;p|d_j^{DIA}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle + \right.$$

$$\left. \langle 0;p|d_j^{(0)}|p;\vec{k},\lambda\rangle\langle p;\vec{k},\lambda|b_k^{DIA}|p;0\rangle \right] + c.c.$$

$$= \frac{e^2}{16\pi\varepsilon_0 m} \varepsilon_{ijk}\varepsilon_{\ell ms}\varepsilon_{nps} \sum_{\substack{\vec{k},\lambda \\ p;n}} \left(\frac{\hbar k}{2V}\right) k^3 q_\ell^{pn} q_n^{np} b_n \bar{b}_\ell e^{-i\vec{k}\cdot\vec{r}} g_{jm}(kr) e^{ikr}$$

$$\frac{-e^2}{16\pi\varepsilon_0 m} \varepsilon_{ijk}\varepsilon_{\ell ms}\varepsilon_{nps} \sum_{\substack{\vec{k},\lambda \\ p;n}} \left(\frac{\hbar k}{2V}\right) k^3 q_\ell^{pn} q_n^{np} e_j \bar{b}_n e^{i\vec{k}\cdot\vec{r}} f_{\ell m}(kr) e^{-ikr} + H.C.$$

$$(3.4.32)$$

using (2.2.69) and (2.2.70). Converting the four terms of (3.4.32) into k-integrals, after carrying out the polarisation sum and angular average, the four terms vanish on addition.

This completes the evaluation of the Poynting vector from a radiating multipole source correct up to terms quadratic in the electric quadrupole coupling term in the multipolar formalism of QED. It has been shown that the only non-zero contributions to the energy flow arise from sources possessing only electric dipole transition moments, or only magnetic dipole or only electric quadrupole transition moments, with contributions from isotropic mixed multipole moments, bilinear in the sources, vanishing.

In all cases the Poynting vector exhibits an inverse square dependence on distance, as expected for an excited source undergoing real photon emission. The r^{-2} dependence is consistent with the local conservation of energy requirement that the energy flow across a spherical surface be independent of the radius. The quantum mechanical rate of spontaneous decay of an excited molecule from which the power loss through a spherical surface is determined, is in agreement with the rate of energy loss by radiation from an oscillating multipole source as calculated by the Poynting vector. It has been confirmed that only the spontaneous allowed transitions contribute to the total power. The importance of the inclusion of the electromagnetic radiation fields second order in the transition moments in the calculation of the

Poynting vector has also been demonstrated. Use of the first order

fields alone gives only one-half of the spontaneous power. Adding the

contribution from the quadratic fields doubled the flow, resulting in

the equality of the spontaneous rate and Poynting energy flow to quantum

fields of second order.

3.5 ENERGY FLUX USING MINIMAL-COUPLING MAXWELL FIELDS

In the previous Section the rate of flow of electromagnetic energy

from a set of oscillating multipole moments was calculated in the

multipolar framework using the electric displacement and magnetic fields

of Section 2.2. In this Section the Maxwell field in the neighbourhood

of a molecule obtained using the minimal-coupling approach, is used to

demonstrate the equivalence of the expectation value for the Poynting

vector with that obtained using the multipolar formalism in the electric

dipole approximation.

In the minimal-coupling approach, the Poynting vector is given by

$$
S_i(\vec{r},t) = \frac{1}{2}\varepsilon_0 c^2 \varepsilon_{ijk}\left[e_j^{TOT}(\vec{r},t)b_k(\vec{r},t) + b_k(\vec{r},t)e_j^{TOT}(\vec{r},t)\right]
$$

$$
\simeq \frac{1}{2}\varepsilon_0 c^2 \varepsilon_{ijk}\left[e_j^{TOT(1)}(\vec{\mu})b_k^{(1)}(\vec{\mu}) + e_j^{TOT(2)}(\vec{\mu}\vec{\mu})b_k^{(0)} + e_j^{(0)}b_k^{(2)}(\vec{\mu}\vec{\mu})\right] + c.c.
$$

$$(3.5.1)$$

concentrating only on terms second order in the electric dipole moments.

The first term above, that arising from the product of the fields linear

in the sources is given by (3.4.4) as the first order minimal-coupling

Maxwell fields are equivalent to their multipolar counterparts. Using

the mode expansions for the zeroth order fields, (3.3.3) and (3.3.12),

the second and third terms above become

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$$\frac{1}{2}\varepsilon_0 c^2 \varepsilon_{ijk} \sum_{\vec{k},\lambda} \left[\langle 0;p|e_j^{TOT(2)}(\overrightarrow{\mu\mu})|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle \right.$$

$$\left. \langle 0;p|e_j^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(2)}(\overrightarrow{\mu\mu})|p;0\rangle \right] + c.c.$$

$$= \frac{c^2}{8\pi\varepsilon_0}\varepsilon_{ijk}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)[e_m A_{mj}\overline{b}_k e^{-i\vec{k}\cdot\vec{r}} + e_j e^{i\vec{k}\cdot\vec{r}}\overline{e}_m\overline{B}_{mk}] + c.c. \qquad (3.5.2)$$

The first term after performing the sum over polarisation, angular average and using (3.3.4) is

$$\frac{-\hbar c^2}{32\pi^2\varepsilon_0}\varepsilon_{ijk}\frac{1}{2\pi i}\int_0^\infty dk k^3[G_{km}(kr)+\overline{G}_{km}(kr)]A_{mj}$$

$$= \frac{c}{32\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_{\tilde{n}}\mu_\ell^{pn}\mu_m^{np}\frac{PV}{2\pi i}\int_0^\infty\frac{dk k^3}{k-k_{np}}\left[k^3 g_{km}(kr)f_{j\ell}(kr)e^{2ikr}\right.$$

$$-(k_{np}^4/k)g_{km}(kr)f_{j\ell}(k_{np}r)e^{ik(r+ct)}e^{ik_{np}(r-ct)}$$

$$\left.-(k_{np}^4/k)\overline{g}_{km}(kr)f_{j\ell}(k_{np}r)e^{-ik(r-ct)}e^{ik_{np}(r-ct)}\right]$$

$$\frac{-c}{32\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_{\tilde{n}}\mu_\ell^{pn}\mu_m^{np}\frac{PV}{2\pi i}\int_0^\infty\frac{dk k^3}{k-k_{pn}}\left[k^3 g_{km}(kr)f_{j\ell}(kr)e^{2ikr}\right.$$

$$-(k_{pn}^4/k)g_{km}(kr)f_{j\ell}(k_{pn}r)e^{ik(r+ct)}e^{ik_{pn}(r-ct)}$$

$$\left.-(k_{pn}^4/k)\overline{g}_{km}(kr)f_{j\ell}(k_{pn}r)e^{-ik(r-ct)}e^{ik_{pn}(r-ct)}\right].$$

$$(3.5.3)$$

Evaluating the time-independent part of the k-integral by extending the limits as before, results in the pole contributions

$$\frac{-c}{64\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_{\tilde{n}}\mu_\ell^{pn}\mu_m^{np}k_{pn}^6 g_{km}(k_{pn}r)\overline{f}_{j\ell}(k_{pn}r) \quad , \quad k_{pn} < 0$$

$$(3.5.4)$$

$$\frac{c}{64\pi^2\varepsilon_0}\varepsilon_{ijk}\sum_{\tilde{n}}\mu_\ell^{pn}\mu_m^{np}k_{pn}^6 \overline{g}_{km}(k_{pn}r)f_{j\ell}(k_{pn}r) \quad , \quad k_{pn} > 0.$$

The second term of (3.5.2), making use of (3.3.13) is

$$\frac{\hbar c^2}{32\pi^2\varepsilon_0}\ \varepsilon_{ijk}\ \frac{1}{2\pi i}\ \int_0^\infty dk k^3 [F_{jm}(kr)-\overline{F}_{jm}(kr)]\overline{B}_{mk}$$

$$= \frac{-c}{32\pi^2\varepsilon_0}\ \varepsilon_{ijk}\ \sum_n \mu_\ell^{pn}\mu_m^{np}\ \frac{PV}{2\pi i}\ \int_0^\infty \frac{dk k^3}{k-k_{np}}\ \left[-k^3\overline{f}_{jm}(kr)\overline{g}_{k\ell}(kr)e^{-2ikr}\right.$$

$$-(k_{np}^4/k)f_{jm}(kr)\overline{g}_{k\ell}(k_{np}r)e^{ik(r-ct)}e^{ik_{pn}(r-ct)}$$

$$\left.+(k_{np}^4/k)\overline{f}_{jm}(kr)\overline{g}_{k\ell}(k_{np}r)e^{-ik(r+ct)}e^{ik_{pn}(r-ct)}\right]$$

$$+ \frac{c}{32\pi^2\varepsilon_0}\ \varepsilon_{ijk}\ \sum_n \mu_\ell^{pn}\mu_m^{np}\ \frac{PV}{2\pi i}\ \int_0^\infty \frac{dk k^3}{k-k_{pn}}\ \left[-k^3\overline{f}_{jm}(kr)\overline{g}_{k\ell}(kr)e^{-2ikr}\right.$$

$$-(k_{pn}^4/k)f_{jm}(kr)\overline{g}_{k\ell}(k_{pn}r)e^{ik(r-ct)}e^{-ik_{pn}(r-ct)}$$

$$\left.+(k_{pn}^4/k)\overline{f}_{jm}(kr)\overline{g}_{k\ell}(k_{pn}r)e^{-ik(r+ct)}e^{-ik_{pn}(r-ct)}\right]$$

$$(3.5.5)$$

giving the contributions

$$\frac{-c}{64\pi^2\varepsilon_0}\ \varepsilon_{ijk}\ \sum_n \mu_\ell^{pn}\mu_m^{np}k_{pn}^6\ \overline{f}_{jm}(k_{pn}r)g_{k\ell}(k_{pn}r)\ ,\ k_{pn}\ <\ 0$$

$$(3.5.6)$$

$$\frac{c}{64\pi^2\varepsilon_0}\ \varepsilon_{ijk}\ \sum_n \mu_\ell^{pn}\mu_m^{np}k_{pn}^6\ f_{jm}(k_{pn}r)\overline{g}_{k\ell}(k_{pn}r)\ ,\ k_{pn}\ >\ 0.$$

Adding (3.5.4) and (3.5.6) and the complex conjugate terms to the contribution from the product of the first order fields, noting that only downward transitions contribute to the radiated energy, the Poynting vector due to an electric dipole source is

$$\frac{c}{16\pi^2\varepsilon_0} \, \varepsilon_{ijk} \sum_{\substack{n \\ E_p > E_n}} \mu_\ell^{pn}\mu_m^{np} k_{pn}^6 \left[\overline{f}_{j\ell}(k_{pn}r)\,g_{\ell m}(k_{pn}r) + \overline{g}_{\ell m}(k_{pn}r)\,f_{j\ell}(k_{pn}r) \right] \qquad (3.5.7)$$

which is seen to be identical to (3.4.12) obtained with the multipolar Hamiltonian. The above calculation provides a demonstration of the equivalence of the expectation value for the Poynting vector using the minimal-coupling and multipolar formalisms.

In this Appendix to Chapter 3, the explicit form of the product of the geometric tensors occurring in the expressions for the energy densities is presented. The tensors are required for the rotationally averaged near- and far-zone limits to be ascertained.

$$h_{i\ell j}(iur)h_{im\ell}(iur) = \left[\frac{A_{jk\ell m}}{u^2 r^2} + \frac{B_{jk\ell m}}{u^3 r^3} + \frac{C_{jk\ell m}}{u^4 r^4} + \frac{D_{jk\ell m}}{u^5 r^5} + \frac{E_{jk\ell m}}{u^6 r^6} + \frac{F_{jk\ell m}}{u^7 r^7} + \frac{G_{jk\ell m}}{u^8 r^8}\right]$$

$$(3.A.1)$$

with

$$A_{jk\ell m} = \alpha_{km}\hat{r}_j\hat{r}_\ell$$

$$B_{jk\ell m} = 4\delta_{km}\hat{r}_j\hat{r}_\ell + \delta_{k\ell}\hat{r}_j\hat{r}_m + \delta_{jm}\hat{r}_k\hat{r}_\ell - 6\hat{r}_j\hat{r}_k\hat{r}_\ell\hat{r}_m$$

$$C_{jk\ell m} = 10\delta_{km}\hat{r}_j\hat{r}_\ell + 5\delta_{k\ell}\hat{r}_j\hat{r}_m + 5\delta_{jm}\hat{r}_k\hat{r}_\ell - 3\delta_{jk}\hat{r}_\ell\hat{r}_m + \delta_{j\ell}\hat{r}_k\hat{r}_m - 3\delta_{\ell m}\hat{r}_j\hat{r}_k +$$

$$\delta_{jk}\delta_{\ell m} - 12\hat{r}_j\hat{r}_k\hat{r}_\ell\hat{r}_m$$

$$D_{jk\ell m} = 18\delta_{km}\hat{r}_j\hat{r}_\ell + 12\delta_{k\ell}\hat{r}_j\hat{r}_m + 12\delta_{jm}\hat{r}_k\hat{r}_\ell - 18\delta_{jk}\hat{r}_\ell\hat{r}_m + 6\delta_{j\ell}\hat{r}_k\hat{r}_m - 18\delta_{\ell m}\hat{r}_j\hat{r}_k +$$

$$6\delta_{jk}\delta_{\ell m} + 6\hat{r}_j\hat{r}_k\hat{r}_\ell\hat{r}_m$$

$$E_{jk\ell m} = 21\delta_{km}\hat{r}_j\hat{r}_\ell + 18\delta_{k\ell}\hat{r}_j\hat{r}_m + 18\delta_{jm}\hat{r}_k\hat{r}_\ell - 45\delta_{jk}\hat{r}_\ell\hat{r}_m + 15\delta_{j\ell}\hat{r}_k\hat{r}_m - 15\delta_{\ell m}\hat{r}_j\hat{r}_k +$$

$$15\delta_{jk}\delta_{\ell m} + 63\hat{r}_j\hat{r}_k\hat{r}_\ell\hat{r}_m$$

$$F_{jk\ell m} = 2(9\delta_{km}\hat{r}_j\hat{r}_\ell + 9\delta_{k\ell}\hat{r}_j\hat{r}_m + 9\delta_{jm}\hat{r}_k\hat{r}_\ell - 27\delta_{jk}\hat{r}_\ell\hat{r}_m + 9\delta_{j\ell}\hat{r}_k\hat{r}_m + 3\delta_{\ell m}\hat{r}_j\hat{r}_k +$$

$$9\delta_{jk}\delta_{\ell m} + 45\hat{r}_j\hat{r}_k\hat{r}_\ell\hat{r}_m)$$

$$G_{jk\ell m} = \frac{1}{2}F_{jk\ell m} \qquad (3.A.2)$$

$$\bar{h}_{i\ell j}(kr)h_{im\ell}(kr) = \left[\frac{a_{jk\ell m}}{k^2 r^2} + \frac{b_{jk\ell m}}{k^3 r^3} + \frac{c_{jk\ell m}}{k^4 r^4} + \frac{d_{jk\ell m}}{k^5 r^5} + \frac{e_{jk\ell m}}{k^6 r^6} + \frac{f_{jk\ell m}}{k^7 r^7} + \frac{g_{jk\ell m}}{k^8 r^8}\right] \quad (3.A.3)$$

with

$$a_{jk\ell m} = \alpha_{km}\hat{r}_j\hat{r}_\ell$$

$$b_{jklm} = \delta_{kl}\hat{r}_j\hat{r}_m - \delta_{jm}\hat{r}_k\hat{r}_l$$

$$c_{jklm} = -2\delta_{km}\hat{r}_j\hat{r}_l - \delta_{kl}\hat{r}_j\hat{r}_m - \delta_{jm}\hat{r}_k\hat{r}_l - 3\delta_{jk}\hat{r}_l\hat{r}_m + \delta_{jl}\hat{r}_k\hat{r}_m - 3\delta_{lm}\hat{r}_j\hat{r}_k +$$
$$\delta_{jk}\delta_{lm} + 12\hat{r}_j\hat{r}_k\hat{r}_l\hat{r}_m$$

$$e_{jklm} = -3\delta_{km}\hat{r}_j\hat{r}_l - 33\delta_{jk}\hat{r}_l\hat{r}_m + 3\delta_{jl}\hat{r}_k\hat{r}_m - 9\delta_{lm}\hat{r}_j\hat{r}_k + 3\delta_{jk}\delta_{lm} + 27\hat{r}_j\hat{r}_k\hat{r}_l\hat{r}_m$$

$$g_{jklm} = 9\delta_{km}\hat{r}_j\hat{r}_l + 9\delta_{kl}\hat{r}_j\hat{r}_m + 9\delta_{jm}\hat{r}_k\hat{r}_l - 27\delta_{jk}\hat{r}_l\hat{r}_m + 9\delta_{jl}\hat{r}_k\hat{r}_m - 27\delta_{lm}\hat{r}_j\hat{r}_k +$$
$$9\delta_{jk}\delta_{lm} + 45\hat{r}_j\hat{r}_k\hat{r}_l\hat{r}_m$$

$$d_{jklm} = f_{jklm} = 0 \qquad (3.A.4)$$

$$\bar{j}_{ijk}(kr)j_{ilm}(kr) = \left[\frac{h_{jklm}}{k^2 r^2} + \frac{i_{jklm}}{k^3 r^3} + \frac{j_{jklm}}{k^4 r^4} + \frac{k_{jklm}}{k^5 r^5} + \frac{l_{jklm}}{k^6 r^6}\right] \qquad (3.A.5)$$

with

$$h_{jklm} = \epsilon_{ijs}\epsilon_{ilt}\hat{r}_k\hat{r}_m\hat{r}_s\hat{r}_t$$

$$i_{jklm} = i\epsilon_{ijs}\epsilon_{ilt}(\beta_{ks}\hat{r}_m\hat{r}_t - \beta_{mt}\hat{r}_k\hat{r}_s)$$

$$j_{jklm} = \epsilon_{ijs}\epsilon_{ilt}(\beta_{mt}\hat{r}_k\hat{r}_s + \beta_{ks}\hat{r}_m\hat{r}_t + \beta_{ks}\beta_{mt})$$

$$k_{jklm} = 0$$

$$l_{jklm} = \epsilon_{ijs}\epsilon_{ilt}\beta_{ks}\beta_{mt} \qquad (3.A.6)$$

$$j_{ijk}(iur)j_{ilm}(iur) = \left[\frac{H_{jklm}}{u^2 r^2} + \frac{I_{jklm}}{u^3 r^3} + \frac{J_{jklm}}{u^4 r^4} + \frac{K_{jklm}}{u^5 r^5} + \frac{L_{jklm}}{u^6 r^6}\right] \qquad (3.A.7)$$

with

$$H_{jklm} = -\epsilon_{ijs}\epsilon_{ilt}\hat{r}_k\hat{r}_m\hat{r}_s\hat{r}_t$$

$$I_{jklm} = \epsilon_{ijs}\epsilon_{ilt}(\beta_{mt}\hat{r}_k\hat{r}_s + \beta_{ks}\hat{r}_m\hat{r}_t)$$

$$J_{jklm} = \epsilon_{ijs}\epsilon_{ilt}(\beta_{mt}\hat{r}_k\hat{r}_s + \beta_{ks}\hat{r}_m\hat{r}_t - \beta_{ks}\beta_{mt})$$

$$K_{jklm} = -2\epsilon_{ijs}\epsilon_{ilt}\beta_{ks}\beta_{mt}$$

$$L_{jklm} = -\epsilon_{ijs}\epsilon_{ilt}\beta_{ks}\beta_{mt} \qquad (3.A.8)$$

CHAPTER 4

INTERACTION OF TWO POLARISABLE MOLECULES

4.1 INTRODUCTION

Intermolecular forces are responsible for almost all of the chemical and physical properties exhibited by matter. Consequently, their understanding through a combination of theoretical prediction and experimental verification is of the greatest importance. The common aim of such study is the evaluation of the interaction energy between atomic and molecular systems and of its inherent dependence upon R, the separation distance between conveniently chosen centres.

The initial quantum mechanical calculation of the interaction between two neutral ground state molecules assumed the coupling between them to be Coulombic in origin. Use of second order perturbation theory then resulted in the characteristic R^{-6} dependence on separation distance of the interaction commonly known as the London-van der Waals dispersion energy [44-46]. The results obtained, however, applied only to intermolecular separations small compared with wavelengths of molecular electronic transitions. This is a direct consequence of the neglect of retardation effects, namely ignoring the fact that electromagnetic phenomena propagate with the finite velocity of light. To deal adequately with intermolecular interactions at all distances outside the regions of overlap of electronic wavefunctions, the inclusion of the radiation field in the total Hamiltonian is essential. Not only is retardation then a natural occurrence, but intermolecular interactions in regions where the separation is of the order of the transition wavelength, where the effects of retardation become important, are also determined correctly.

By fully incorporating the radiation field and retardation effects, Casimir and Polder [43], prompted by the experimental observations of Overbeek and Verwey [47], first showed that the retarded dispersion energy obeyed an R^{-7} power law dependence at large intermolecular separations. The London result was found to be applicable only at short separation distances. The use of the Coulomb potential energy term alone is therefore not sufficient to describe the interaction in the radiation zone. That a weakening of the potential occurred at large separations and could be attributed to retardation effects has been firmly established theoretically [48-52] and also confirmed experimentally [53,54].

By treating both radiation and matter on an equal footing, QED is ideally suited to the investigation of retarded dispersion forces and the interaction between molecules in electronically excited states. The commonly held picture is one where all intermolecular interactions are viewed as arising from radiation-molecule couplings. Intermolecular interaction is mediated by the radiation field through the exchange of transverse virtual photons. In this exchange, the absorption and emission processes violate the principle of energy conservation. This is rationalised by appeal to the time-energy Heisenberg uncertainty principle; for small intervals of time, energy maybe "borrowed" from the electromagnetic vacuum permitting the participation of virtual states. Dispersion interactions are seen as being caused by vacuum fluctuations, a direct manifestation of the ever present zero-point energy of the quantised electromagnetic field.

The dispersion interaction between neutral molecules has been investigated thoroughly in the Schrödinger picture of QED, at first solely within the electric dipole approximation giving the Casimir-Polder result [5,6,55], and later by including magnetic dipole

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and electric quadrupole couplings |38|. Use of the multipolar form of the theory is advantageous as neutral molecules couple among themselves solely via the radiation field since all electrostatic, and therefore instantaneous interactions, have been eliminated from the multipolar Hamiltonian. The dispersion force was interpreted as arising from the exchange of two virtual photons, the energy shift calculation requiring the use of fourth order time-dependent perturbation theory. Results were expressed in terms of molecular polarisability tensors, and were valid for the entire range of separation outside electron overlap. The limiting values at long and short separation distances were also given.

In this Chapter, an alternative approach to the calculation of the energy shift between two neutral molecules is presented. This method relies on the use of the time dependent Maxwell fields evaluated in Chapter 2. The picture is one in which a molecule is thought of as a polarisable test body placed in the electromagnetic field produced by a second, source molecule. The response of the first to the Maxwell field of the second is then calculated directly using the quantum mechanical analogue of the expression for the classical interaction energy. The leading term, corresponding to the use of the electric dipole source fields, gives the historically important Casimir-Polder potential |32,34|. This response formalism is now extended, by presenting for the first time in the Heisenberg method, a comprehensive calculation of the energy of interaction between neutral molecules in the ground state and in electronically excited states for molecules possessing a variety of multipole polarisability characteristics up to and including the diamagnetic coupling term. These higher order interactions are important when considering molecules with a small electric dipole polarisability and for molecules whose optically allowed levels are accessible from the ground state by non-zero magnetic dipole and electric quadrupole matrix

elements. The inclusion of multipole moments other than the electric dipole is also important when the interaction between chiral molecules is examined. In such optically active species, the dispersion force depends on the relative handedness of the pair, a phenomenon termed chiral discrimination [56]. The derivation of the complete potential in the Heisenberg representation is given for the first time. The equivalence of this result and of others obtained in this Chapter, including their asymptotic behaviour at the limits of large and small separation, is shown with previous work carried out in the Schrödinger picture.

In order to express the energy of interaction between two molecules in terms of their molecular polarisabilities, it is necessary to include the second order source fields which are quadratic in the transition moments as in the determination of the energy density and the Poynting vector. In the calculation of interaction energies, contributions arise from the product of the first order fields, which are linear in the moments, and from the interference of the vacuum field with the second order field. To evaluate the latter contribution, use is made of the diagonal electron space matrix elements of the electromagnetic field operators given in Section 3.1.

The energy shift between two neutral polarisable molecules is given by the expression

$$\Delta E = -\frac{1}{2}\alpha\vec{d}^2 - G\vec{b}\vec{d} - \frac{1}{2}\chi\vec{b}^2 - A\vec{d}\nabla\vec{d} - T\vec{b}\nabla\vec{d} - \frac{1}{2}\theta(\nabla\vec{d})^2 + \ldots \qquad (4.1.1)$$

representing the interaction of a molecule possessing a specific polarisability characteristic with the radiation field of a second source molecule. The leading term, corresponding to electric dipole coupling has been treated by Power and Thirunamachandran [32,34] and is

given here for the sake of completeness and as an introduction to the response formalism. The calculation of higher order terms follows.

4.2 THE INTERACTION BETWEEN TWO ELECTRIC DIPOLE POLARISABLE MOLECULES

The first interaction to be considered is that between two electric dipole polarisable molecules. Recalling that the electromagnetic fields in the vicinity of a molecule can be expressed as series in powers of the multipole moments, the interaction energy between two non-identical electric dipole polarisable molecules A and B in initial states $|p\rangle$ and $|q\rangle$ respectively, with A-B separation $R = |\vec{R}_A - \vec{R}_B|$, correct to second order in the moments, is

$$
\begin{aligned}
\Delta E = & \frac{-1}{2\varepsilon_0^2} \sum_m \alpha_{ij}^A(\omega_{qm}) d_i^{(1)B}(\vec{\mu};\omega_{qm}) d_j^{(1)B}(\vec{\mu};\omega_{qm}) \\
& \frac{-1}{2\varepsilon_0^2} \sum_n \alpha_{k\ell}^B(\omega_{pn}) d_k^{(1)A}(\vec{\mu};\omega_{pn}) d_\ell^{(1)A}(\vec{\mu};\omega_{pn}) + \\
& \left\{ \frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \alpha_{ij}^A(\omega) \left[d_i^{(0)}(\omega) d_j^{(2)B}(\vec{\mu}\vec{\mu};\omega) + d_i^{(2)B}(\vec{\mu}\vec{\mu};\omega) d_j^{(0)}(\omega) \right] \right. \\
& \left. \frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \alpha_{k\ell}^B(\omega) \left[d_k^{(0)}(\omega) d_\ell^{(2)A}(\vec{\mu}\vec{\mu};\omega) + d_k^{(2)A}(\vec{\mu}\vec{\mu};\omega) d_\ell^{(0)}(\omega) \right] \right\}' .
\end{aligned}
$$
 (4.2.1)

The prime superscript in (4.2.1) implies that the virtual photon (non-resonant) contributions are not double counted, and applies to all interactions considered in this Chapter. The first term of (4.2.1) represents the response of molecule A through its dynamic polarisability $\alpha_{ij}(\omega_{qm})$, at frequency ω_{qm} for molecule A in state $|p\rangle$, to the first-order electromagnetic fields associated with the electric dipole transitions to the intermediate states $|m\rangle$ from the initial state $|q\rangle$ of

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molecule B. A similar interpretation applies to the remaining terms of (4.2.1). The dynamic polarisability at frequency ω is defined by

$$\alpha_{ij}(\omega) = \sum_{n} \left\{ \frac{\mu_i^{pn}\mu_j^{np}}{E_{np}-\hbar\omega} + \frac{\mu_j^{pn}\mu_i^{np}}{E_{np}+\hbar\omega} \right\} = \sum_{m} \frac{2E_{np}\mu_i^{pn}\mu_j^{np}}{E_{np}^2-(\hbar\omega)^2} .$$

(4.2.2)

The terms listed in (4.2.1) are the important contributions to the interaction energy as the first three terms arising from the expansion of the field in series of powers of the moments do not contribute. The product of the free field is independent of the source, simply being the zero-point energy contribution, while the term arising from the interference of the zeroth order field with the first order field does not contribute to the expectation value since the number of photons change. The first contribution to be retained and evaluated is that arising from the product of the field linear in the source. Using the electric dipole dependent part of the first order electric displacement field (2.2.34), the expectation value of the first two terms of (4.2.1) over the molecular state $|q\rangle$ and $|p\rangle$ respectively, with the radiation field in the vacuum state, is

$$\Delta E = \frac{-1}{32\pi^2\varepsilon_0^2} \sum_{m} \alpha_{ij}^A(k_{qm})\mu_k^{qm}\mu_\ell^{mq}k_{qm}^6 \bar{f}_{i\ell}(k_{qm}R)f_{j\ell}(k_{qm}R)$$

$$\frac{-1}{32\pi^2\varepsilon_0^2} \sum_{n} \alpha_{k\ell}^B(k_{pn})\mu_i^{pn}\mu_j^{np}k_{pn}^6 \bar{f}_{\ell i}(k_{pn}R)f_{\ell j}(k_{pn}R) .$$

(4.2.3)

To determine the contribution to the energy shift from the product of the vacuum field with the second order field, use is made of the diagonal matrix elements of the electromagnetic field operators quadratic in the moments given in Section 3.1. Using the definition of the free field (2.2.15) and (3.1.1), the contribution from the last two

terms of (4.2.1) can be written as

$$\Delta E = \frac{-1}{8\pi\epsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right) \alpha_{ij}^A(\omega) [e_i e^{i\vec{k}\cdot\vec{R}} \bar{e}_\ell \bar{\mathscr{A}}_{\ell j} + e_\ell \mathscr{A}_{\ell i} \bar{e}_j e^{-i\vec{k}\cdot\vec{R}}] +$$

$$\frac{-1}{8\pi\epsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right) \alpha_{\ell\ell}^B(\omega) [e_\ell e^{-i\vec{k}\cdot\vec{R}} \bar{e}_i \bar{\mathscr{A}}_{i\ell} + e_i \mathscr{A}_{i\ell} \bar{e}_\ell e^{i\vec{k}\cdot\vec{R}}].\qquad(4.2.4)$$

For the moment, concentrating on the very first term of (4.2.4), the
polarisation sum (2.2.19) and angular average (2.2.24), give

$$\frac{-1}{8\pi\epsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right) \alpha_{ij}^A(\omega) e_i \bar{e}_\ell e^{i\vec{k}\cdot\vec{R}} \bar{\mathscr{A}}_{\ell j}$$

$$= \frac{-\hbar c}{32\pi^2\epsilon_0^2} \frac{1}{2\pi i} \int_0^\infty dk\, k^3 \alpha_{ij}^A(\omega) [F_{i\ell}(kR) - \bar{F}_{i\ell}(kR)] \bar{\mathscr{A}}_{\ell j}.\qquad(4.2.5)$$

Using the definition (3.1.13) for $\mathscr{A}_{\ell j}$, (4.2.5) becomes

$$\frac{-1}{32\pi^2\epsilon_0^2} \sum_{m} \mu_\ell^{qm} \mu_\ell^{mq} \frac{PV}{2\pi i} \int_0^\infty dk\, k^3 \alpha_{ij}^A(\omega) \times$$

$$\left\{ \frac{[F_{i\ell}(kR) - \bar{F}_{i\ell}(kR)][k^3 \bar{F}_{j\ell}(kR) - k_{mq}^3 \bar{F}_{j\ell}(k_{mq}R)] e^{-i(k_{qm}+k)ct}}{(k_{mq}-k)} \right. +$$

$$\left. \frac{[F_{i\ell}(kR) - \bar{F}_{i\ell}(kR)][k^3 \bar{F}_{j\ell}(kR) - k_{qm}^3 \bar{F}_{j\ell}(k_{qm}R)] e^{i(k_{qm}-k)ct}}{(k_{mq}+k)} \right\}$$

$$= \frac{1}{32\pi^2\epsilon_0^2} \sum_{m} \mu_\ell^{qm} \mu_\ell^{mq} \frac{PV}{2\pi i} \int_0^\infty \frac{dk\, k^3}{k-k_{mq}} \alpha_{ij}^A(\omega) \left[-k^3 \bar{f}_{i\ell}(kR) \bar{f}_{j\ell}(kR) e^{-2ikR} \right.$$

$$-k_{mq}^3 f_{i\ell}(kR) \bar{f}_{j\ell}(k_{mq}R) e^{ik(R-ct)} e^{ik_{qm}(R-ct)}$$

$$\left. +k_{mq}^3 \bar{f}_{i\ell}(kR) \bar{f}_{j\ell}(k_{mq}R) e^{-ik(R+ct)} e^{ik_{qm}(R-ct)} \right]$$

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$$-\frac{1}{32\pi^2\epsilon_0^2}\sum_m \mu_k^{qm}\mu_\ell^{mq}\frac{PV}{2\pi i}\int_0^\infty\frac{dk\,k^3}{k-k_{qm}}\,\alpha_{ij}^A(\omega)\left[-k^3\bar{f}_{i\ell}(kR)\bar{f}_{jk}(kR)e^{-2ikR}\right.$$

$$-k_{qm}^3 f_{i\ell}(kR)\bar{f}_{jk}(k_{qm}R)e^{ik(R-ct)}e^{-ik_{qm}(R-ct)}$$

$$\left.+k_{qm}^3\bar{f}_{i\ell}(kR)\bar{f}_{jk}(k_{qm}R)e^{-ik(R+ct)}e^{-ik_{qm}(R-ct)}\right]$$

$$(4.2.6)$$

where use has been made of the k,ℓ-index symmetry to eliminate the term without an exponential dependence. For a state for which $E_q > E_m$, after making the substitution $k = -iu$, the time-independent part of (4.2.6) is

$$\frac{-1}{64\pi^2\epsilon_0^2}\sum_m \alpha_{ij}^A(k_{qm})\mu_k^{qm}\mu_\ell^{mq}k_{qm}^5\,\bar{f}_{ik}(k_{qm}R)f_{j\ell}(k_{qm}R)$$

$$+\frac{hc}{64\pi^3\epsilon_0^2}\int_0^\infty duu^6e^{-2uR}\alpha_{ij}^A(icu)\alpha_{k\ell}^B(icu)f_{ik}(iuR)f_{j\ell}(iuR) \qquad (4.2.7)$$

and the time-dependent part is given by

$$-\frac{1}{64\pi^3\epsilon_0^2}\sum_m \mu_k^{qm}\mu_\ell^{mq}(-k_{qm}^3)\int_0^\infty duu^3\alpha_{ij}^A(icu)\times$$

$$\left[\bar{f}_{i\ell}(k_{mq}R)e^{ik_{qm}(R-ct)}f_{jk}(-iuR)\frac{e^{-uc(t-R/c)}}{u+ik_{qm}}\right.$$

$$-\bar{f}_{i\ell}(k_{mq}R)e^{ik_{qm}(R-ct)}\bar{f}_{jk}(-iuR)\frac{e^{-uc(t+R/c)}}{u+ik_{qm}}$$

$$+\bar{f}_{i\ell}(k_{qm}R)e^{ik_{mq}(R-ct)}f_{jk}(-iuR)\frac{e^{-uc(t-R/c)}}{u-ik_{qm}}$$

$$\left.-\bar{f}_{i\ell}(k_{qm}R)e^{ik_{mq}(R-ct)}\bar{f}_{jk}(-iuR)\frac{e^{-uc(t+R/c)}}{u-ik_{qm}}\right].$$

$$(4.2.8)$$

The time-dependent terms tend to zero for $t \gg R/c$ as the integrals have exponentially decreasing values for large t. In addition, the average of (4.2.8) over a finite time interval tends to zero because of the

modulation factors $e^{\pm ik_{qm}ct}$. These oscillatory terms are ignored henceforth. Returning to (4.2.6) and evaluating the integral for the case $k_{mq} > 0$, the pole contribution is found to be

$$\frac{1}{64\pi^2\varepsilon_0^2} \sum_m \alpha_{ij}^A(k_{qm})\mu_k^{qm}\mu_\ell^{mq}k_{qm}^6 f_{ik}(k_{qm}R)\bar{f}_{j\ell}(k_{qm}R). \qquad (4.2.9)$$

The u-integral part is identical to that obtained in the second term of (4.2.7). Use has been made of the relations (2.A.3) and (2.A.4) given in the Appendix to Chapter 2 for the geometrical tensors.

It is important to note that the first term of (4.2.7) has the same sign as the corresponding term arising from the first order fields (4.2.3). However, for those states m with $E_m > E_q$, the pole contribution has opposite sign as indicated by (4.2.9), and cancels the corresponding term of (4.2.3). This addition and cancellation of pole contributions from the zeroth and second order fields with terms from the product of the first order fields is once again a common characteristic throughout the calculations carried out in this Chapter.

After evaluating all the remaining terms in (4.2.4), the energy of interaction between two excited electric dipole polarisable molecules is

$$\Delta E = \frac{-1}{16\pi^2\varepsilon_0^2} \sum_{\substack{m \\ E_q > E_m}} \alpha_{ij}^A(k_{qm})\mu_k^{qm}\mu_\ell^{mq}k_{qm}^6 \bar{f}_{ik}(k_{qm}R)f_{j\ell}(k_{qm}R)$$

$$\frac{-1}{16\pi^2\varepsilon_0^2} \sum_{\substack{n \\ E_p > E_n}} \alpha_{k\ell}^B(k_{pn})\mu_i^{pn}\mu_j^{np}k_{pn}^6 \bar{f}_{ik}(k_{pn}R)f_{j\ell}(k_{pn}R)$$

$$+ \frac{\hbar c}{32\pi^3\varepsilon_0^2} \int_0^\infty du\, u^6 e^{-2uR}\alpha_{ij}^A(icu)\alpha_{k\ell}^B(icu)f_{ik}(iuR)f_{j\ell}(iuR). \qquad (4.2.10)$$

When both molecules are in the ground electronic state, the first two terms of (4.2.10) disappear since only upward transitions from the initial state are possible, leaving the u-integral as the sole contribution to the dispersion interaction. After multiplying the geometric tensors and averaging, this term can be expressed as

$$
\Delta E = \frac{-1}{36\pi^3 \epsilon_0^2 \hbar c} \sum_{m,n} |\vec{\mu}^{0m}|^2 |\vec{\mu}^{n0}|^2 \int_0^\infty \frac{du\, u^6 e^{-2uR} k_{m0} k_{n0}}{(k_{m0}^2 + u^2)(k_{n0}^2 + u^2)} \times
$$

$$
\left[\frac{1}{u^2 R^2} + \frac{2}{u^3 R^3} + \frac{5}{u^4 R^4} + \frac{6}{u^5 R^5} + \frac{3}{u^6 R^6} \right] \tag{4.2.11}
$$

and is the familiar Casimir-Polder potential [43]. It is instructive to examine the asymptotic behaviour of (4.2.11) in the limits of large and small intermolecular separation. In the far-zone limit the molecules are separated by a distance R much larger than the wavelengths of the molecular transitions. In the denominators of (4.2.11) u^2 may be ignored in relation to k_{m0} and k_{n0}. After performing the u-integral, the far-zone result is found to be

$$
\frac{-23\hbar c \alpha^B(0) \alpha^A(0)}{64\pi^3 \epsilon_0^2 R^7} \tag{4.2.12}
$$

where now the ground state static polarisabilities appear. In the near-zone the separation is much smaller than characteristic transition wavelengths, resulting in $kR \ll 1$. Retaining the leading term of (4.2.11) after setting the exponential factor to unity gives the near-zone shift

$$
\frac{-1}{24\pi^2 \epsilon_0^2 R^6} \sum_{m,n} \frac{|\vec{\mu}^{0m}|^2 |\vec{\mu}^{n0}|^2}{(E_{m0} + E_{n0})} \;, \tag{4.2.13}
$$

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more commonly known as the London dispersion energy. It is worth pointing out at this stage, that the near-zone result may be obtained from second order perturbation theory when the interaction is represented by an electric dipolar coupling term. This is examined in more detail in the final Section of this Chapter. The dispersion potential is identical to that obtained in previous studies using both methods [6,32], and is in agreement with the interaction energies obtained in Section 3.2 resulting from the response of a test molecule to the displacement field of the source.

If for example molecule A is taken to be in its ground state while B remains excited [57], only the first and third terms of (4.2.10) survive. Examining the first term of (4.2.10), after multiplying the tensors and rotational averaging, the additional contribution from downward transitions is found to be

$$
\frac{-1}{24\pi^2\epsilon_0^2} \sum_{\substack{m \\ E_q > E_m}} \alpha^A(k_{qm}) |\vec{\mu}^{qm}|^2 k_{qm}^6 \left[\frac{1}{k_{qm}^2 R^2} + \frac{1}{k_{qm}^4 R^4} + \frac{3}{k_{qm}^6 R^6}\right].
\tag{4.2.14}
$$

It is important to note that for large R the leading term of (4.2.14) has an R^{-2} dependence corresponding to real photon emission, given by

$$
\frac{-1}{24\pi^2\epsilon_0^2 R^2} \sum_{\substack{m \\ E_q > E_m}} \alpha^A(k_{qm}) |\vec{\mu}^{qm}|^2 k_{qm}^4.
\tag{4.2.15}
$$

This is the dominant contribution to the interaction energy at large separations since the virtual photon terms exhibit the familiar R^{-7} dependence in this limit. The virtual photon contribution is essentially the same as that of the upward transitions given in (4.2.11)

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$$\Delta E = \frac{-1}{36\pi^3 \epsilon_0^2 \hbar c} \sum_{m,n} |\vec{\mu}^{qm}|^2 |\vec{\mu}^{no}|^2 \int_0^\infty \frac{du\, u^6 e^{-2uR} k_{mq} k_{no}}{(k_{mq}^2 + u^2)(k_{no}^2 + u^2)} \times$$

$$\left[\frac{1}{u^2 R^2} + \frac{2}{u^3 R^3} + \frac{5}{u^4 R^4} + \frac{6}{u^5 R^5} + \frac{3}{u^6 R^6} \right] \qquad (4.2.16)$$

where the summation over m includes both upward and downward transitions. The asymptotic behaviour of (4.2.16) at large R is

$$\frac{-23 \hbar c \alpha^B(0) \alpha^A(0)}{64 \pi^3 \epsilon_0^2 R^7} \qquad (4.2.17)$$

where now the static excited polarisability of B appears. For small R, the dominant term of (4.2.16) is

$$\frac{-1}{24\pi^2 \epsilon_0^2 R^6} \sum_{m,n} \mathrm{sgn}(E_{mq}) \frac{|\vec{\mu}^{qm}|^2 |\vec{\mu}^{no}|^2}{(E_{no} + |E_{mq}|)} \qquad (4.2.18)$$

while that from (4.2.14) is

$$\frac{-1}{8\pi^2 \epsilon_0^2 R^6} \sum_{\substack{m \\ E_q > E_m}} \alpha^A(k_{qm}) |\vec{\mu}^{qm}|^2. \qquad (4.2.19)$$

Adding the last two expressions results in the total small R limit

$$\frac{-1}{24\pi^2 \epsilon_0^2 R^6} \sum_{m,n} \frac{|\vec{\mu}^{qm}|^2 |\vec{\mu}^{no}|^2}{(E_{no} + E_{mq})} \qquad (4.2.20)$$

in which both real- and virtual-photon terms contribute to the interaction energy. The limits (4.2.15) and (4.2.20) are in agreement with the energy shifts (3.2.22) and (3.2.23) respectively, obtained when

a test polarisable body interacts with the electric energy density due to an electric dipole source.

If both molecules are in electronically excited states, all three terms occurring in (4.2.10) contribute to the energy shift. The first term is given by (4.2.14), the second term of (4.2.10) can similarly be written as

$$\frac{-1}{24\pi^2\varepsilon_0^2} \sum_{\substack{n \\ E_p > E_n}} \alpha^B(k_{pn}) |\vec{\mu}^{pn}|^2 k_{pn}^6 \left[\frac{1}{k_{pn}^2 R^2} + \frac{1}{k_{pn}^4 R^4} + \frac{3}{k_{pn}^6 R^6}\right] \qquad (4.2.21)$$

while the third term of (4.2.10) can be expressed as

$$\frac{-\hbar c}{16\pi^3\varepsilon_0^2} \int_0^\infty du\, u^6 e^{-2uR} \alpha^A(icu)\alpha^B(icu)\left[\frac{1}{u^2 R^2} + \frac{2}{u^3 R^3} + \frac{5}{u^4 R^4} + \frac{6}{u^5 R^5} + \frac{3}{u^6 R^6}\right].$$

$$(4.2.22)$$

This interaction energy can be decomposed into three types of terms depending on whether the transitions m ⟵ q and n ⟵ p are both upward, one upward and one downward, or both downward. The first two cases have already been examined, respectively giving the dispersion interaction and the energy shift between one ground and one excited state molecule. For the third type due to downward transitions, the near-zone limits of (4.2.14), (4.2.21) and (4.2.22) are respectively

$$\frac{-1}{12\pi^2\varepsilon_0^2\hbar cR^6} \sum_{\substack{m \\ E_q > E_m}} k_{np} \frac{|\vec{\mu}^{pn}|^2 |\vec{\mu}^{qm}|^2}{k_{np}^2 - k_{qm}^2} - \frac{1}{12\pi^2\varepsilon_0^2\hbar cR^6} \sum_{\substack{n \\ E_p > E_n}} k_{mq} \frac{|\vec{\mu}^{pn}|^2 |\vec{\mu}^{qm}|^2}{k_{mq}^2 - k_{np}^2} -$$

$$\frac{1}{24\pi^2\varepsilon_0^2\hbar cR^6} \sum_{m,n} \frac{(sgn\,k_{mq})(sgn\,k_{np})|\vec{\mu}^{qm}|^2 |\vec{\mu}^{pn}|^2}{(|k_{mq}| + |k_{np}|)}$$

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$$= \frac{-1}{24\pi^2 \epsilon_0^2 R^6} \sum_{\substack{m,n \\ E_q > E_m \\ E_p > E_n}} \frac{|\vec{\mu}^{qm}|^2 |\vec{\mu}^{np}|^2}{(E_{np} + E_{mq})}. \tag{4.2.23}$$

For large R the dominant term is proportional to R^{-2} and arises solely from the real-photon exchange terms of (4.2.14) and (4.2.21), giving

$$\frac{-1}{36\pi^2 \epsilon_0^2 (\hbar c)^4 R^2} \sum_{\substack{m,n \\ E_q > E_m \\ E_p > E_n}} \frac{|\vec{\mu}^{qm}|^2 |\vec{\mu}^{np}|^2}{(E_{pn} + E_{qm})} E_{qm} E_{pn} (E_{qm}^2 + E_{qm} E_{pn} + E_{pn}^2). \tag{4.2.24}$$

The response method [34,57] described above has the additional advantage of being able to treat the interaction of electronically excited molecules in a single formulation from which the dispersion interaction is also easily obtainable. These potentials are not readily calculable by more conventional methods due to the presence of intermediate state resonances. In the response formalism these resonances are easily isolated and automatically accounted for since the source fields include contributions arising from real transitions. This completes the derivation of the energy shift between two electric dipole polarisable molecules in both ground and electronically excited states. The methods outlined form the basis of the rest of the calculations carried out in this Chapter.

4.3 THE INTERACTION BETWEEN A CHIRAL MOLECULE AND AN ELECTRIC DIPOLE POLARISABLE MOLECULE

The dominant transitions occurring in most atoms and molecules that undergo optical processes are those due to electric dipole allowed transitions. However, the inclusion of the magnetic dipole coupling term is necessary for the satisfactory treatment of optically active molecules. The energy shift between an electric dipole polarisable molecule A and a molecule B with electric and magnetic dipole moments is given by

$$
\frac{-1}{2\varepsilon_0^2} \sum_m \alpha_{ij}^A(\omega_{qm}) \left[d_i^{(1)}(\vec{\mu};\omega_{qm}) d_j^{(1)}(\vec{m};\omega_{qm}) + d_i^{(1)}(\vec{m};\omega_{qm}) d_j^{(1)}(\vec{\mu};\omega_{qm}) \right]
$$

$$
\frac{-1}{2\varepsilon_0} \sum_n G_{k\ell}^B(\omega_{pn}) \left[b_\ell^{(1)}(\vec{\mu};\omega_{pn}) d_k^{(1)}(\vec{\mu};\omega_{pn}) - d_k^{(1)}(\vec{\mu};\omega_{pn}) b_\ell^{(1)}(\vec{\mu};\omega_{pn}) \right]
$$

$$
\frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \alpha_{ij}^A(\omega) \left[d_i^{(0)} d_j^{(2)}(\vec{\mu}\vec{m}) + d_i^{(2)}(\vec{\mu}\vec{m}) d_j^{(0)} \right]
$$

$$
\frac{-1}{2\varepsilon_0} \sum_{\vec{k},\lambda} G_{k\ell}^B(\omega) \left[b_\ell^{(0)} d_k^{(2)}(\vec{\mu}\vec{\mu}) + b_\ell^{(2)}(\vec{\mu}\vec{\mu}) d_k^{(0)} - d_k^{(0)} b_\ell^{(2)}(\vec{\mu}\vec{\mu}) - d_k^{(2)}(\vec{\mu}\vec{\mu}) b_\ell^{(0)} \right]
$$

(4.3.1)

with mixed electric-magnetic dipole dynamic polarisability

$$
G_{k\ell}(\omega) = \sum_m \left\{ \frac{\mu_k^{qm} m_\ell^{mq}}{E_{mq} - \hbar\omega} + \frac{m_\ell^{qm} \mu_k^{mq}}{E_{mq} + \hbar\omega} \right\} = \sum_m \frac{2\hbar\omega \mu_k^{qm} m_\ell^{mq}}{E_{mq}^2 - (\hbar\omega)^2} .
$$

(4.3.2)

Using the $\vec{\mu}$- and $\vec{m}$-dependent parts of the first order displacement field (2.2.34) and the $\vec{\mu}$-dependent term of the magnetic field linear in the sources (2.2.55), the contribution to the energy shift (4.3.1) from the first order fields is

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$$\Delta E = \frac{1}{32\pi^2\varepsilon_0^2 c} \sum_m \alpha^A_{ij}(k_{qm})\mu^{qm}_k m^{mq}_\ell k^6_{qm} [\bar{f}_{i\ell}(k_{qm}R)g_{j\ell}(k_{qm}R)+\bar{g}_{j\ell}(k_{qm}R)f_{i\ell}(k_{qm}R)]$$

$$\frac{-1}{32\pi^2\varepsilon_0^2 c} \sum_n G^B_{k\ell}(k_{pn})\mu^{pn}_i \mu^{np}_j k^6_{pn} [\bar{f}_{kj}(k_{pn}R)g_{\ell i}(k_{pn}R)+\bar{g}_{\ell i}(k_{pn}R)f_{kj}(k_{pn}R)].$$

$$(4.3.3)$$

The remaining two terms of (4.3.1), the contribution from the zeroth and second order fields, making use of (3.1.1), (3.1.2) and (3.1.7), are

$$\frac{-1}{8\pi\varepsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right)\alpha^A_{ij}(\omega)\left[e_i e^{i\vec{k}.\vec{R}}(\bar{b}_\ell\mathcal{B}_{\ell j}+\bar{e}_\ell\mathcal{E}_{\ell j}) + (b_\ell\mathcal{B}_{\ell i}+e_\ell\mathcal{E}_{\ell i})\bar{e}_j e^{-i\vec{k}.\vec{R}}\right]$$

$$\frac{-1}{8\pi\varepsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right)G^B_{k\ell}(\omega)\left[b_\ell e^{-i\vec{k}.\vec{R}}\bar{e}_j\mathcal{A}_{j k} - e_j\mathcal{J}_{j\ell}\bar{e}_k e^{i\vec{k}.\vec{R}}+\right.$$

$$\left. e_k e^{-i\vec{k}.\vec{R}}\bar{e}_j\mathcal{J}_{j\ell} - e_j\mathcal{A}_{j k}\bar{b}_\ell e^{i\vec{k}.\vec{R}}\right].$$

$$(4.3.4)$$

On evaluating the terms of (4.3.4) in the familiar manner, noting that the last two terms in each expression are complex conjugates of the first two, and adding the contribution from the first order fields (4.3.3), the energy of interaction between a chiral molecule and an electric dipole polarisable molecule is

$$\frac{1}{16\pi^2\varepsilon_0^2 c} \sum_m \alpha^A_{ij}(k_{qm})\mu^{qm}_k m^{mq}_\ell k^6_{qm} [\bar{f}_{i\ell}(k_{qm}R)g_{j\ell}(k_{qm}R)+\bar{g}_{j\ell}(k_{qm}R)f_{i\ell}(k_{qm}R)]$$
$$E_q > E_m$$

$$\frac{-1}{16\pi^2\varepsilon_0^2 c} \sum_n G^B_{k\ell}(k_{pn})\mu^{pn}_i \mu^{np}_j k^6_{pn} [\bar{f}_{kj}(k_{pn}R)g_{\ell i}(k_{pn}R)+\bar{g}_{\ell i}(k_{pn}R)f_{kj}(k_{pn}R)] +$$
$$E_p > E_n$$

$$\frac{\hbar}{16\pi^3\varepsilon_0^2} \int_0^\infty du\, u^6 e^{-2uR}\alpha^A_{ij}(icu)G^B_{k\ell}(icu)f_{i\ell}(iuR)g_{j\ell}(iuR).$$

$$(4.3.5)$$

When both molecules are in their ground states, only the u-integral term of (4.3.5) survives, and is

$$\frac{-\hbar}{16\pi^3\varepsilon_0^2} \varepsilon_{j\ell m}\hat{R}_m\int_0^\infty duu^6 e^{-2uR}\alpha_{ij}^A(icu)G_{\ell\ell}^B(icu)\left[\frac{\alpha_{ik}}{u^2R^2} + \frac{\alpha_{ik}+\beta_{ik}}{u^3R^3} + \frac{2\beta_{ik}}{u^4R^4} + \frac{\beta_{ik}}{u^5R^5}\right]$$

$$(4.3.6)$$

with the dyadics α_{ij} and β_{ij} defined as

$$\alpha_{ij} = (\delta_{ij}-\hat{R}_i\hat{R}_j) \quad ; \quad \beta_{ij} = (\delta_{ij}-3\hat{R}_i\hat{R}_j), \qquad (4.3.7)$$

after multiplication of the geometric tensors, and is in agreement with the result obtained using diagrammatic techniques [38]. The dispersion potential (4.3.6) disappears on averaging, resulting in no discrimination in the fluid phase.

If molecule B is in an excited state while A remains in the ground state, only the first and third terms of (4.3.5) contribute. The energy shift for an oriented pair is then

$$\Delta E = \frac{-1}{8\pi^2\varepsilon_0^2 cR^2} \sum_{\substack{m \\ E_q>E_m}} \alpha_{ij}^A(k_{qm})\mu_\ell^{qm}m_\ell^{mq}k_{qm}^4\varepsilon_{j\ell m}\hat{R}_m\alpha_{ik}$$

$$\frac{-i}{4\pi^3\varepsilon_0^2\hbar c^2} \varepsilon_{j\ell m}\hat{R}_m\sum_{m,n}\mu_i^{0n}\mu_j^{n0}\mu_\ell^{qm}m_\ell^{mq}\int_0^\infty\frac{duu^6e^{-2uR}}{(u^2+k_{qm}^2)(u^2+k_{no}^2)}uk_{no} \times$$

$$\left[\frac{\alpha_{ik}}{u^2R^2} + \frac{\alpha_{ik}+\beta_{ik}}{u^3R^3} + \frac{2\beta_{ik}}{u^4R^4} + \frac{\beta_{ik}}{u^5R^5}\right]. \qquad (4.3.8)$$

On rotational averaging, both terms of (4.3.8) vanish since $\varepsilon_{ij\ell}$ is antisymmetric to index interchange in contrast to α_{ik} and β_{ik} which are symmetric. When both molecules are excited, all three terms of (4.3.5) contribute with the geometric part of the second term of (4.3.5) similar to that of the first term of (4.3.8), while the u-integral term is identical to that occurring in (4.3.6), but with both molecules now

excited. Once again the energy shift vanishes for isotropic source and test bodies.

4.4 THE INTERACTION BETWEEN AN ELECTRIC DIPOLE POLARISABLE MOLECULE AND AN ELECTRIC DIPOLE-QUADRUPOLE POLARISABLE MOLECULE

For a consistent treatment of intermolecular interaction energies between neutral molecules, the effects arising from the inclusion of the electric quadrupole coupling term is now investigated. The magnetic dipole and electric quadrupole are both of the same order, being a factor of the fine structure constant smaller than the electric dipole interaction.

By utilising the Maxwell fields which depend upon an electric quadrupole source, the number of interaction energy shifts to be determined between molecules with differing polarisability characteristics, now greatly increases. Bearing in mind that only terms of a comparable order are being studied, the number of electric dipole dependent interactions occurring between the two centres is restricted to a minimum of two. The energy shift is determined from

$$
\begin{aligned}
\Delta E = &\ \frac{-1}{2\varepsilon_0^2} \sum_m \alpha_{ij}^A(\omega_{qm}) \left[d_i^{(1)}(\vec{\mu};\omega_{qm}) d_j^{(1)}(\vec{Q};\omega_{qm}) + d_i^{(1)}(\vec{Q};\omega_{qm}) d_j^{(1)}(\vec{\mu};\omega_{qm}) \right] \\
&\ \frac{-1}{2\varepsilon_0^2} \sum_n A_{k\ell m}^B(\omega_{pn}) \left[d_k^{(1)}(\vec{\mu};\omega_{pn}) \nabla_m d_\ell^{(1)}(\vec{\mu};\omega_{pn}) + \nabla_m d_\ell^{(1)}(\vec{\mu};\omega_{pn}) d_k^{(1)}(\vec{\mu};\omega_{pn}) \right] \\
&\ \frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \alpha_{ij}^A(\omega) \left[d_i^{(0)} d_j^{(2)}(\vec{\mu}\vec{Q}) + d_i^{(2)}(\vec{\mu}\vec{Q}) d_j^{(0)} \right] \\
&\ \frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} A_{k\ell m}^B(\omega) \left[d_k^{(0)} \nabla_m d_\ell^{(2)}(\vec{\mu}\vec{\mu}) + d_k^{(2)}(\vec{\mu}\vec{\mu}) \nabla_m d_\ell^{(0)} + \right. \\
&\ \left. \nabla_m d_\ell^{(0)} d_k^{(2)}(\vec{\mu}\vec{\mu}) + \nabla_m d_\ell^{(2)}(\vec{\mu}\vec{\mu}) d_k^{(0)} \right]
\end{aligned}
\qquad (4.4.1)
$$

where $A_{k\ell m}(\omega)$ is the mixed electric dipole-quadrupole tensor defined by

$$A_{ijk}(\omega) = \sum_{r} \left\{ \frac{\mu_i^{qr} Q_{jk}^{rq}}{E_{rq}-\hbar\omega} + \frac{Q_{jk}^{qr}\mu_i^{rq}}{E_{rq}+\hbar\omega} \right\} = \sum_{r} \frac{2E_{rq}\mu_i^{qr} Q_{jk}^{rq}}{E_{rq}^2-(\hbar\omega)^2} . \tag{4.4.2}$$

Using the $\vec{\mu}$- and $\vec{Q}$-dependent parts of the displacement field linear in the sources (2.2.34), the contribution from the product of the first order fields is found to be

$$\frac{1}{32\pi^2\varepsilon_0^2} \sum_{m} \alpha_{ij}^A(k_{qm})\mu_k^{qm}Q_{\ell m}^{mq}k_{qm}^7 \left[\bar{f}_{ik}(k_{qm}R)h_{j\ell m}(k_{qm}R)-\bar{h}_{j\ell m}(k_{qm}R)f_{ik}(k_{qm}R) \right] +$$

$$\frac{1}{32\pi^2\varepsilon_0^2} \sum_{n} A_{k\ell m}^B(k_{pn})\mu_i^{pn}\mu_j^{np}k_{pn}^7 \left[\bar{f}_{ki}(k_{pn}R)h_{m\ell j}(k_{pn}R)-\bar{h}_{m\ell j}(k_{pn}R)f_{ki}(k_{pn}R) \right] .$$

$$\tag{4.4.3}$$

Employing (3.1.1) and (3.1.4), the contribution from the zeroth and second order fields is

$$\frac{i}{8\pi\varepsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right) \alpha_{ij}^A(\omega) [e_i e^{i\vec{k}.\vec{R}}(\bar{e}_m k_\ell \bar{\mathcal{E}}_{\ell m j}+i\bar{e}_k \bar{\mathcal{F}}_{kj})+(e_m k_\ell \bar{\mathcal{E}}_{\ell m i}+ie_k \bar{\mathcal{F}}_{ki})\bar{e}_j e^{-i\vec{k}.\vec{R}}]$$

$$+ \frac{1}{8\pi\varepsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right) A_{k\ell m}^B(\omega) [e_k e^{-i\vec{k}.\vec{R}}\bar{e}_j(\nabla_m \bar{\mathcal{A}}_{j\ell}) - ie_j k_m \mathcal{A}_{j k}\bar{e}_\ell e^{i\vec{k}.\vec{R}}$$

$$+ie_\ell k_m e^{-i\vec{k}.\vec{R}}\bar{e}_j \bar{\mathcal{A}}_{jk} + e_j(\nabla_m \mathcal{A}_{j\ell})\bar{e}_k e^{i\vec{k}.\vec{R}}] . \tag{4.4.4}$$

Evaluating (4.4.4) in the usual manner and taking account of (4.4.3)

$$\Delta E = \frac{1}{16\pi^2\varepsilon_0^2} \sum_{\substack{m \\ E_q > E_m}} \alpha_{ij}^A(k_{qm})\mu_k^{qm}Q_{\ell m}^{mq}k_{qm}^7\left[\bar{f}_{i\ell}(k_{qm}R)h_{j\ell m}(k_{qm}R)-\bar{h}_{j\ell m}(k_{qm}R)f_{i\ell}(k_{qm}R)\right]$$

$$+ \frac{1}{16\pi^2\varepsilon_0^2} \sum_{\substack{n \\ E_n < E_p}} A_{\ell\ell m}^B(k_{pn})\mu_i^{pn}\mu_j^{np}k_{pn}^7\left[\bar{f}_{\ell i}(k_{pn}R)h_{m\ell j}(k_{pn}R)-\bar{h}_{m\ell j}(k_{pn}R)f_{\ell i}(k_{pn}R)\right]$$

$$+ \frac{i\hbar c}{16\pi^3\varepsilon_0^2} \int_0^\infty du\, u^7 e^{-2uR}\alpha_{ij}^A(icu)A_{\ell\ell m}^B(icu)f_{i\ell}(iuR)h_{j\ell m}(iuR). \qquad (4.4.5)$$

Examining the u-integral term of (4.4.5), the sole contribution if both molecules are in the ground state, leads to the dispersion potential

$$\frac{-1}{4\pi^3\varepsilon_0^2\hbar c}\sum_{m,n}\mu_i^{0n}\mu_j^{n0}\mu_k^{0m}Q_{\ell m}^{m0}\int_0^\infty\frac{du\, u^7 e^{-2uR}}{(u^2+k_{mo}^2)(u^2+k_{no}^2)}k_{mo}k_{no}\times$$

$$\left[\frac{A_{ij\ell\ell m}}{u^2R^2}+\frac{B_{ij\ell\ell m}}{u^3R^3}+\frac{C_{ij\ell\ell m}}{u^4R^4}+\frac{D_{ij\ell\ell m}}{u^5R^5}+\frac{E_{ij\ell\ell m}}{u^6R^6}+\frac{F_{ij\ell\ell m}}{u^7R^7}\right] \qquad (4.4.6)$$

with the tensors $A_{ij\ell\ell m}$ to $F_{ij\ell\ell m}$ given in the Appendix to this Chapter. Expression (4.4.6) vannishes on averaging. If B is in an excited state, the second term of (4.4.5) does not contribute. The first term of (4.4.5) however, after multiplying the geometric tensors, can be written

$$\frac{1}{16\pi^2\varepsilon_0^2}\sum_{\substack{m \\ E_q > E_m}}\alpha_{ij}^A(k_{qm})\mu_k^{qm}Q_{\ell m}^{mq}k_{qm}^7\left[\frac{a_{ij\ell\ell m}}{k_{qm}^2R^2}+\frac{b_{ij\ell\ell m}}{k_{qm}^3R^3}+\frac{c_{ij\ell\ell m}}{k_{qm}^4R^4}+\frac{d_{ij\ell\ell m}}{k_{qm}^5R^5}+\frac{e_{ij\ell\ell m}}{k_{qm}^6R^6}+\frac{f_{ij\ell\ell m}}{k_{qm}^7R^7}\right].$$

$$(4.4.7)$$

The near-zone result has an R^{-7} dependence while the far-zone varies as R^{-2}, with (4.4.7) vanishing on averaging. The u-integral term from (4.4.5) is analogous to (4.4.6) with B excited. When both molecules are excited, all three terms of (4.4.5) contribute for oriented A and B.

4.5 THE INTERACTION BETWEEN TWO CHIRAL MOLECULES

The energy shift between two non-identical chiral molecules with each centre possessing an electric and a magnetic dipole moment, is given by

$$
\begin{aligned}
\Delta E = \ & \mathrm{Im}\ \frac{i}{\varepsilon_0} \sum_m G^A_{ij}(\omega_{qm})\left[d^{(1)}_i(\vec{\mu};\omega_{qm})b^{(1)}_j(\vec{m};\omega_{qm})+d^{(1)}_i(\vec{m};\omega_{qm})b^{(1)}_j(\vec{\mu};\omega_{qm})\right] + \\
& \mathrm{Im}\ \frac{i}{\varepsilon_0} \sum_n G^B_{k\ell}(\omega_{pn})\left[d^{(1)}_k(\vec{\mu};\omega_{pn})b^{(1)}_\ell(\vec{m};\omega_{pn})+d^{(1)}_k(\vec{m};\omega_{pn})b^{(1)}_\ell(\vec{\mu};\omega_{pn})\right] - \\
& \mathrm{Im}\ \frac{i}{\varepsilon_0} \sum_{\vec{k},\lambda} G^A_{ij}(\omega)\left[b^{(0)}_j d^{(2)}_i(\vec{\mu}\vec{m}) +b^{(2)}_j(\vec{\mu}\vec{m})d^{(0)}_i\right] - \\
& \mathrm{Im}\ \frac{i}{\varepsilon_0} \sum_{\vec{k},\lambda} G^B_{k\ell}(\omega)\left[b^{(0)}_\ell d^{(2)}_k(\vec{\mu}\vec{m}) +b^{(2)}_\ell(\vec{\mu}\vec{m})d^{(0)}_k\right] ,
\end{aligned}
\qquad (4.5.1)
$$

including all terms second order in the transition moments. The contribution to the interaction energy from the product of the first order fields is evaluated using the electric and magnetic dipole dependent terms of the Maxwell fields linear in the sources (2.2.34) and (2.2.55), and is

$$
\begin{aligned}
\Delta E = \ & \mathrm{Im}\left\{\frac{-i}{16\pi^2\varepsilon_0^2 c^2}\sum_m G^A_{ij}(k_{qm})k^6_{qm}\left[\mu^{qm}_k m^{mq}_\ell f_{i\ell}(k_{qm}R)f_{j\ell}(k_{qm}R) - \right.\right. \\
& \left.\left. m^{qm}_k \mu^{mq}_\ell g_{i\ell}(k_{qm}R)g_{j\ell}(k_{qm}R)\right]\right\} + \\
& \mathrm{Im}\left\{\frac{-i}{16\pi^2\varepsilon_0^2 c^2}\sum_n G^B_{k\ell}(k_{pn})k^6_{pn}\left[\mu^{pn}_i m^{np}_j f_{ki}(k_{pn}R)f_{\ell j}(k_{pn}R) - \right.\right. \\
& \left.\left. m^{pn}_j \mu^{np}_i g_{ki}(k_{pn}R)g_{\ell j}(k_{pn}R)\right]\right\} .
\end{aligned}
\qquad (4.5.2)
$$

For the contribution from the zeroth and second order fields, use is made of the free fields (2.2.15) and (2.2.52), and the diagonal matrix elements of the quadratic fields (3.1.2) and (3.1.8), giving

$$- \operatorname{Im}\left\{ \sum_{\vec{k},\lambda} \frac{i\hbar k}{8\pi\varepsilon_0^2 cV} G^A_{ij}(\omega) [b_j e^{i\vec{k}\cdot\vec{R}} (\bar{b}_\ell \mathcal{B}_{\ell i} + \bar{e}_\ell \mathcal{E}_{\ell i}) + (b_\ell \mathcal{X}_{\ell j} + e_\ell \mathcal{L}_{\ell j}) \bar{e}_i e^{-i\vec{k}\cdot\vec{R}}] \right\}$$

$$- \operatorname{Im}\left\{ \sum_{\vec{k},\lambda} \frac{i\hbar k}{8\pi\varepsilon_0^2 cV} G^B_{k\ell}(\omega) [b_\ell e^{-i\vec{k}\cdot\vec{R}} (\bar{b}_i \mathcal{B}_{i k} + \bar{e}_i \mathcal{E}_{i k}) + (b_i \mathcal{X}_{i\ell} + e_i \mathcal{L}_{i\ell}) \bar{e}_k e^{i\vec{k}\cdot\vec{R}}] \right\}.$$

$$(4.5.3)$$

Evaluating the terms of (4.5.3) using the appropriate polarisation sums, angular integrals and definitions of the tensor fields and adding the contribution from the first order fields (4.5.2), the interaction energy between two chiral molecules is

$$\Delta E = \frac{-1}{8\pi^2 \varepsilon_0^2 c^2} \sum_{\substack{m \\ E_q > E_m}} G^A_{ij}(k_{qm}) k^6_{qm} \left[\mu^{qm}_k m^{mq}_\ell \bar{f}_{ik}(k_{qm}R) f_{j\ell}(k_{qm}R) - \right.$$

$$\left. m^{qm}_k \mu^{mq}_\ell \bar{g}_{ik}(k_{qm}R) g_{j\ell}(k_{qm}R) \right] +$$

$$\frac{-1}{8\pi^2 \varepsilon_0^2 c^2} \sum_{\substack{n \\ E_p > E_n}} G^B_{k\ell}(k_{pn}) k^6_{pn} \left[\mu^{pn}_i m^{np}_j \bar{f}_{ki}(k_{pn}R) f_{\ell j}(k_{pn}R) - \right.$$

$$\left. m^{pn}_j \mu^{np}_i \bar{g}_{ki}(k_{pn}R) g_{\ell j}(k_{pn}R) \right]$$

$$- \frac{1}{16\pi^3 \varepsilon_0^2 c^2} \sum_{\substack{m \\ \text{ALL } E_m}} \mu^{qm}_k m^{mq}_\ell \int_0^\infty \frac{2i du\, u^7 e^{-2uR}}{u^2 + k^2_{qm}} G^A_{ij}(icu) \times$$

$$\left[f_{ik}(iuR) f_{j\ell}(iuR) - g_{ik}(iuR) g_{j\ell}(iuR) \right]. \qquad (4.5.4)$$

When both molecules are in the ground state only the u-integral term of (4.5.4) survives, which when written explicitly in terms of transition moments after multiplication of the geometric tensors, is

$$- \frac{1}{4\pi^3\varepsilon_0^2\hbar c^3} \sum_{m,n} \mu_i^{0n}m_j^{n0}\mu_k^{0m}m_\ell^{m0} \int_0^\infty \frac{du\, u^8 e^{-2uR}}{(u^2+k_{0m}^2)(u^2+k_{0n}^2)} \times$$

$$\left\{ \frac{a_{ij k\ell}}{u^2 R^2} + \frac{b_{ij k\ell}}{u^3 R^3} + \frac{c_{ij k\ell}}{u^4 R^4} + \frac{d_{ij k\ell}}{u^5 R^5} + \frac{e_{ij k\ell}}{u^6 R^6} \right\} \qquad (4.5.5)$$

with

$$a_{ij k\ell} = \alpha_{ik}\alpha_{j\ell} - \varepsilon_{i\ell s}\varepsilon_{jkt}\hat{R}_s\hat{R}_t$$

$$b_{ij k\ell} = \alpha_{ik}\beta_{j\ell} + \beta_{ik}\alpha_{j\ell} - 2\varepsilon_{i\ell s}\varepsilon_{jkt}\hat{R}_s\hat{R}_t$$

$$c_{ij k\ell} = \alpha_{ik}\beta_{j\ell} + \beta_{ik}\alpha_{j\ell} + \beta_{ik}\beta_{j\ell} - \varepsilon_{i\ell s}\varepsilon_{jkt}\hat{R}_s\hat{R}_t$$

$$d_{ij k\ell} = 2\beta_{ik}\beta_{j\ell}$$

$$e_{ij k\ell} = \beta_{ik}\beta_{j\ell} \qquad (4.5.6)$$

The expression (4.5.5) applies when the orientations of molecules A and B are fixed relative to each other. It may also be written in terms of the molecular polarisability tensor $G_{ij}(\omega)$,

$$\frac{\hbar}{16\pi^3\varepsilon_0^2 c} \int_0^\infty du\, u^6 e^{-2uR} G_{ij}^A(icu) G_{k\ell}^B(icu) \times$$

$$\left\{ \frac{a_{ij k\ell}}{u^2 R^2} + \frac{b_{ij k\ell}}{u^3 R^3} + \frac{c_{ij k\ell}}{u^4 R^4} + \frac{d_{ij k\ell}}{u^5 R^5} + \frac{e_{ij k\ell}}{u^6 R^6} \right\} \qquad (4.5.7)$$

or in terms of the rotatory strength $R_{ij}^{s0} = \mathrm{Im}\mu_i^{0s}m_j^{s0}$. To deal with molecules in the fluid phase, a rotational average of (4.5.5) is needed. By following the standard procedure [41], the dispersion interaction for two freely rotating chiral molecules valid for all separation distances beyond electron overlap, is

$$- \frac{1}{18\pi^3\varepsilon_0^2\hbar c^3 R^4} \sum_{m,n} |\vec{\mu}^{0m}\cdot\vec{m}^{m0}| |\vec{\mu}^{0n}\cdot\vec{m}^{n0}| \int_0^\infty \frac{du\, u^4 e^{-2uR}}{(u^2+k_{0m}^2)(u^2+k_{0n}^2)} \left[4 + \frac{6}{uR} + \frac{3}{u^2 R^2} \right].$$

$$(4.5.8)$$

After the usual approximations, the far-zone limit is [48]

$$\Delta E_{FZ} = \frac{-\hbar^3 c}{3\pi^3 \varepsilon_0^2 R^9} \sum_{m,n} \frac{|\vec{\mu}^{0m}.\vec{m}^{m0}||\vec{\mu}^{0n}.\vec{m}^{n0}|}{E_{m0}^2 E_{n0}^2} \qquad (4.5.9)$$

while the near-zone shift is [48,58]

$$\Delta E_{NZ} = \frac{-1}{12\pi^2 \varepsilon_0^2 c^2 R^6} \sum_{m,n} \frac{|\vec{\mu}^{0m}.\vec{m}^{m0}||\vec{\mu}^{0n}.\vec{m}^{n0}|}{E_{m0}+E_{n0}} . \qquad (4.5.10)$$

This completes the evaluation of the dispersion interaction between two chiral molecules, originating from the third term of (4.5.4). The result for all R is given by (4.5.8) while the results at large and small intermolecular separations are respectively given by (4.5.9) and (4.5.10). This interaction potential is discriminatory, dependent upon the relative chirality of the molecules of the pair. The polarisability tensor $G_{ij}(\omega)$ changes sign with enantiomer since $\vec{\mu}$, a polar vector, is antisymmetric to inversion, in contrast to $\vec{m}$ which is symmetric. For molecules with absolute configurations R and S, the A(R)-B(R) and A(R)-B(S) interactions differ in sign. Since the rotatory strength maybe either greater or less than zero, it is not possible to determine the absolute sign of the interaction when the molecules are chemically distinct. For chemically identical molecules however, the energy shift for opposite isomers is attractive while that for like isomers is repulsive. The complete ground state interaction, along with the R^{-9} far-zone and R^{-6} short range dependences agree with work carried out in the Schrödinger picture [6,38,58] and the calculation performed by Mavroyannis and Stephen [48] in the Lorentz gauge, in which only the limiting results were given. It is worth noting that the near-zone

result may be obtained from second order perturbation theory when the interaction is represented by an electric and a magnetic dipolar coupling term and the mixed electric-magnetic cross term is extracted [58]. This is examined in more detail in the final Section to this Chapter.

Returning to the general result (4.5.4) and examining the case in which molecule B is in the ground state and A is excited, the additional contribution from downward transitions from $|p\rangle$ from the second term of (4.5.4) is

$$
\frac{-1}{8\pi^2 \varepsilon_0^2 c^2} \sum_{\substack{n \\ E_p > E_n}} G_{k\ell}^B (k_{pn}) \mu_i^{pn} m_j^{np} k_{pn}^6 \left[\frac{(\alpha_{ik}\alpha_{j\ell} + \varepsilon_{j\ell s}\varepsilon_{ik t}\hat{R}_s\hat{R}_t)}{k_{pn}^2 R^2} + \right.
$$
$$
\left. \frac{i(\beta_{ik}\alpha_{j\ell} - \alpha_{ik}\beta_{j\ell})}{k_{pn}^3 R^3} + \frac{(\beta_{ik}\beta_{j\ell} - \alpha_{ik}\alpha_{j\ell} - \beta_{ik}\alpha_{j\ell} + \varepsilon_{ik t}\varepsilon_{j\ell s}\hat{R}_s\hat{R}_t)}{k_{pn}^4 R^4} + \frac{\beta_{ik}\beta_{j\ell}}{k_{pn}^6 R^6} \right] \qquad (4.5.11)
$$

which for an isotropic source and test becomes

$$
- \frac{1}{12\pi^2 \varepsilon_0^2 c^2} \sum_{\substack{n \\ E_p > E_n}} G^B(k_{pn}) |\vec{\mu}^{pn} \cdot \vec{m}^{np}| k_{pn}^6 \left[\frac{2}{k_{pn}^2 R^2} + \frac{2}{k_{pn}^4 R^4} + \frac{3}{k_{pn}^6 R^6} \right]. \qquad (4.5.12)
$$

The far-zone limit of (4.5.12) is

$$
- \frac{1}{6\pi^2 \varepsilon_0^2 c^2 R^2} \sum_{\substack{n \\ E_p > E_n}} G^B(k_{pn}) |\vec{\mu}^{pn} \cdot \vec{m}^{np}| k_{pn}^4 \qquad (4.5.13)
$$

exhibiting an R^{-2} dependence, being associated with real photon emission. This is also the dominant contribution as the asymptotic behaviour of the u-integral term shows an R^{-9} dependence as demonstrated

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earlier. For small R, the near-zone limit of (4.5.12) is

$$- \frac{1}{4\pi^2 \varepsilon_0^2 c^2 R^6} \sum_{\substack{n \\ E_p > E_n}} G^B(k_{pn}) \, |\vec{\mu}^{pn} . \vec{m}^{np}| \qquad (4.5.14)$$

while that from the u-integral is

$$\frac{-1}{12\pi^2 \varepsilon_0^2 c^2 R^6} \sum_{m,n} \text{sgn}(E_{np}) \, \frac{|\vec{\mu}^{0m} . \vec{m}^{m0}| \, |\vec{\mu}^{pn} . \vec{m}^{np}|}{(E_{m0} + |E_{np}|)} \qquad (4.5.15)$$

both terms exhibiting R^{-6} dependences. The sum of (4.5.14) and (4.5.15) gives the total small R limit

$$\frac{-1}{12\pi^2 \varepsilon_0^2 c^2 R^6} \sum_{\substack{m,n \\ \text{ALL } E_n}} \frac{|\vec{\mu}^{0m} . \vec{m}^{m0}| \, |\vec{\mu}^{pn} . \vec{m}^{np}|}{(E_{m0} + E_{np})} , \qquad (4.5.16)$$

which is composed of both real and virtual photon terms.

If both molecules are in electronically excited states, all three terms of (4.5.4) contribute. The first term of (4.5.4), the additional contribution due to excited molecule B is

$$- \frac{1}{12\pi^2 \varepsilon_0^2 c^2} \sum_{\substack{m \\ E_q > E_m}} G^A(k_{qm}) \, |\vec{\mu}^{qm} . \vec{m}^{mq}| \, k_{qm}^6 \left[\frac{2}{k_{qm}^2 R^2} + \frac{2}{k_{qm}^4 R^4} + \frac{3}{k_{qm}^6 R^6} \right] \qquad (4.5.17)$$

with the second term of (4.5.4) given by (4.5.12), remembering that B is now excited, while the u-integral term can be written analogous to (4.5.8) as

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$$-\frac{1}{18\pi^3\varepsilon_0^2\hbar c^3 R^4}\sum_{m,n}|\vec{\mu}^{qm}.\vec{m}^{mq}||\vec{\mu}^{pn}.\vec{m}^{np}|\int_0^\infty\frac{du\,u^4e^{-2uR}}{(k_{qm}^2+u^2)(k_{pn}^2+u^2)}\left[4+\frac{6}{uR}+\frac{3}{u^2R^2}\right].$$

$$(4.5.18)$$

For large R the interaction energy has an inverse square dependence on separation, arising from the addition of the real photon exchange terms (4.5.12) and (4.5.17). In the near-zone, the downward transition contributions to the interaction energy shift are

$$-\frac{1}{4\pi^2\varepsilon_0^2c^2R^6}\sum_{\substack{m\\E_q>E_m}}G^A(k_{qm})|\vec{\mu}^{qm}.\vec{m}^{mq}|-\frac{1}{4\pi^2\varepsilon_0^2c^2R^6}\sum_{\substack{n\\E_p>E_n}}G^B(k_{pn})|\vec{\mu}^{pn}.\vec{m}^{np}|$$

$$\frac{-1}{12\pi^2\varepsilon_0^2c^2R^6}\sum_{m,n}\mathrm{sgn}(E_{np})\mathrm{sgn}(E_{mq})\frac{|\vec{\mu}^{qm}.\vec{m}^{mq}||\vec{\mu}^{pn}.\vec{m}^{np}|}{(|E_{mq}|+|E_{np}|)}\qquad(4.5.19)$$

which simplifies to

$$\frac{-1}{12\pi^2\varepsilon_0^2c^2R^6}\sum_{\substack{m,n\\E_p>E_n\\E_q>E_m}}\frac{|\vec{\mu}^{qm}.\vec{m}^{mq}||\vec{\mu}^{pn}.\vec{m}^{np}|}{(E_{mq}+E_{np})}.\qquad(4.5.20)$$

4.6 THE INTERACTION BETWEEN AN ELECTRIC DIPOLE POLARISABLE MOLECULE AND A MAGNETIC DIPOLE POLARISABLE MOLECULE

For molecules with small electric dipole polarisability and large magnetic susceptibility, the most important interaction is that between an electric dipole polarisable molecule and a magnetic dipole polarisable molecule, which is now examined. The energy of interaction is given by

$$\Delta E = \frac{-1}{2\varepsilon_0^2} \sum_m \alpha_{ij}^A(\omega_{qm}) d_i^{(1)}(\vec{m};\omega_{qm}) d_j^{(1)}(\vec{m};\omega_{qm})$$

$$-\frac{1}{2} \sum_n \chi_{k\ell}^B(\omega_{pn}) b_k^{(1)}(\vec{\mu};\omega_{pn}) b_\ell^{(1)}(\vec{\mu};\omega_{pn})$$

$$\frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \alpha_{ij}^A(\omega) \left[d_i^{(0)} d_j^{(2)}(\vec{m}\vec{m}) + d_i^{(2)}(\vec{m}\vec{m}) d_j^{(0)} \right]$$

$$-\frac{1}{2} \sum_{\vec{k},\lambda} \chi_{k\ell}^B(\omega) \left[b_k^{(0)} b_\ell^{(2)}(\vec{\mu}\vec{\mu}) + b_k^{(2)}(\vec{\mu}\vec{\mu}) b_\ell^{(0)} \right] \qquad (4.6.1)$$

where the magnetic susceptibility tensor $\chi_{ij}(\omega)$ is defined as

$$\chi_{ij}(\omega) = \sum_r \left\{ \frac{m_i^{qr} m_j^{rq}}{E_{rq} - \hbar\omega} + \frac{m_j^{qr} m_i^{rq}}{E_{rq} + \hbar\omega} \right\} = \sum_r \frac{2 E_{rq} m_i^{qr} m_j^{rq}}{E_{rq}^2 - (\hbar\omega)^2} . \qquad (4.6.2)$$

Using (2.2.34) for the electric displacement field of a magnetic dipole and (2.2.55) for the magnetic field of an electric dipole source, the contribution to the energy shift from the product of the first order fields is

$$\frac{-1}{32\pi^2 \varepsilon_0^2 c^2} \sum_m \alpha_{ij}^A(k_{qm}) m_k^{qm} m_\ell^{mq} k_{qm}^6 \bar{g}_{ik}(k_{qm}R) g_{j\ell}(k_{qm}R)$$

$$\frac{-1}{32\pi^2 \varepsilon_0^2 c^2} \sum_n \chi_{k\ell}^B(k_{pn}) \mu_i^{pn} \mu_j^{np} k_{pn}^6 \bar{g}_{ik}(k_{pn}R) g_{j\ell}(k_{pn}R). \qquad (4.6.3)$$

Employing (3.1.4) and (3.1.7), the contribution from the free and second order fields is

$$\frac{-1}{8\pi\varepsilon_0^2 c} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) \alpha_{ij}^A(\omega) [e_i e^{i\vec{k}\cdot\vec{R}} \bar{b}_\ell \mathcal{D}_{\ell j} + b_\ell \mathcal{D}_{\ell i} \bar{e}_j e^{-i\vec{k}\cdot\vec{R}}]$$

$$\frac{-1}{8\pi\varepsilon_0^2 c} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) \chi_{k\ell}^B(\omega) [b_k e^{-i\vec{k}\cdot\vec{R}} \bar{e}_i \mathcal{J}_{i\ell} + e_i \mathcal{J}_{ik} \bar{b}_\ell e^{i\vec{k}\cdot\vec{R}}]. \qquad (4.6.4)$$

Evaluating the terms of (4.6.4), noting that upward and downward transitions from both $|q\rangle$ and $|p\rangle$ respectively cancel and reinforce with the corresponding terms from (4.6.3), the energy shift is

$$\Delta E = \frac{-1}{16\pi^2\varepsilon_0^2 c^2} \sum_{\substack{m \\ E_q > E_m}} \alpha_{ij}^A(k_{qm}) m_k^{qm} m_\ell^{mq} k_{qm}^6 \bar{g}_{ik}(k_{qm}R) g_{j\ell}(k_{qm}R)$$

$$\frac{-1}{16\pi^2\varepsilon_0^2 c^2} \sum_{\substack{n \\ E_p > E_n}} \chi_{k\ell}^B(k_{pn}) \mu_i^{pn} \mu_j^{np} k_{pn}^6 \bar{g}_{ik}(k_{pn}R) g_{j\ell}(k_{pn}R)$$

$$\frac{-\hbar}{32\pi^3\varepsilon_0^2 c} \int_0^\infty du\, u^6 e^{-2uR} \alpha_{ij}^A(icu) \chi_{k\ell}^B(icu) g_{j\ell}(iuR) g_{ik}(iuR). \tag{4.6.5}$$

When both molecules are excited, all three terms of (4.6.5) contribute, which after expanding the geometrical tensors, becomes

$$\frac{-1}{16\pi^2\varepsilon_0^2 c^2} \sum_{\substack{m \\ E_q > E_m}} \alpha_{ij}^A(k_{qm}) m_k^{qm} m_\ell^{mq} k_{qm}^6 \varepsilon_{iks}\varepsilon_{j\ell t}\hat{R}_s\hat{R}_t\left[\frac{1}{k_{qm}^2 R^2} + \frac{1}{k_{qm}^4 R^4}\right]$$

$$\frac{-1}{16\pi^2\varepsilon_0^2 c^2} \sum_{\substack{n \\ E_p > E_n}} \chi_{k\ell}^B(k_{pn}) \mu_i^{pn} \mu_j^{np} k_{pn}^6 \varepsilon_{iks}\varepsilon_{j\ell t}\hat{R}_s\hat{R}_t\left[\frac{1}{k_{pn}^2 R^2} + \frac{1}{k_{pn}^4 R^4}\right] +$$

$$\frac{1}{8\pi^3\varepsilon_0^2 \hbar c^3}\varepsilon_{j\ell t}\varepsilon_{iks}\hat{R}_s\hat{R}_t \sum_{m,n} \mu_i^{pn}\mu_j^{np} m_k^{qm} m_\ell^{mq} \times$$

$$\int_0^\infty \frac{du\, u^6 e^{-2uR}}{(u^2+k_{qm}^2)(u^2+k_{pn}^2)} k_{mq}k_{np}\left[\frac{1}{u^2 R^2} + \frac{2}{u^3 R^3} + \frac{1}{u^4 R^4}\right] \tag{4.6.6}$$

which after rotational averaging becomes for isotropic source and test bodies

$$\frac{-1}{24\pi^2\varepsilon_0^2 c^2} \sum_{\substack{m \\ E_q > E_m}} \alpha^A(k_{qm}) |\vec{m}^{qm}|^2 k_{qm}^6 \left[\frac{1}{k_{qm}^2 R^2} + \frac{1}{k_{qm}^4 R^4}\right]$$

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$$\frac{-1}{24\pi^2\varepsilon_0^2 c^2} \sum_{\substack{n \\ E_p > E_n}} \chi^B(k_{pn}) |\vec{\mu}^{pn}|^2 k_{pn}^6 \left[\frac{1}{k_{pn}^2 R^2} + \frac{1}{k_{pn}^4 R^4}\right] +$$

$$\frac{1}{36\pi^3\varepsilon_0^2 \hbar c^3} \sum_{m,n} |\vec{\mu}^{pn}|^2 |\vec{m}^{qm}|^2 \times$$

$$\int_0^\infty \frac{du\, u^6 e^{-2uR}}{(u^2+k_{qm}^2)(u^2+k_{np}^2)} k_{mq} k_{np} \left[\frac{1}{u^2 R^2} + \frac{2}{u^3 R^3} + \frac{1}{u^4 R^4}\right]. \qquad (4.6.7)$$

The first two terms of (4.6.7) exhibit R^{-2} far-zone and R^{-4} near-zone dependences, in agreement (3.2.58) and (3.2.59), the energy shifts resulting from a test magnetic dipole polarisable molecule to the magnetic energy density of an electric dipole source field. The asymptotic behaviour of the u-integral term of (4.6.7) is readily found to be

$$\Delta E_{NZ} = \frac{1}{72\pi^2\varepsilon_0^2 \hbar^2 c^4 R^4} \sum_{m,n} (\operatorname{sgn}E_{np})(\operatorname{sgn}E_{mq}) |E_{np}| |E_{mq}| \frac{|\vec{\mu}^{pn}|^2 |\vec{m}^{qm}|^2}{(|E_{np}| + |E_{mq}|)}$$

$$(4.6.8)$$

$$\Delta E_{FZ} = \frac{7\hbar}{64\pi^3\varepsilon_0^2 cR^7} \alpha^A(0)\chi^B(0) \qquad (4.6.9)$$

where $\alpha(0)$ and $\chi(0)$ represent isotropic static susceptibility tensors for the excited molecules. The far-zone limit of the intermolecular interaction energy (4.6.9) is identical to (3.2.33), the latter having been derived from the energy density. The R^{-4} near-zone dependence is a direct consequence of the absence of static coupling between an electric and a magnetic dipole, in contrast to the R^{-6} small limit found in Section 4.2 when dealing with two electric dipole polarisable molecules.

The overall far-zone behaviour is dominated by the additional contributions from downward transitions, exhibiting R^{-2} distance

dependence due to real photon emission, since the u-integral term was shown to produce an R^{-7} dependence as seen in (4.6.9). From the first two terms of (4.6.7), the far-zone limit is

$$\frac{-1}{36\pi^2 \epsilon_0^2 c^2 R^2 (\hbar c)^4} \sum_{\substack{m,n \\ E_p > E_n \\ E_q > E_m}} \frac{|\vec{\mu}^{pn}|^2 |\vec{m}^{qm}|^2}{E_{np}^2 - E_{qm}^2} \left[E_{qm}^4 E_{np} + E_{np}^4 E_{mq} \right]. \tag{4.6.10}$$

The overall near-zone behaviour for two excited molecules arises from contributions from all three terms of (4.6.7).

If, for instance molecule B is in the ground state while A remains excited, the second and third terms of (4.6.7) contribute to the energy shift with $|q\rangle = 0$, the behaviour of the two terms having already been discussed. When both molecules are in the ground state, the u-integral term of (4.6.7) survives to give the dispersion potential

$$\frac{1}{36\pi^3 \epsilon_0^2 \hbar c^3} \sum_{m,n} |\vec{\mu}^{no}|^2 |\vec{m}^{mo}|^2 \int_0^\infty \frac{du\, u^6 e^{-2uR}}{(u^2 + k_{mo}^2)(u^2 + k_{no}^2)} k_{mo} k_{no} \left[\frac{1}{u^2 R^2} + \frac{2}{u^3 R^3} + \frac{1}{u^4 R^4} \right]$$

$$\tag{4.6.11}$$

giving the limiting results

$$\Delta E_{NZ} = \frac{1}{72\pi^2 \epsilon_0^2 \hbar^2 c^4 R^4} \sum_{m,n} \frac{|\vec{\mu}^{no}|^2 |\vec{m}^{mo}|^2}{E_{no} + E_{mo}} E_{no} E_{mo} \tag{4.6.12}$$

$$\Delta E_{FZ} = \frac{7\hbar}{64\pi^3 \epsilon_0^2 c R^7} \alpha^A(0) \chi^B(0) \tag{4.6.13}$$

where the susceptibility tensors now signify molecules in the ground state. These asymptotic values could of course have been obtained

directly from (4.6.8) and (4.6.9) on inserting $|p\rangle = |q\rangle = |0\rangle$. The calculation of the dispersion energy between an electric dipole polarisable molecule and a magnetic dipole polarisable molecule when both molecules are in their ground electronic states, is in agreement with previous studies [35,38,48]. It should be noted that this intermolecular interaction energy is repulsive. Further, the above result is incomplete since no account has been taken of the diamagnetic coupling term, which is one of the same order. This interaction term will be considered in a later Section.

4.7 THE INTERACTION BETWEEN AN ELECTRIC DIPOLE POLARISABLE MOLECULE AND AN ELECTRIC QUADRUPOLE POLARISABLE MOLECULE

The next interaction to be discussed is that between an electric dipole polarisable molecule and an electric quadrupole polarisable species. The energy of interaction between the two is given by

$$
\begin{aligned}
\Delta E = &\frac{-1}{2\varepsilon_0^2} \sum_m \alpha_{ij}^A(\omega_{qm}) d_i^{(1)}(\vec{Q};\omega_{qm}) d_j^{(1)}(\vec{Q};\omega_{qm}) \\
&\frac{-1}{2\varepsilon_0^2} \sum_n \theta_{k\ell mn}^B(\omega_{pn}) [\nabla_\ell d_k^{(1)}(\vec{\mu};\omega_{pn})][\nabla_n d_m^{(1)}(\vec{\mu};\omega_{pn})] \\
&\frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \alpha_{ij}^A(\omega) \left[d_i^{(0)} d_j^{(2)}(\vec{Q}\vec{Q}) + d_i^{(2)}(\vec{Q}\vec{Q}) d_j^{(0)} \right] \\
&\frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \theta_{k\ell mn}^B(\omega) \left[[\nabla_\ell d_k^{(0)}][\nabla_n d_m^{(2)}(\vec{\mu}\vec{\mu})] + [\nabla_\ell d_k^{(2)}(\vec{\mu}\vec{\mu})][\nabla_n d_m^{(0)}] \right]
\end{aligned}
$$

(4.7.1)

where the definition of the quadrupole polarisability tensor is given by

$$\theta_{ijk\ell}(\omega) = \sum_{r}\left\{\frac{Q_{ij}^{qr}Q_{k\ell}^{rq}}{E_{rq}-\hbar\omega}+\frac{Q_{k\ell}^{qr}Q_{ij}^{rq}}{E_{rq}+\hbar\omega}\right\} = \sum_{r}\frac{2E_{rq}Q_{ij}^{qr}Q_{k\ell}^{rq}}{E_{rq}^{2}-(\hbar\omega)^{2}} . \qquad (4.7.2)$$

The contribution arising from the product of the first order fields is obtained from the $\vec{\mu}$- and $\vec{Q}$-dependent parts of (2.2.34), and is

$$\Delta E = \frac{-1}{32\pi^{2}\varepsilon_{0}^{2}} \sum_{m} \alpha_{ij}^{A}(k_{qm})Q_{k\ell}^{qm}Q_{mn}^{mq}k_{qm}^{8}\bar{h}_{ik\ell}(k_{qm}R)h_{jmn}(k_{qm}R)$$

$$\frac{-1}{32\pi^{2}\varepsilon_{0}^{2}} \sum_{n} \theta_{k\ell mn}^{B}(k_{pn})\mu_{i}^{pn}\mu_{j}^{np}k_{pn}^{8}\bar{h}_{\ell k i}(k_{pn}R)h_{nmj}(k_{pn}R) . \qquad (4.7.3)$$

The contribution to the energy shift from the zeroth and second order fields using (3.1.1) and (3.1.6) is

$$\Delta E = \frac{i}{8\pi\varepsilon_{0}^{2}} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right)\alpha_{ij}^{A}(\omega)[e_{i}e^{i\vec{k}\cdot\vec{R}}\bar{e}_{n}k_{m}\mathcal{T}_{mnj}+e_{n}k_{m}\mathcal{T}_{mni}\bar{e}_{j}e^{-i\vec{k}\cdot\vec{R}}]$$

$$\frac{-1}{8\pi\varepsilon_{0}^{2}} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V}\right)\theta_{k\ell mn}^{B}(\omega)[-ik_{\ell}e_{k}e^{-i\vec{k}\cdot\vec{R}}\bar{e}_{i}(\nabla_{n}\bar{\mathcal{A}}_{im})+ie_{i}(\nabla_{\ell}\mathcal{A}_{ik})k_{n}\bar{e}_{m}e^{i\vec{k}\cdot\vec{R}}] . $$

$$(4.7.4)$$

Evaluating the terms of (4.7.4) using the tensor field definitions (3.1.13) and (3.1.21) and adding to the contribution from the first order fields (4.7.3), results in the energy shift

$$\Delta E = \frac{-1}{16\pi^{2}\varepsilon_{0}^{2}} \sum_{\substack{m \\ E_{q}>E_{m}}} \alpha_{ij}^{A}(k_{qm})Q_{k\ell}^{qm}Q_{mn}^{mq}k_{qm}^{8}\bar{h}_{ik\ell}(k_{qm}R)h_{jmn}(k_{qm}R)$$

$$\frac{-1}{16\pi^{2}\varepsilon_{0}^{2}} \sum_{\substack{n \\ E_{p}>E_{n}}} \theta_{k\ell mn}^{B}(k_{pn})\mu_{i}^{pn}\mu_{j}^{np}k_{pn}^{8}\bar{h}_{\ell k i}(k_{pn}R)h_{nmj}(k_{pn}R)$$

$$\frac{-\hbar c}{32\pi^{3}\varepsilon_{0}^{2}} \int_{0}^{\infty}du\, u^{8}e^{-2uR}\alpha_{ij}^{A}(icu)\theta_{k\ell mn}^{B}(icu)h_{ik\ell}(iuR)h_{jnm}(iuR) . \qquad (4.7.5)$$

When both molecules are in the ground state, only the final term of (4.7.5) remains, which when expressed in terms of transition moments is

$$\frac{-1}{8\pi^3\epsilon_0^2\hbar c}\sum_{m,n}\mu_i^{0n}\mu_j^{n0}Q_{k\ell}^{0m}Q_{mn}^{m0}\int_0^{\infty}\frac{du\,u^8\,e^{-2uR}}{(u^2+k_{mo}^2)(u^2+k_{no}^2)}\,k_{mo}k_{no}\times$$

$$\left[\frac{A_{ijk\ell mn}}{u^2R^2}+\frac{B_{ijk\ell mn}}{u^3R^3}+\frac{C_{ijk\ell mn}}{u^4R^4}+\frac{D_{ijk\ell mn}}{u^5R^5}+\frac{E_{ijk\ell mn}}{u^6R^6}+\frac{F_{ijk\ell mn}}{u^7R^7}+\frac{G_{ijk\ell mn}}{u^8R^8}\right]$$

$$(4.7.6)$$

after multiplication of the geometric tensors, whose explicit form in terms of $A_{ijk\ell mn}$ etc., are given in the Appendix at the end of this Chapter. Expression (4.7.6) is applicable at all separation distances outside electron overlap for an oriented molecular pair. To obtain the interaction in the fluid phase, a rotational average is taken. The average entails the product of $\delta_{ij}(-2\delta_{k\ell}\delta_{mn}+3\delta_{km}\delta_{\ell n}+3\delta_{kn}\delta_{\ell m})$ with each of $A_{ijk\ell mn}$ to $G_{ijk\ell mn}$. After the usual approximations, the u-integrals can be evaluated to give the asymptotic values

$$\Delta E_{FZ}=\frac{-1593\hbar c}{1280\pi^3\epsilon_0^2R^9}\,\alpha^A(0)\theta^B_{\lambda\mu\lambda\mu}(0)\qquad\qquad(4.7.7)$$

$$\Delta E_{NZ}=\frac{-3}{8\pi^2\epsilon_0^2R^8}\sum_{m,n}\frac{|\vec{\mu}^{n0}|^2Q_{\lambda\mu}^{0m}Q_{\lambda\mu}^{m0}}{E_{mo}+E_{no}}\qquad\qquad(4.7.8)$$

where the ground state static polarisabilities appear in (4.7.7). These results are in agreement with previous studies [35,38], and with that obtained from the response of an electric dipole polarisable test body to the electric energy density due to a quadrupole source (3.2.46).

If molecule A is in the ground state, the second term of (4.7.5)does not contribute. The first term of (4.7.5) is

$$\frac{-1}{16\pi^2\epsilon_0^2} \sum_{\substack{m \\ E_q > E_m}} \alpha^A_{ij}(k_{qm}) Q^{qm}_{k\ell} Q^{mq}_{mn} k_{qm}^8 \times$$

$$\left[\frac{a_{ijk\ell mn}}{k_{qm}^2 R^2} + \frac{b_{ijk\ell mn}}{k_{qm}^3 R^3} + \frac{c_{ijk\ell mn}}{k_{qm}^4 R^4} + \frac{d_{ijk\ell mn}}{k_{qm}^5 R^5} + \frac{e_{ijk\ell mn}}{k_{qm}^6 R^6} + \frac{f_{ijk\ell mn}}{k_{qm}^7 R^7} + \frac{g_{ijk\ell mn}}{k_{qm}^8 R^8}\right]$$

$$(4.7.9)$$

with tensors $a_{ijk\ell mn}$ to $g_{ijk\ell mn}$ given in the Appendix. After rotational averaging, (4.7.9) becomes

$$\frac{-1}{80\pi^2\epsilon_0^2} \sum_{\substack{m \\ E_q > E_m}} \alpha^A(k_{qm}) Q^{qm}_{\lambda\mu} Q^{mq}_{\lambda\mu} k_{qm}^8 \left[\frac{1}{k_{qm}^2 R^2} + \frac{3}{k_{qm}^4 R^4} + \frac{18}{k_{qm}^6 R^6} + \frac{90}{k_{qm}^8 R^8}\right] \qquad (4.7.10)$$

exhibiting R^{-8} near-zone behaviour,

$$\frac{-9}{8\pi^2\epsilon_0^2 R^8} \sum_{\substack{m \\ E_q > E_m}} \alpha^A(k_{qm}) Q^{qm}_{\lambda\mu} Q^{mq}_{\lambda\mu} \qquad (4.7.11)$$

in agreement with (3.2.47), and R^{-2} far-zone behaviour,

$$\frac{-1}{80\pi^2\epsilon_0^2 R^2} \sum_{\substack{m \\ E_q > E_m}} \alpha^A(k_{qm}) Q^{qm}_{\lambda\mu} Q^{mq}_{\lambda\mu} k_{qm}^6 \qquad (4.7.12)$$

in agreement with (3.2.48). The term (4.7.12) is the dominant contribution to the interaction energy at large separations since the virtual photon contribution from the u-integral produces an R^{-9} dependence as seen in (4.7.7). The small R limit obtained from the analogue of the u-integral (4.7.6) when B is excited is

$$\frac{-3}{8\pi^2\varepsilon_0^2 R^8}\sum_{m,n}\mathrm{sgn}(E_{mq})\frac{|\vec{\mu}^{no}|^2 Q_{\lambda\mu}^{qm}Q_{\lambda\mu}^{mq}}{(E_{no}+|E_{mq}|)}\ . \tag{4.7.13}$$

Adding (4.7.11) and (4.7.13) results in the total small R limit

$$\frac{-3}{8\pi^2\varepsilon_0^2 R^8}\sum_{m,n}\frac{|\vec{\mu}^{no}|^2 Q_{\lambda\mu}^{qm}Q_{\lambda\mu}^{mq}}{(E_{no}+E_{mq})}\ . \tag{4.7.14}$$

When both molecules are excited, all three terms occurring in (4.7.5) contribute to the energy shift. The first term is given by (4.7.10), with the second term of (4.7.5) similarly expressed as

$$\frac{-1}{6\pi^2\varepsilon_0^2}\sum_{\substack{n\\E_p>E_n}}\Theta_{\lambda\mu\lambda\mu}^{B}(k_{pn})|\vec{\mu}^{pn}|^2 k_{pn}^8\left[\frac{1}{k_{pn}^2 R^2}+\frac{3}{k_{pn}^4 R^4}+\frac{18}{k_{pn}^6 R^6}+\frac{90}{k_{pn}^8 R^8}\right] \tag{4.7.15}$$

while the u-integral part is given by

$$\frac{-1}{720\pi^3\varepsilon_0^2 \hbar c}\sum_{m,n}|\vec{\mu}^{pn}|^2 Q_{\lambda\mu}^{qm}Q_{\lambda\mu}^{mq}\int_0^\infty\frac{du\,u^8 e^{-2uR}}{(u^2+k_{qm}^2)(u^2+k_{pn}^2)}k_{np}k_{mq}\times$$
$$\left[\frac{6}{u^2 R^2}+\frac{36}{u^3 R^3}+\frac{162}{u^4 R^4}+\frac{504}{u^5 R^5}+\frac{972}{u^6 R^6}+\frac{1080}{u^7 R^7}+\frac{540}{u^8 R^8}\right]\ . \tag{4.7.16}$$

The total near-zone limit is obtained from the addition of the leading small R terms from the last two expressions to the limit (4.7.11), resulting in

$$\frac{-3}{4\pi^2\varepsilon_0^2 R^8}\sum_{\substack{m,n\\E_q>E_m}}\frac{|\vec{\mu}^{pn}|^2 Q_{\lambda\mu}^{qm}Q_{\lambda\mu}^{mq}E_{np}}{E_{np}^2-E_{qm}^2}-\frac{3}{4\pi^2\varepsilon_0^2 R^8}\sum_{\substack{n,m\\E_p>E_n}}\frac{|\vec{\mu}^{pn}|^2 Q_{\lambda\mu}^{qm}Q_{\lambda\mu}^{mq}E_{mq}}{E_{qm}^2-E_{np}^2}\ +$$

$$\frac{-3}{8\pi^2\varepsilon_0^2R^8} \sum_{m,n} (sgnE_{mq})(sgnE_{np}) \frac{|\vec{\mu}^{pn}|^2 Q_{\lambda\mu}^{qm}Q_{\lambda\mu}^{mq}}{(|E_{mq}|+|E_{np}|)}$$

$$= \frac{-3}{8\pi^2\varepsilon_0^2R^8} \sum_{\substack{m,n \\ E_q>E_m \\ E_p>E_n}} \frac{|\vec{\mu}^{pn}|^2 Q_{\lambda\mu}^{qm}Q_{\lambda\mu}^{mq}}{(E_{mq}+E_{np})} \ . \qquad (4.7.17)$$

For large R the dominant term is proportional to R^{-2}, obtained from the addition of (4.7.12) to the large R limit of (4.7.15).

4.8 THE INTERACTION BETWEEN TWO ELECTRIC DIPOLE-ELECTRIC QUADRUPOLE POLARISABLE MOLECULES

In the last interaction to be considered, that between a dipole polarisable molecule and a quadrupole polarisable body, each centre consisted of pure multipole moments. In this Section, the possibility of splitting up that particular configuration is examined with each centre now possessing both an electric dipole moment and an electric quadrupole moment. The energy shift is

$$\Delta E = \frac{-1}{2\varepsilon_0^2} \sum_{m} A_{ijk}^A(\omega_{qm}) \left[d_i^{(1)}(\vec{\mu};\omega_{qm})\nabla_k d_j^{(1)}(\vec{Q};\omega_{qm})+d_i^{(1)}(\vec{Q};\omega_{qm})\nabla_k d_j^{(1)}(\vec{\mu};\omega_{qm}) \right. +$$

$$\left. \nabla_k d_j^{(1)}(\vec{\mu};\omega_{qm})d_i^{(1)}(\vec{Q};\omega_{qm})+\nabla_k d_j^{(1)}(\vec{Q};\omega_{qm})d_i^{(1)}(\vec{\mu};\omega_{qm}) \right.$$

$$\frac{-1}{2\varepsilon_0^2} \sum_{n} A_{\ell mn}^B(\omega_{pn}) \left[d_\ell^{(1)}(\vec{\mu};\omega_{pn})\nabla_n d_m^{(1)}(\vec{Q};\omega_{pn})+d_\ell^{(1)}(\vec{Q};\omega_{pn})\nabla_n d_m^{(1)}(\vec{\mu};\omega_{pn}) \right.$$

$$\left. +\nabla_n d_m^{(1)}(\vec{\mu};\omega_{pn})d_\ell^{(1)}(\vec{Q};\omega_{pn}) +\nabla_n d_m^{(1)}(\vec{Q};\omega_{pn})d_\ell^{(1)}(\vec{\mu};\omega_{pn}) \right]$$

$$\frac{-1}{2\varepsilon_0^2} \sum_{k,\lambda} A_{ijk}^A(\omega) \left[d_i^{(0)}\nabla_k d_j^{(2)}(\vec{\mu Q})+d_i^{(2)}(\vec{\mu Q})\nabla_k d_j^{(0)} \right. +$$

$$\nabla_\ell d_j^{(0)} d_i^{(2)}(\vec{\mu}\vec{Q}) + \nabla_\ell d_j^{(2)}(\vec{\mu}\vec{Q}) d_i^{(0)}\Big]$$

$$\frac{-1}{2\epsilon_0^2}\sum_{\vec{k},\lambda} A_{\ell mn}^{B}(\omega)\Big[d_\ell^{(0)}\nabla_n d_m^{(2)}(\vec{\mu}\vec{Q}) + d_\ell^{(2)}(\vec{\mu}\vec{Q})\nabla_n d_m^{(0)} +$$

$$\nabla_n d_m^{(0)} d_\ell^{(2)}(\vec{\mu}\vec{Q}) + \nabla_n d_m^{(2)}(\vec{\mu}\vec{Q}) d_\ell^{(0)}\Big]. \qquad (4.8.1)$$

Using the $\vec{\mu}$- and $\vec{Q}$-dependent parts of (2.2.34), the contribution to the energy shift from the product of the field linear in the moments is

$$\frac{1}{32\pi^2\epsilon_0^2}\sum_{\overline{m}} A_{ij\ell}^{A}(k_{qm})\mu_\ell^{qm}Q_{mn}^{mq}k_{qm}^{B}[\overline{f}_{\ell i}(k_{qm}R)l_{jnm\ell}(k_{qm}R) + \overline{l}_{jnm\ell}(k_{qm}R)f_{\ell i}(k_{qm}R)$$

$$+\overline{h}_{\ell\ell j}(k_{qm}R)h_{min}(k_{qm}R) + \overline{h}_{min}(k_{qm}R)h_{\ell\ell j}(k_{qm}R)] +$$

$$\frac{1}{32\pi^2\epsilon_0^2}\sum_{\overline{n}} A_{\ell mn}^{B}(k_{pn})\mu_i^{pn}Q_{j\ell}^{np}k_{pn}^{B}[\overline{f}_{\ell i}(k_{pn}R)l_{m\ell jn}(k_{pn}R) + \overline{l}_{m\ell jn}(k_{pn}R)f_{\ell i}(k_{pn}R)$$

$$+\overline{h}_{\ell\ell j}(k_{pn}R)h_{min}(k_{pn}R) + \overline{h}_{min}(k_{pn}R)h_{\ell\ell j}(k_{pn}R)]. \qquad (4.8.2)$$

Using (3.1.4), the contribution from the free and quadratic fields is

$$\frac{-1}{8\pi\epsilon_0^2}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V}\right)A_{ij\ell}^{A}(\omega)\Big[ie_i e^{i\vec{k}\cdot\vec{R}}(\overline{e}_m k_\ell(\nabla_\ell\overline{\mathscr{E}}_{\ell mj}) - i\overline{e}_\ell(\nabla_\ell\overline{\mathscr{F}}_{\ell j})) +$$

$$(e_m k_\ell\mathscr{E}_{\ell mi} - ie_\ell\mathscr{F}_{i\ell})k_\ell\overline{e}_j e^{-i\vec{k}\cdot\vec{R}} + e_j k_\ell e^{i\vec{k}\cdot\vec{R}}(\overline{e}_m k_\ell\overline{\mathscr{E}}_{\ell mi} + i\overline{e}_\ell\overline{\mathscr{F}}_{\ell i})$$

$$- i(e_m k_\ell(\nabla_\ell\overline{\mathscr{E}}_{\ell mj}) + ie_\ell(\nabla_\ell\overline{\mathscr{F}}_{\ell j}))\overline{e}_i e^{-i\vec{k}\cdot\vec{R}}\Big]$$

$$\frac{-1}{8\pi\epsilon_0^2}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V}\right)A_{\ell mn}^{B}(\omega)\Big[ie_\ell e^{i\vec{k}\cdot\vec{R}}(\overline{e}_\ell k_j(\nabla_n\overline{\mathscr{E}}_{j\ell m}) - i\overline{e}_i(\nabla_n\overline{\mathscr{F}}_{im})) +$$

$$(e_\ell k_j\mathscr{E}_{j\ell\ell} - ie_i\mathscr{F}_{\ell i})k_n\overline{e}_m e^{-i\vec{k}\cdot\vec{R}} + e_m k_n e^{i\vec{k}\cdot\vec{R}}(\overline{e}_\ell k_j\overline{\mathscr{E}}_{j\ell\ell} + i\overline{e}_i\overline{\mathscr{F}}_{i\ell})$$

$$- i(e_\ell k_j(\nabla_n\overline{\mathscr{E}}_{j\ell m}) + ie_i(\nabla_n\overline{\mathscr{F}}_{im}))\overline{e}_\ell e^{-i\vec{k}\cdot\vec{R}}\Big]. \qquad (4.8.3)$$

Evaluating the terms of (4.8.3) using the tensor fields (3.1.17) and (3.1.18) and the additional angular integral

$$\frac{1}{4\pi}\int(\delta_{ij}-\hat{k}_i\hat{k}_j)\hat{k}_\ell\hat{k}_\ell e^{\pm i\vec{k}\cdot\vec{r}}d\Omega = \frac{1}{2i}[L_{ij\ell\ell}(kr)-\bar{L}_{ij\ell\ell}(kr)] \qquad (4.8.4)$$

with $L_{ij\ell\ell}(kr)$ defined at the end of the Appendix to Chapter 2, the interaction energy is

$$\Delta E = \frac{1}{16\pi^2\varepsilon_0^2}\sum_{\substack{m\\E_q>E_m}}A^A_{ij\ell}(k_{qm})\mu_\ell^{qm}Q^{mq}_{mn}k^8_{qm}[\bar{f}_{\ell i}(k_{qm}R)l_{jnmk}(k_{qm}R)+$$

$$l_{jnmk}(k_{qm}R)f_{\ell i}(k_{qm}R)+\bar{h}_{\ell kj}(k_{qm}R)h_{min}(k_{qm}R)+\bar{h}_{min}(k_{qm}R)h_{\ell kj}(k_{qm}R)] +$$

$$\frac{1}{16\pi^2\varepsilon_0^2}\sum_{\substack{n\\E_p>E_n}}A^B_{\ell mn}(k_{pn})\mu_i^{pn}Q^{np}_{jk}k^8_{pn}[\bar{f}_{\ell i}(k_{pn}R)l_{mkjn}(k_{pn}R)+$$

$$l_{mkjn}(k_{pn}R)f_{\ell i}(k_{pn}R)+\bar{h}_{\ell kj}(k_{pn}R)h_{min}(k_{pn}R)+\bar{h}_{min}(k_{pn}R)h_{\ell kj}(k_{pn}R)]$$

$$\frac{-\hbar c}{32\pi^3\varepsilon_0^2}\int_0^\infty duu^8e^{-2uR}A^A_{ij\ell}(icu)A^B_{\ell mn}(icu) \times$$

$$[f_{\ell i}(iuR)l_{mkjn}(iuR)+h_{\ell kj}(iuR)h_{min}(iuR)], \qquad (4.8.5)$$

and applies when both molecules are excited. If for example A is in the ground state, the second term of (4.8.5) vanishes, with the additional contribution from downward transitions from B being

$$\frac{1}{16\pi^2\varepsilon_0^2}\sum_{\substack{m\\E_q>E_m}}A^A_{ij\ell}(k_{qm})\mu_\ell^{qm}Q^{mq}_{mn}k^8_{qm} \times$$

$$\left[\frac{p_{ij\ell\ell mn}}{k^2_{qm}R^2}+\frac{q_{ij\ell\ell mn}}{k^3_{qm}R^3}+\frac{r_{ij\ell\ell mn}}{k^4_{qm}R^4}+\frac{s_{ij\ell\ell mn}}{k^5_{qm}R^5}+\frac{t_{ij\ell\ell mn}}{k^6_{qm}R^6}+\frac{u_{ij\ell\ell mn}}{k^7_{qm}R^7}+\frac{v_{ij\ell\ell mn}}{k^8_{qm}R^8}\right]$$

$$(4.8.6)$$

with $p_{ijk\ell mn} - v_{ijk\ell mn}$ defined in the Appendix. For freely rotating molecules, this result, like that when both molecules are excited, vanishes after averaging. Examining the third term of (4.8.5), which is the sole contribution when considering the interaction between molecules in the ground state,

$$\frac{-1}{8\pi^3\varepsilon_0^2\hbar c}\sum_{m,n}\mu_i^{on}Q_{jk}^{no}\mu_\ell^{om}Q_{mn}^{mo}\int_0^\infty\frac{du\,u^8 e^{-2uR}}{(u^2+k_{mo}^2)(u^2+k_{no}^2)}\,k_{no}k_{mo}\times$$

$$\left[\frac{P_{ijk\ell mn}}{u^2R^2}+\frac{Q_{ijk\ell mn}}{u^3R^3}+\frac{R_{ijk\ell mn}}{u^4R^4}+\frac{S_{ijk\ell mn}}{u^5R^5}+\frac{T_{ijk\ell mn}}{u^6R^6}+\frac{U_{ijk\ell mn}}{u^7R^7}+\frac{V_{ijk\ell mn}}{u^8R^8}\right]$$

$$(4.8.7)$$

is obtained. This is the general result for oriented molecules which also vanishes on averaging, as expected for a dipole-quadrupole coupling at each centre.

4.9 THE INTERACTION BETWEEN AN ELECTRIC DIPOLE POLARISABLE MOLECULE AND A MAGNETIC DIPOLE-ELECTRIC QUADRUPOLE POLARISABLE MOLECULE

In Section 4.7 the interaction between an electric dipole polarisable molecule and an electric quadrupole polarisable molecule was discussed. An interaction of a similar order to that is obtained if one of the electric quadrupoles is replaced by a magnetic dipole moment, resulting in the interaction between an electric dipole polarisable body with a mixed magnetic dipole-electric quadrupole molecule, which is now calculated. The energy shift is

$$\Delta E = \frac{-1}{2\varepsilon_0^2}\sum_m\alpha_{ij}^A(\omega_{qm})\left[d_i^{(1)}(\vec{m};\omega_{qm})d_j^{(1)}(\vec{Q};\omega_{qm}) + d_i^{(1)}(\vec{Q};\omega_{qm})d_j^{(1)}(\vec{m};\omega_{qm})\right]$$

$$\frac{-1}{2\varepsilon_0^2}\sum_n T_{k\ell m}^B(\omega_{pn})\left[b_k^{(1)}(\vec{\mu};\omega_{pn})\nabla_m d_\ell^{(1)}(\vec{\mu};\omega_{pn})-\nabla_m d_\ell^{(1)}(\vec{\mu};\omega_{pn})b_k^{(1)}(\vec{\mu};\omega_{pn})\right]$$

$$\frac{-1}{2\varepsilon_0^2} \sum_{\vec{k},\lambda} \alpha_{ij}^A(\omega) \left[d_i^{(0)} d_j^{(2)}(\vec{m}\vec{Q}) + d_i^{(2)}(\vec{m}\vec{Q}) d_j^{(0)} \right]$$

$$\frac{-1}{2\varepsilon_0} \sum_{\vec{k},\lambda} T_{k\ell m}^B(\omega) \left[b_k^{(0)} \nabla_m d_\ell^{(2)}(\vec{\mu}\vec{\mu}) + b_k^{(2)}(\vec{\mu}\vec{\mu}) \nabla_m d_\ell^{(0)} + \right.$$

$$\left. \nabla_m d_\ell^{(0)} b_k^{(2)}(\vec{\mu}\vec{\mu}) + \nabla_m d_\ell^{(2)}(\vec{\mu}\vec{\mu}) b_k^{(0)} \right] \tag{4.9.1}$$

where $T_{k\ell m}(\omega)$, the mixed magnetic dipole-electric quadrupole tensor is defined as

$$T_{ijk}(\omega) = \sum_{\vec{r}} \left\{ \frac{m_i^{qr} Q_{jk}^{rq}}{E_{rq}-\hbar\omega} + \frac{Q_{jk}^{qr} m_i^{rq}}{E_{rq}+\hbar\omega} \right\} = \sum_{\vec{r}} \frac{2\hbar\omega m_i^{qr} Q_{jk}^{rq}}{E_{rq}^2-(\hbar\omega)^2} . \tag{4.9.2}$$

Employing the displacement field (2.2.34) and the $\vec{\mu}$-dependent part of the magnetic field (2.2.55), the contribution from the product of the first order fields is

$$\frac{-1}{32\pi^2\varepsilon_0^2 c} \sum_{\vec{m}} \alpha_{ij}^A(k_{qm}) m_k^{qm} Q_{\ell m}^{mq} k_{qm}^7 \left[\bar{g}_{ik}(k_{qm}R) h_{jm\ell}(k_{qm}R) - \bar{h}_{jm\ell}(k_{qm}R) g_{ik}(k_{qm}R) \right]$$

$$\frac{-1}{32\pi^2\varepsilon_0^2 c} \sum_{\vec{n}} T_{k\ell m}^B(k_{pn}) \mu_i^{pn} \mu_j^{np} k_{pn}^7 \left[\bar{g}_{ik}(k_{pn}R) h_{\ell jm}(k_{pn}R) - \bar{h}_{\ell jm}(k_{pn}R) g_{ik}(k_{pn}R) \right].$$

$$\tag{4.9.3}$$

The contribution to the energy shift from the interference of the zeroth and second order fields is obtained using (3.1.1), (3.1.5) and (3.1.7),

$$\frac{-1}{8\pi\varepsilon_0^2 c} \sum_{\vec{k},\lambda} \left(\frac{\hbar ck}{2V} \right) \alpha_{ij}^A(\omega) \left[ie_i e^{i\vec{k}\cdot\vec{R}} (\bar{e}_m k_\ell \bar{\mathscr{G}}_{\ell mj} - i\bar{b}_k \bar{\mathscr{H}}_{kj}) - \right.$$

$$\left. i(e_m k_\ell \mathscr{G}_{\ell mi} + ib_k \mathscr{H}_{ki}) \bar{e}_j e^{-i\vec{k}\cdot\vec{R}} \right]$$

$$\frac{-1}{8\pi\epsilon_0^2} \sum_{\vec{k},\lambda} \left(\frac{\hbar k}{2V}\right) T^B_{k\ell m}(\omega)[b_{k}e^{-i\vec{k}\cdot\vec{R}}\bar{e}_j(\nabla_m \bar{\mathscr{A}}_{j\ell}) + ik_m e_j \mathscr{J}_{j k}\bar{e}_{\ell}e^{i\vec{k}\cdot\vec{R}}$$

$$+ ik_m e_{\ell}e^{-i\vec{k}\cdot\vec{R}}\bar{e}_j \bar{\mathscr{J}}_{jk} - e_j(\nabla_m \mathscr{A}_{j\ell})\bar{b}_{k}e^{i\vec{k}\cdot\vec{R}}]. \qquad (4.9.4)$$

Evaluating the terms of (4.9.4) using the tensor field definitions (3.1.13), (3.1.19), (3.1.20) and (3.1.22), and adding the contribution from (4.9.3), the energy shift is

$$\Delta E =$$

$$\frac{-1}{16\pi^2\epsilon_0^2 c} \sum_{\substack{m \\ E_q > E_m}} \alpha^A_{ij}(k_{qm})m_{k}^{qm}Q_{\ell m}^{mq}k_{qm}^7[\bar{g}_{ik}(k_{qm}R)h_{jm\ell}(k_{qm}R)-\bar{h}_{jm\ell}(k_{qm}R)g_{ik}(k_{qm}R)]$$

$$\frac{-1}{16\pi^2\epsilon_0^2 c} \sum_{\substack{n \\ E_p > E_n}} T^B_{k\ell m}(k_{pn})\mu_i^{pn}\mu_j^{np}k_{pn}^7[\bar{g}_{ik}(k_{pn}R)h_{\ell jm}(k_{pn}R)-\bar{h}_{\ell jm}(k_{pn}R)g_{ik}(k_{pn}R)]$$

$$\frac{-1}{4\pi^3\epsilon_0^2 \hbar c^2} \sum_{m,n} \mu_i^{pn}\mu_j^{np}m_{k}^{qm}Q_{\ell m}^{mq} \int_0^{\infty} \frac{duu^7 e^{-2uR}}{(u^2+k_{qm}^2)(u^2+k_{pn}^2)}uk_{np} [g_{jk}(iuR)h_{i\ell m}(iuR)].$$

$$(4.9.5)$$

If molecule A is in the ground state, the second term of (4.9.5) disappears. The first term, the additional contribution from downward transitions from B, can be written as

$$\frac{-1}{16\pi^2\epsilon_0^2 c} \sum_{\substack{m \\ E_q > E_m}} \alpha^A_{ij}(k_{qm})m_{k}^{qm}Q_{\ell m}^{mq}k_{qm}^7 \times$$

$$\left[\frac{g_{ijk\ell m}}{k_{qm}^2 R^2} + \frac{h_{ijk\ell m}}{k_{qm}^3 R^3} + \frac{i_{ijk\ell m}}{k_{qm}^4 R^4} + \frac{j_{ijk\ell m}}{k_{qm}^5 R^5} + \frac{k_{ijk\ell m}}{k_{qm}^6 R^6}\right] \qquad (4.9.6)$$

exhibiting R^{-2} far-zone and R^{-6} near-zone behaviour. This result vanishes on orientational averaging, as does the u-integral term. When

both molecules are in the ground state, the u-integral is the only

contribution, the potential for oriented molecules being

$$\frac{-\hbar}{16\pi^3\varepsilon_0^2}\int_0^\infty du\, u^7 e^{-2uR}\alpha_{ij}^A(icu)T_{k\ell m}^B(icu) \times$$

$$\left[\frac{G_{ijk\ell m}}{u^2R^2} + \frac{H_{ijk\ell m}}{u^3R^3} + \frac{I_{ijk\ell m}}{u^4R^4} + \frac{J_{ijk\ell m}}{u^5R^5} + \frac{K_{ijk\ell m}}{u^6R^6}\right] \qquad (4.9.7)$$

and which also vanishes on averaging.

4.10 THE INTERACTION BETWEEN A CHIRAL MOLECULE AND AN ELECTRIC DIPOLE-QUADRUPOLE POLARISABLE MOLECULE

The final interaction to be considered is that between an electric

dipole-magnetic dipole polarisable molecule and an electric

dipole-quadrupole polarisable molecule, the last possible case where at

least two electric dipole moments are present, either entirely at one

centre, or as in this example, split between the two. The interaction

energy is calculated from

$$\Delta E = \frac{-1}{2\varepsilon_0^2}\sum_m A_{ijk}^A(\omega_{qm})\left[d_i^{(1)}(\vec{\mu};\omega_{qm})\nabla_\ell d_j^{(1)}(\vec{m};\omega_{qm})+d_i^{(1)}(\vec{m};\omega_{qm})\nabla_\ell d_j^{(1)}(\vec{\mu};\omega_{qm}) + \right.$$

$$\left. \nabla_\ell d_j^{(1)}(\vec{\mu};\omega_{qm})d_i^{(1)}(\vec{m};\omega_{qm})+\nabla_\ell d_j^{(1)}(\vec{m};\omega_{qm})d_i^{(1)}(\vec{\mu};\omega_{qm})\right] +$$

$$\frac{1}{\varepsilon_0}\sum_n G_{\ell m}^B(\omega_{pn})\left[d_\ell^{(1)}(\vec{\mu};\omega_{pn})b_m^{(1)}(\vec{Q};\omega_{pn})+d_\ell^{(1)}(\vec{Q};\omega_{pn})b_m^{(1)}(\vec{\mu};\omega_{pn})\right]$$

$$\frac{-1}{2\varepsilon_0^2}\sum_{\vec{k},\lambda} A_{ijk}^A(\omega)\left[d_i^{(0)}\nabla_\ell d_j^{(2)}(\vec{\mu m}) + d_i^{(2)}(\vec{\mu m})\nabla_\ell d_j^{(0)}+\right.$$

$$\left. \nabla_\ell d_j^{(2)}(\vec{\mu m})d_i^{(0)} + \nabla_\ell d_j^{(0)}d_i^{(2)}(\vec{\mu m})\right]$$

$$\frac{-1}{\varepsilon_0}\sum_{\vec{k},\lambda} G_{\ell m}^B(\omega)\left[b_m^{(0)}d_\ell^{(2)}(\vec{\mu Q}) + b_m^{(2)}(\vec{\mu Q})d_\ell^{(0)}\right]. \qquad (4.10.1)$$

The contribution to the energy shift from the first order displacement field (2.2.34) and the $\vec{\mu}$- and $\vec{Q}$-dependent part of the first order magnetic field (2.2.55) is

$$\frac{1}{32\pi^2\varepsilon_0^2 c}\sum_m A^{A}_{ijk}(k_{qm})\mu^{qm}_{\ell}m^{mq}_{m}k_{qm}^7[\bar{h}_{j\ell k}(k_{qm}R)g_{im}(k_{qm}R) - \bar{g}_{im}(k_{qm}R)h_{j\ell k}(k_{qm}R)$$

$$-i(\bar{f}_{i\ell}(k_{qm}R)j_{jm k}(k_{qm}R) + \bar{j}_{jm k}(k_{qm}R)f_{i\ell}(k_{qm}R))]$$

$$\frac{-1}{16\pi^2\varepsilon_0^2 c}\sum_n G^{B}_{\ell m}(k_{pn})\mu^{pn}_{i}Q^{np}_{jk}k_{pn}^7[i\bar{f}_{\ell i}(k_{pn}R)j_{m j k}(k_{pn}R)+\bar{h}_{\ell k j}(k_{pn}R)g_{mi}(k_{pn}R)].$$

$$(4.10.2)$$

Using (3.1.2), (3.1.4) and (3.1.10), the contribution to the interaction energy from the zeroth and second order fields is determined from

$$\frac{-1}{8\pi\varepsilon_0^2}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)A^{A}_{ijk}(\omega) \times$$

$$[e_i e^{i\vec{k}\cdot\vec{R}}(\bar{b}_m(\nabla_k\bar{\mathcal{B}}_{mj}+\bar{e}_{\ell}(\nabla_k\bar{\mathcal{E}}_{\ell j})-i(b_m\mathcal{B}_{mi}+e_{\ell}\mathcal{E}_{\ell i})k_k\bar{e}_j e^{-i\vec{k}\cdot\vec{R}}$$

$$+(b_m(\nabla_k\mathcal{B}_{mj})+e_{\ell}(\nabla_k\mathcal{E}_{\ell j}))\bar{e}_i e^{-i\vec{k}\cdot\vec{R}}+ik_k e_j e^{i\vec{k}\cdot\vec{R}}(\bar{b}_m\bar{\mathcal{B}}_{mi}+\bar{e}_{\ell}\bar{\mathcal{E}}_{\ell i})]$$

$$\frac{-1}{4\pi\varepsilon_0^2}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)G^{B}_{\ell m}(\omega)[-ib_m e^{i\vec{k}\cdot\vec{R}}(\bar{e}_k k_j\bar{\mathcal{E}}_{j k\ell}+i\bar{e}_i\bar{\mathcal{F}}_{i\ell})-$$

$$i(e_k k_j \mathcal{N}_{j k m}+e_i\mathcal{P}_{im})\bar{e}_{\ell}e^{-i\vec{k}\cdot\vec{R}}].\qquad(4.10.3)$$

Evaluating the terms of (4.10.3) in the usual manner, the energy shift is found to be

$$\Delta E = \frac{1}{16\pi^2\varepsilon_0^2 c}\sum_{\substack{m\\ E_q>E_m}} A^{A}_{ijk}(k_{qm})\mu^{qm}_{\ell}m^{mq}_{m}k_{qm}^7[\bar{h}_{j\ell k}(k_{qm}R)g_{im}(k_{qm}R) -$$

$$\bar{g}_{im}(k_{qm}R)h_{j\ell k}(k_{qm}R)-i(\bar{f}_{i\ell}(k_{qm}R)j_{jmk}(k_{qm}R) + \bar{j}_{jmk}(k_{qm}R)f_{i\ell}(k_{qm}R))]$$

$$\frac{-1}{8\pi^2\epsilon_0^2 c}\sum_{\substack{n\\E_p>E_n}}G^B_{\ell m}(k_{pn})\mu_i^{pn}Q_{jk}^{np}k_{pn}^7[if_{\ell i}(k_{pn}R)j_{mjk}(k_{pn}R)+\bar{h}_{\ell kj}(k_{pn}R)g_{mi}(k_{pn}R)]$$

$$\frac{-1}{8\pi^3\epsilon_0^2\hbar c^2}\sum_{m,n}\mu_i^{pn}Q_{jk}^{np}\mu_\ell^{qm}m_m^{mq}\int_0^\infty\frac{duu^7e^{-2uR}}{(u^2+k_{qm}^2)(u^2+k_{pn}^2)}uk_{np}\times$$

$$[if_{i\ell}(iuR)j_{jmk}(iuR)+g_{mi}(iuR)h_{jk\ell}(iuR)].\qquad(4.10.4)$$

The first term of (4.10.4) can be expressed as

$$\frac{1}{16\pi^2\epsilon_0^2 c}\sum_{\substack{m\\E_q>E_m}}A^A_{ijk}(k_{qm})\mu_\ell^{qm}m_m^{mq}k_{qm}^7\times$$

$$\left[\frac{q_{ijk\ell m}}{k_{qm}^2R^2}+\frac{r_{ijk\ell m}}{k_{qm}^3R^3}+\frac{s_{ijk\ell m}}{k_{qm}^4R^4}+\frac{t_{ijk\ell m}}{k_{qm}^5R^5}+\frac{u_{ijk\ell m}}{k_{qm}^6R^6}\right]\qquad(4.10.5)$$

the explicit form of $q_{ijk\ell m}-u_{ijk\ell m}$ given in the Appendix, which is the additional contribution from excited B, with a similar term occurring from the second term of (4.10.4) when A is excited. The result (4.10.5) disappears after orientational averaging. When both molecules are in the ground state, only the u-integral of (4.10.5) survives, which is

$$\frac{-i\hbar}{32\pi^3\epsilon_0^2}\int_0^\infty duu^7e^{-2uR}A^A_{ijk}(icu)G^B_{\ell m}(icu)\left[\frac{Q_{ijk\ell m}}{u^2R^2}+\frac{R_{ijk\ell m}}{u^3R^3}+\frac{S_{ijk\ell m}}{u^4R^4}+\frac{T_{ijk\ell m}}{u^5R^5}+\frac{U_{ijk\ell m}}{u^6R^6}\right]$$

$$(4.10.6)$$

with $Q_{ijk\ell m}$ etc., given in full in the Appendix. This also vanishes after rotational averaging.

4.11 CONTRIBUTION FROM THE DIAMAGNETIC COUPLING TERM

The discussion outlined so far in this Chapter is still incomplete in the sense that no account has yet been taken of the diamagnetic coupling term which is one of a similar order as the electric quadrupole and magnetic dipole interaction terms. For a comprehensive treatment of intermolecular interactions to this order of approximation, the effects arising from the inclusion of the diamagnetic coupling term in the interaction Hamiltonian must therefore be investigated.

For a freely rotating source, the diamagnetic coupling term is

$$\frac{e^2}{12m} \, q^2 b^2(\vec{r})$$ (4.11.1)

with the resulting interaction energy arising from (4.11.1) for a molecule in the ground state given by

$$\frac{e^2}{12m} \, \langle 0;0| \langle q^2 \rangle^B (\vec{b}^{(0)}.\vec{b}^{(2)} + \vec{b}^{(2)}.\vec{b}^{(0)}) |0;0 \rangle ;$$ (4.11.2)

(4.11.2) is seen to be similar to the last term of (4.6.1) from the interaction between an electric dipole polarisable molecule and a magnetic dipole polarisable molecule. The field dependent part above is identical to that occurring in Section 4.6, resulting in

$$\frac{-e^2}{144\pi^3 \varepsilon_o^2 c^2 m} \sum_n |\vec{\mu}^{no}|^2 \langle q^2 \rangle^B \int_o^\infty \frac{duu^6 e^{-2ur}}{(u^2+k_{no}^2)} k_{no} \left[\frac{1}{u^2 r^2} + \frac{2}{u^3 r^3} + \frac{1}{u^4 r^4} \right] .$$ (4.11.3)

In the far-zone, (4.11.3) reduces to [35]

$$\Delta E_{FZ} = \frac{-3e^2 \hbar}{128\pi^3 \varepsilon_o^2 mcR^7} \, \alpha^A(0) \langle q^2 \rangle^B$$ (4.11.4)

illustrating that at large intermolecular separations, the diamagnetic contribution to the dispersion interaction varies as R^{-7}. This result may be combined with that obtained in Section 4.6 where the far-zone limit was also expressed in terms of the static polarisability of molecule A. From (4.6.13) and (4.11.4),

$$\Delta E_{FZ}^{TOT} = \frac{7\hbar}{64\pi^3 \epsilon_o^2 cR^7} \alpha^A(0)\chi'^B(0) \qquad (4.11.5)$$

where the new, modified magnetic susceptibility tensor takes the definition

$$\chi'^B(0) = \chi^B(0) - \frac{e^2}{6m} \langle q^2 \rangle^B . \qquad (4.11.6)$$

Although both $\alpha(0)$ and $\chi(0)$ are positive for molecules in the ground state, $\chi'(0)$ maybe either positive or negative depending on the relative sizes of the two terms in (4.11.6). A molecule is termed diamagnetic if $\chi'(0) < 0$. Returning to (4.11.3) and examining the near-zone behaviour, after the usual approximations, the leading term is found to be

$$\Delta E_{NZ} = \frac{-e^2}{288\pi^3 \epsilon_o^2 c^2 mR^5} \sum_{\bar{n}} |\vec{\mu}^{n0}|^2 \langle q^2 \rangle^B k_{no} . \qquad (4.11.7)$$

Comparing (4.11.7) with the corresponding limit (4.6.12) obtained between electric dipole and magnetic dipole polarisable molecules, the ratio of the two is given by

$$\frac{\Delta E_{NZ}(\alpha\chi)}{\Delta E_{NZ}(DIA)} \simeq kR . \qquad (4.11.8)$$

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In the near-zone, where $kR \ll 1$, the contribution from the diamagnetic coupling term dominates the interaction.

4.12 NEAR-ZONE LIMIT TO THE DISPERSION INTERACTION

So far throughout this Chapter, the dispersion interaction and the interaction between two molecules in electronically excited levels has been investigated using the multipolar formalism of QED in the Heisenberg picture. Results for oriented and completely rotationally averaged molecules, valid for the entire range of separation distance beyond electron overlap have been obtained for molecules possessing a variety of multipole polarisability characteristics up to and including the magnetic dipole and electric quadrupole moments with complete account being taken of all retardation effects. The asymptotic behaviour of the energy shift between two neutral molecules in the limits of large and small intermolecular separation has also been studied.

It was mentioned in Section 4.2 that the near-zone results may be obtained from second order perturbation theory when the interaction term is represented by a Coulomb's law type coupling [59]. In this Section, second order perturbation theory with an electrostatic multipolar interaction term is used to obtain the near-zone limits to the energy shifts calculated in Sections 4.2, 4.4 - 4.5 and 4.7 - 4.8.

The attraction between two neutral molecules in ground electronic states was first discussed by London in terms of virtual molecular transitions. For intermolecular separations small compared with characteristic wavelengths of molecular electronic transitions, use of second order perturbation theory with electrostatic dipolar coupling resulted in the R^{-6} dependence on distance of the dispersion energy.

This interaction was interpreted as arising from the induction of a dipole in one molecule by a dipolar fluctuation of electric charge in the other molecule. In the present treatment the static electric dipole coupling approximation is relaxed with the effects of static magnetic dipole-magnetic dipole, electric dipole-electric quadrupole and electric quadrupole-electric quadrupole couplings fully incorporated.

Molecules A and B are again taken to be non-identical many-level systems separated by a distance $\vec{R}$, with intermediate states n and m respectively. The dispersion energy is easily calculated using second order perturbation theory,

$$\Delta E = -\sum_{m,n} \frac{\langle E_0^A, E_0^B | H_{INT} | E_n^A, E_m^B \rangle \langle E_m^B, E_n^A | H_{INT} | E_0^A, E_0^B \rangle}{E_{mo} + E_{no}} \qquad (4.12.1)$$

with the interaction Hamiltonian representing the static multipolar coupling given by

$$H_{INT} = H_{\vec{\mu}\vec{\mu}} + H_{\vec{m}\vec{m}} + H_{\vec{\mu}\vec{Q}} + H_{\vec{Q}\vec{Q}} \qquad (4.12.2)$$

where

$$H_{\vec{\mu}\vec{\mu}} = \frac{\mu_i^A \mu_j^B}{4\pi\varepsilon_0 R^3} \beta_{ij} , \qquad (4.12.3)$$

$$H_{\vec{m}\vec{m}} = \frac{m_i^A m_j^B}{4\pi\varepsilon_0 c^2 R^3} \beta_{ij} , \qquad (4.12.4)$$

$$H_{\vec{\mu}\vec{Q}} = \frac{\mu_i^A Q_{jk}^B}{4\pi\varepsilon_0} \nabla_k \frac{\beta_{ij}}{R^3} = \frac{\mu_i^A Q_{jk}^B}{4\pi\varepsilon_0 R^4} \alpha_{ijk} , \qquad (4.12.5)$$

$$H_{\overrightarrow{QQ}} = \frac{Q^A_{ij}Q^B_{k\ell}}{4\pi\varepsilon_0} \, \nabla_\ell \, \frac{\alpha_{ijk}}{R^4} = \frac{Q^A_{ij}Q^B_{k\ell}}{4\pi\varepsilon_0 R^5} \, \alpha_{ijk\ell} \, , \tag{4.12.6}$$

where

$$\alpha_{ijk} = - \, [3(\delta_{ij}\hat{R}_k + \delta_{jk}\hat{R}_i + \delta_{ik}\hat{R}_j) - 15\hat{R}_i\hat{R}_j\hat{R}_k] \tag{4.12.7}$$

and

$$\alpha_{ijk\ell} = [-3(\delta_{ij}\delta_{k\ell} + \delta_{jk}\delta_{i\ell} + \delta_{ik}\delta_{j\ell}) - 105\hat{R}_i\hat{R}_j\hat{R}_k\hat{R}_\ell +$$
$$15(\delta_{ij}\hat{R}_k\hat{R}_\ell + \delta_{jk}\hat{R}_i\hat{R}_\ell + \delta_{ik}\hat{R}_j\hat{R}_\ell + \delta_{j\ell}\hat{R}_i\hat{R}_k + \delta_{i\ell}\hat{R}_j\hat{R}_k + \delta_{k\ell}\hat{R}_i\hat{R}_j)] \, . \tag{4.12.8}$$

The leading contribution to the dispersion interaction for small separation distances corresponds to the use of the first term of (4.12.2) in (4.12.1), giving

$$\Delta E = \frac{-1}{16\pi^2\varepsilon_0^2 R^6} \, \beta_{ik}\beta_{j\ell} \sum_{m,n} \frac{\langle E^B_0,E^A_0|\mu^A_i\mu^B_k|E^A_n,E^B_m\rangle\langle E^B_m,E^A_n|\mu^A_j\mu^B_\ell|E^A_0,E^B_0\rangle}{E_{m0}+E_{n0}}$$

$$= \frac{-1}{16\pi^2\varepsilon_0^2 R^6} \sum_{m,n} \frac{\mu^{0n}_i\mu^{n0}_j\mu^{0m}_k\mu^{m0}_\ell}{E_{m0}+E_{n0}} \, \beta_{ik}\beta_{j\ell} \tag{4.12.9}$$

which after rotational averaging results in

$$\Delta E = \frac{-1}{24\pi^2\varepsilon_0^2 R^6} \sum_{m,n} \frac{|\vec{\mu}^{0n}|^2|\vec{\mu}^{m0}|^2}{E_{m0}+E_{n0}} \tag{4.12.10}$$

which is the familiar London dispersion energy [44], identical to the near-zone result (4.2.13) obtained from the full quantum electrodynamical expression.

The next short range interaction to be evaluated corresponds to the near-zone limit of the chiral discrimination dispersion potential determined in Section 4.5. This is obtained by extracting the cross term after including the first two contributions to the interaction Hamiltonian (4.12.2). The leading term has already been derived above, being the pure electric dipole case, while the pure magnetic analogue is ignored to this order of approximation. The electric-magnetic cross term is given by

$$\Delta E = \frac{-1}{16\pi^2\varepsilon_0^2 c^2 R^6}\,\beta_{ik}\beta_{j\ell}\sum_{m,n}\left[\frac{\langle E_0^B,E_0^A|\mu_i^A\mu_k^B|E_n^A,E_m^B\rangle\langle E_m^B,E_n^A|m_j^A m_\ell^B|E_0^A,E_0^B\rangle}{E_{mo}+E_{no}}\right.$$

$$\left.+\frac{\langle E_0^B,E_0^A|m_j^A m_\ell^B|E_n^A,E_m^B\rangle\langle E_m^B,E_n^A|\mu_i^A\mu_k^B|E_0^B,E_0^A\rangle}{E_{mo}+E_{no}}\right]$$

$$=\frac{-1}{8\pi^2\varepsilon_0^2 c^2 R^6}\,\beta_{ik}\beta_{j\ell}\sum_{m,n}\frac{\mu_i^{On}m_j^{no}\mu_k^{Om}m_\ell^{mo}}{E_{mo}+E_{no}} \qquad (4.12.11)$$

which after averaging becomes [58]

$$\Delta E = \frac{-1}{12\pi^2\varepsilon_0^2 c^2 R^6}\sum_{m,n}\frac{|\vec{\mu}^{On}\cdot\vec{m}^{no}||\vec{\mu}^{Om}\cdot\vec{m}^{mo}|}{E_{mo}+E_{no}} \qquad (4.12.12)$$

in agreement with (4.5.10).

If the first and third terms of the interaction (4.12.2) are retained, and the cross term extracted again, the resulting interaction corresponds to the near-zone limit obtained in Section 4.4 between an electric dipole polarisable body and a mixed electric dipole-quadrupole polarisable molecule. The energy shift is given by

$$\Delta E = \frac{-1}{16\pi^2\varepsilon_0^2 R^7}\,\beta_{ik}\alpha_{j\ell m}\sum_{m,n}\left[\frac{\langle E_0^B,E_0^A|\mu_i^A\mu_k^B|E_n^A,E_m^B\rangle\langle E_m^B,E_n^A|\mu_j^A Q_{\ell m}^B|E_0^A,E_0^B\rangle}{E_{mo}+E_{no}}+\right.$$

$$\frac{\langle E_0^B, E_0^A | \mu_j^A Q_{\ell m}^B | E_n^A, E_m^B \rangle \langle E_m^B, E_n^A | \mu_i^A \mu_k^B | E_0^A, E_0^B \rangle}{E_{mo} + E_{no}} \Bigg]$$

$$= \frac{-1}{8\pi^2 \varepsilon_0^2 R^7} \sum_{m,n} \frac{\mu_i^{on} \mu_j^{no} \mu_k^{om} Q_{\ell m}^{mo}}{E_{mo} + E_{no}} \beta_{ik} \alpha_{j\ell m} . \qquad (4.12.13)$$

On using the definition of $\alpha_{ij\ell}$ from (4.12.7) and comparing (4.12.13) with the $F_{ij k\ell m}$ term of (4.4.6), after performing the u-integral, with $F_{ij k\ell m}$ given in the Appendix under (4.A.5), the two results are seen to be identical. (4.12.13) like its counterpart from Section 4.4, vanishes on averaging.

If only the third term of (4.12.2) is retained and used in the second order perturbation theory expression, the resulting energy shift corresponds to the near-zone result of the interaction energy between an electric dipole polarisable molecule and an electric quadrupole polarisable molecule investigated in Section 4.7. Using (4.12.5) in (4.12.1), the energy shift is

$$\Delta E = \frac{-1}{16\pi^2 \varepsilon_0^2 R^8} \alpha_{ik\ell} \alpha_{jmn} \sum_{m,n} \frac{\langle E_0^B, E_0^A | \mu_i^A Q_{k\ell}^B | E_n^A, E_m^B \rangle \langle E_m^B, E_n^A | \mu_j^A Q_{mn}^B | E_0^A, E_0^B \rangle}{E_{mo} + E_{no}}$$

$$= \frac{-1}{16\pi^2 \varepsilon_0^2 R^8} \sum_{m,n} \frac{\mu_i^{on} \mu_j^{no} Q_{k\ell}^{om} Q_{mn}^{mo}}{E_{mo} + E_{no}} \alpha_{ik\ell} \alpha_{jmn}. \qquad (4.12.14)$$

Using the definition (4.12.7), the above is seen to be identical to the $G_{ij k\ell mn}$ part of (4.7.6), after performing the u-integral, with $G_{ij k\ell mn}$ given in full in the Appendix under (4.A.6). Rotationally averaging (4.12.14), and contracting the geometrical tensors results in

$$\Delta E = \frac{-3}{8\pi^2 \varepsilon_0^2 R^8} \sum_{m,n} \frac{|\vec{\mu}^{on}|^2 Q_{\lambda\mu}^{om} Q_{\lambda\mu}^{mo}}{E_{mo} + E_{no}} \qquad (4.12.15)$$

which is equivalent to the near-zone shift (4.7.8).

When the second term of (4.12.2) is excluded and the electric dipole-dipole electric quadrupole-quadrupole cross term extracted along with the mixed electric dipole-quadrupole contribution, the resulting interaction corresponds to the near-zone result obtained in Section 4.8 between two electric dipole-electric quadrupole polarisable molecules. The total energy shift from the two contributions is given by

$$
\Delta E = \frac{-1}{16\pi^2 \epsilon_0^2 R^8} \sum_{m,n} \left\{ \left[\frac{\langle E_0^B, E_0^A | \mu_i^A \mu_\ell^B | E_n^A, E_m^B \rangle \langle E_m^B, E_n^A | Q_{j\ell}^A Q_{mn}^B | E_0^A, E_0^B \rangle}{E_{mo}+E_{no}} + \right. \right.
$$

$$
\left. \frac{\langle E_0^B, E_0^A | Q_{j\ell}^A Q_{mn}^B | E_n^A, E_m^B \rangle \langle E_m^B, E_n^A | \mu_i^A \mu_\ell^B | E_0^A, E_0^B \rangle}{E_{mo}+E_{no}} \right] \beta_{i\ell}^\alpha{}_{j\ell mn} +
$$

$$
\left[\frac{\langle E_0^B, E_0^A | \mu_i^A Q_{mn}^B | E_n^A, E_m^B \rangle \langle E_m^B, E_n^A | Q_{j\ell}^A \mu_\ell^B | E_0^A, E_0^B \rangle}{E_{mo}+E_{no}} + \right.
$$

$$
\left. \left. \frac{\langle E_0^B, E_0^A | Q_{j\ell}^A \mu_\ell^B | E_n^A, E_m^B \rangle \langle E_m^B, E_n^A | \mu_i^A Q_{mn}^B | E_0^A, E_0^B \rangle}{E_{mo}+E_{no}} \right] \alpha_{imn}^\alpha{}_{j\ell\ell} \right\}
$$

$$
= \frac{-1}{8\pi^2 \epsilon_0^2 R^8} \sum_{m,n} \frac{\mu_i^{On} Q_{j\ell}^{no} \mu_\ell^{Om} Q_{mn}^{mO}}{E_{mo}+E_{no}} [\beta_{i\ell}^\alpha{}_{j\ell mn} + \alpha_{imn}^\alpha{}_{j\ell\ell}] \qquad (4.12.16)
$$

which corresponds to the $V_{ij\ell\ell mn}$ term of (4.8.7) and which similarly vanishes after orientational averaging.

In this Chapter, the energy of interaction between two neutral polarisable molecules has been calculated using molecular response theory. The response of a test body through its dynamic polarisability to the Maxwell field of a second source molecule is determined for ground state and electronically excited molecules. In all the examples considered, the energy shift for two excited molecules consists of three terms: a u-integral term applicable for both upward and downward transitions from the initial state, corresponding to virtual and real photon transitions, and two additional unmodulated terms applicable only

to downward transitions from the initial state, corresponding to real photon emission. For two molecules in the ground state, the u-integral term is the sole contribution to the dispersion energy, intermolecular interaction mediated by the electromagnetic field through virtual transitions. The energy shifts are expressed in terms of generalised molecular polarisabilities and are valid for the entire range of separation distance beyond regions of overlap of molecular electronic wavefunctions for both oriented and completely rotationally averaged source and test bodies. The asymptotic behaviour in the limits of large and small intermolecular separation, where the effects of retardation are most clearly distinguished, is also investigated. This is evident in the dispersion interaction between two electric dipole polarisable molecules and two chiral molecules, amongst others, where the far-zone dependences are respectively R^{-7} and R^{-9}, in direct contrast to the R^{-6} power law predicted for both cases by a London type calculation using static intermolecular coupling, which applies only to small separation distances, and which is the near-zone limit to the fully retarded interaction.

When both molecules are excited, the additional contributions to the energy shift arising from downward transitions dominate, and can result in a repulsive force. In the far-zone an inverse square distance dependence is found in all the cases examined, corresponding to real photon emission from a molecule in an excited state. If only one of the pair is excited, the sign of the potential depends on the relative magnitudes of the relevant transition energies of the two molecules.

The use of time dependent Maxwell fields in the vicinity of a source and molecular response theory leads directly to the intermolecular energy shift for a pair of molecules, and has obvious physical appeal.

APPENDIX

Throughout this Chapter, the energy of interaction between two polarisable molecules has been expressed in terms of molecular susceptibility tensors, whose definitions were given in the text, and in terms of products of various geometric tensors. The definitions of each of the tensors used here were given in the Appendix to Chapter 2. In this Appendix to Chapter 4, the explicit form of the product of the geometric tensors is given; the definitions of the various tensors denoted by $A_{ij k\ell}$ etc., in the text, are stated here in complete form. These are required in order to determine the dependence of the interaction energy on separation distance in the near- and far-zones. The number of indices associated with each tensor is sufficient to remove any ambiguity regarding the use of any particular tensor in any specific calculation.

In Section 4.2 the products $f_{ij}(kR)\bar{f}_{k\ell}(kR)$ and $f_{ij}(iuR)f_{k\ell}(iuR)$ are required. From their definition (2.A.1),

$$f_{ij}(kR)\bar{f}_{k\ell}(kR) = \left[\frac{-\alpha_{ij}}{kR} + \beta_{ij}\left(\frac{-i}{k^2R^2} + \frac{1}{k^3R^3}\right)\right]\left[\frac{-\alpha_{k\ell}}{kR} + \beta_{k\ell}\left(\frac{i}{k^2R^2} + \frac{1}{k^3R^3}\right)\right]$$

$$= \left[\frac{a_{ij k\ell}}{k^2R^2} + \frac{b_{ij k\ell}}{k^3R^3} + \frac{c_{ij k\ell}}{k^4R^4} + \frac{d_{ij k\ell}}{k^5R^5} + \frac{e_{ij k\ell}}{k^6R^6}\right] \qquad (4.A.1)$$

where

$$a_{ij k\ell} = \alpha_{ij}\alpha_{k\ell}$$

$$b_{ij k\ell} = -i\alpha_{ij}\beta_{k\ell} + i\beta_{ij}\alpha_{k\ell}$$

$$c_{ij k\ell} = -\alpha_{ij}\beta_{k\ell} + \beta_{ij}\beta_{k\ell} - \beta_{ij}\alpha_{k\ell}$$

$$d_{ij k\ell} = -i\beta_{ij}\beta_{k\ell} + i\beta_{ij}\beta_{k\ell} = 0$$

$$e_{ij k\ell} = \beta_{ij}\beta_{k\ell} \qquad (4.A.2)$$

$$f_{ij}(iuR)f_{k\ell}(iuR) = -\left[\frac{A_{ijk\ell}}{u^2R^2} + \frac{B_{ijk\ell}}{u^3R^3} + \frac{C_{ijk\ell}}{u^4R^4} + \frac{D_{ijk\ell}}{u^5R^5} + \frac{E_{ijk\ell}}{u^6R^6}\right]$$

where

$$A_{ijk\ell} = \alpha_{ij}\alpha_{k\ell}$$

$$B_{ijk\ell} = \alpha_{ij}\beta_{k\ell} + \beta_{ij}\alpha_{k\ell}$$

$$C_{ijk\ell} = \alpha_{ij}\beta_{k\ell} + \beta_{ij}\alpha_{k\ell} + \beta_{ij}\beta_{k\ell}$$

$$D_{ijk\ell} = 2\beta_{ij}\beta_{k\ell}$$

$$E_{ijk\ell} = \beta_{ij}\beta_{k\ell} \tag{4.A.3}$$

In Section 4.4, the following products are required

$$\bar{f}_{ij}(kR)h_{k\ell m}(kR) = \left[\frac{a_{ijk\ell m}}{k^2R^2} + \frac{b_{ijk\ell m}}{k^3R^3} + \frac{c_{ijk\ell m}}{k^4R^4} + \frac{d_{ijk\ell m}}{k^5R^5} + \frac{e_{ijk\ell m}}{k^6R^6} + \frac{f_{ijk\ell m}}{k^7R^7}\right]$$

where

$$a_{ijk\ell m} = -i\alpha_{ij}\alpha_{k\ell}\hat{R}_m$$

$$b_{ijk\ell m} = \alpha_{ij}[(2\delta_{k\ell}\hat{R}_m + \delta_{\ell m}\hat{R}_k + \delta_{km}\hat{R}_\ell) - 6\hat{R}_k\hat{R}_\ell\hat{R}_m] - \beta_{ij}\alpha_{k\ell}\hat{R}_m$$

$$c_{ijk\ell m} = i\alpha_{ij}[3(\delta_{k\ell}\hat{R}_m + \delta_{\ell m}\hat{R}_k + \delta_{km}\hat{R}_\ell) - 15\hat{R}_k\hat{R}_\ell\hat{R}_m] + i\beta_{ij}\alpha_{k\ell}\hat{R}_m$$

$$\qquad -i\beta_{ij}[(2\delta_{k\ell}\hat{R}_m + \delta_{\ell m}\hat{R}_k + \delta_{km}\hat{R}_\ell) - 6\hat{R}_k\hat{R}_\ell\hat{R}_m]$$

$$d_{ijk\ell m} = (\beta_{ij} - \alpha_{ij})[3(\delta_{k\ell}\hat{R}_m + \delta_{\ell m}\hat{R}_k + \delta_{km}\hat{R}_\ell) - 15\hat{R}_k\hat{R}_\ell\hat{R}_m]$$

$$\qquad -\beta_{ij}[(2\delta_{k\ell}\hat{R}_m + \delta_{\ell m}\hat{R}_k + \delta_{km}\hat{R}_\ell) - 6\hat{R}_k\hat{R}_\ell\hat{R}_m]$$

$$e_{ijk\ell m} = 0$$

$$f_{ijk\ell m} = \beta_{ij}[3(\delta_{k\ell}\hat{R}_m + \delta_{\ell m}\hat{R}_k + \delta_{km}\hat{R}_\ell) - 15\hat{R}_k\hat{R}_\ell\hat{R}_m] \tag{4.A.4}$$

and

$$f_{ij}(iuR)h_{k\ell m}(iuR) = i\left[\frac{A_{ijk\ell m}}{u^2R^2} + \frac{B_{ijk\ell m}}{u^3R^3} + \frac{C_{ijk\ell m}}{u^4R^4} + \frac{D_{ijk\ell m}}{u^5R^5} + \frac{E_{ijk\ell m}}{u^6R^6} + \frac{F_{ijk\ell m}}{u^7R^7}\right]$$

$$A_{ijk\ell m} = \alpha_{ij}\alpha_{k\ell}\hat{R}_m$$

$$B_{ijk\ell m} = \beta_{ij}\alpha_{k\ell}\hat{R}_m + \alpha_{ij}(2\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k - 6\hat{R}_k\hat{R}_\ell\hat{R}_m)$$

$$C_{ijk\ell m} = \beta_{ij}\alpha_{k\ell}\hat{R}_m + \delta_{k\ell}\hat{R}_m(3\alpha_{ij}+2\beta_{ij}) + \delta_{km}\hat{R}_\ell(3\alpha_{ij}+\beta_{ij}) + \delta_{\ell m}\hat{R}_k(3\alpha_{ij}+\beta_{ij})$$
$$- (15\alpha_{ij}+6\beta_{ij})\hat{R}_k\hat{R}_\ell\hat{R}_m$$

$$D_{ijk\ell m} = \delta_{k\ell}\hat{R}_m(3\alpha_{ij}+5\beta_{ij}) + (\delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k)(3\alpha_{ij}+4\beta_{ij}) - (15\alpha_{ij}+21\beta_{ij})\hat{R}_k\hat{R}_\ell\hat{R}_m$$

$$E_{ijk\ell m} = 6\beta_{ij}(\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k) - 30\beta_{ij}\hat{R}_k\hat{R}_\ell\hat{R}_m$$

$$F_{ijk\ell m} = 3\beta_{ij}(\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k) - 15\beta_{ij}\hat{R}_k\hat{R}_\ell\hat{R}_m \ . \tag{4.A.5}$$

In Section 4.7, the following products are required

$$h_{ijk}(iuR)h_{\ell mn}(iuR) =$$

$$\left[\frac{A_{ijk\ell mn}}{u^2R^2} + \frac{B_{ijk\ell mn}}{u^3R^3} + \frac{C_{ijk\ell mn}}{u^4R^4} + \frac{D_{ijk\ell mn}}{u^5R^5} + \frac{E_{ijk\ell mn}}{u^6R^6} + \frac{F_{ijk\ell mn}}{u^7R^7} + \frac{G_{ijk\ell mn}}{u^8R^8}\right]$$

where

$$A_{ijk\ell mn} = \alpha_{ij}\alpha_{\ell m}\hat{R}_k\hat{R}_n$$

$$B_{ijk\ell mn} = \alpha_{ij}\hat{R}_k(2\delta_{\ell m}\hat{R}_n + \delta_{\ell n}\hat{R}_m + \delta_{mn}\hat{R}_\ell - 6\hat{R}_\ell\hat{R}_m\hat{R}_n) +$$
$$\alpha_{\ell m}\hat{R}_n(2\delta_{ij}\hat{R}_k + \delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i - 6\hat{R}_i\hat{R}_j\hat{R}_k)$$

$$C_{ijk\ell mn} = \alpha_{ij}\hat{R}_k[3(\delta_{\ell m}\hat{R}_n + \delta_{\ell n}\hat{R}_m + \delta_{mn}\hat{R}_\ell) - 15\hat{R}_\ell\hat{R}_m\hat{R}_n] +$$
$$\alpha_{\ell m}\hat{R}_n[3(\delta_{ij}\hat{R}_k + \delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i) - 15\hat{R}_i\hat{R}_j\hat{R}_k] +$$
$$(2\delta_{ij}\hat{R}_k + \delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i - 6\hat{R}_i\hat{R}_j\hat{R}_k)(2\delta_{\ell m}\hat{R}_n + \delta_{\ell n}\hat{R}_m + \delta_{mn}\hat{R}_\ell - 6\hat{R}_\ell\hat{R}_m\hat{R}_n)$$

$$D_{ijk\ell mn} = \alpha_{ij}\hat{R}_k[3(\delta_{\ell m}\hat{R}_n + \delta_{\ell n}\hat{R}_m + \delta_{mn}\hat{R}_\ell) - 15\hat{R}_\ell\hat{R}_m\hat{R}_n] +$$
$$\alpha_{\ell m}\hat{R}_n[3(\delta_{ij}\hat{R}_k + \delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i) - 15\hat{R}_i\hat{R}_j\hat{R}_k] +$$
$$(2\delta_{ij}\hat{R}_k + \delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i - 6\hat{R}_i\hat{R}_j\hat{R}_k)[3(\delta_{\ell m}\hat{R}_n + \delta_{mn}\hat{R}_\ell + \delta_{n\ell}\hat{R}_m) - 15\hat{R}_\ell\hat{R}_m\hat{R}_n] +$$
$$[3(\delta_{ij}\hat{R}_k + \delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i) - 15\hat{R}_i\hat{R}_j\hat{R}_k](2\delta_{\ell m}\hat{R}_n + \delta_{\ell n}\hat{R}_m + \delta_{mn}\hat{R}_\ell - 6\hat{R}_\ell\hat{R}_m\hat{R}_n)$$

$$E_{ijk\ell mn} = (2\delta_{ij}\hat{R}_k+\delta_{ik}\hat{R}_j+\delta_{jk}\hat{R}_i-6\hat{R}_i\hat{R}_j\hat{R}_k)[3(\delta_{\ell m}\hat{R}_n+\delta_{\ell n}\hat{R}_m+\delta_{mn}\hat{R}_\ell)-15\hat{R}_\ell\hat{R}_m\hat{R}_n]+$$

$$[3(\delta_{ij}\hat{R}_k+\delta_{jk}\hat{R}_i+\delta_{ik}\hat{R}_j)-15\hat{R}_i\hat{R}_j\hat{R}_k][3(\delta_{\ell m}\hat{R}_n+\delta_{\ell n}\hat{R}_m+\delta_{mn}\hat{R}_\ell)-15\hat{R}_\ell\hat{R}_m\hat{R}_n]$$

$$+ [3(\delta_{ij}\hat{R}_k+\delta_{ik}\hat{R}_j+\delta_{jk}\hat{R}_i)-15\hat{R}_i\hat{R}_j\hat{R}_k](2\delta_{\ell m}\hat{R}_n+\delta_{\ell n}\hat{R}_m+\delta_{mn}\hat{R}_\ell-6\hat{R}_\ell\hat{R}_m\hat{R}_n)$$

$$F_{ijk\ell mn}= 2[3(\delta_{ij}\hat{R}_k+\delta_{ik}\hat{R}_j+\delta_{jk}\hat{R}_i)-15\hat{R}_i\hat{R}_j\hat{R}_k][3(\delta_{\ell m}\hat{R}_n+\delta_{\ell n}\hat{R}_m+\delta_{mn}\hat{R}_\ell)-15\hat{R}_\ell\hat{R}_m\hat{R}_n]$$

$$G_{ijk\ell mn} = [3(\delta_{ij}\hat{R}_k+\delta_{ik}\hat{R}_j+\delta_{jk}\hat{R}_i)-15\hat{R}_i\hat{R}_j\hat{R}_k][3(\delta_{\ell m}\hat{R}_n+\delta_{\ell n}\hat{R}_m+\delta_{mn}\hat{R}_\ell)-15\hat{R}_\ell\hat{R}_m\hat{R}_n]$$

$$(4.A.6)$$

and

$$\bar{h}_{ik\ell}(kR)h_{jmn}(kR) =$$

$$\left[\frac{a_{ijk\ell mn}}{k^2R^2} + \frac{b_{ijk\ell mn}}{k^3R^3} + \frac{c_{ijk\ell mn}}{k^4R^4} + \frac{d_{ijk\ell mn}}{k^5R^5} + \frac{e_{ijk\ell mn}}{k^6R^6} + \frac{f_{ijk\ell mn}}{k^7R^7} + \frac{g_{ijk\ell mn}}{k^8R^8}\right]$$

where

$$a_{ijk\ell mn} = \alpha_{ik}\alpha_{jm}\hat{R}_\ell\hat{R}_n$$

$$b_{ijk\ell mn} = i\alpha_{ik}\hat{R}_\ell(2\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m-6\hat{R}_j\hat{R}_m\hat{R}_n) -$$

$$i\alpha_{jm}\hat{R}_n(2\delta_{ik}\hat{R}_\ell+\delta_{k\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_k-6\hat{R}_i\hat{R}_k\hat{R}_\ell)$$

$$c_{ijk\ell mn} = -\alpha_{ik}\hat{R}_\ell[3(\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{nj}\hat{R}_m)-15\hat{R}_j\hat{R}_m\hat{R}_n] -$$

$$\alpha_{jm}\hat{R}_n[3(\delta_{ik}\hat{R}_\ell+\delta_{k\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_k)-15\hat{R}_i\hat{R}_k\hat{R}_\ell] +$$

$$(2\delta_{ik}\hat{R}_\ell+\delta_{k\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_k-6\hat{R}_i\hat{R}_k\hat{R}_\ell)(2\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m-6\hat{R}_j\hat{R}_m\hat{R}_n)$$

$$d_{ijk\ell mn} = -i\alpha_{ik}\hat{R}_\ell[3(\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m)-15\hat{R}_j\hat{R}_m\hat{R}_n] +$$

$$i(2\delta_{ik}\hat{R}_\ell+\delta_{i\ell}\hat{R}_k+\delta_{k\ell}\hat{R}_i-6\hat{R}_i\hat{R}_k\hat{R}_\ell)[3(\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m)-15\hat{R}_j\hat{R}_m\hat{R}_n]-$$

$$i[3(\delta_{ik}\hat{R}_\ell+\delta_{k\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_k)-15\hat{R}_i\hat{R}_k\hat{R}_\ell](2\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m-6\hat{R}_j\hat{R}_m\hat{R}_n)+$$

$$i\alpha_{jm}\hat{R}_n[3(\delta_{ik}\hat{R}_\ell+\delta_{k\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_k)-15\hat{R}_i\hat{R}_k\hat{R}_\ell]$$

$$e_{ijk\ell mn} = -(2\delta_{ik}\hat{R}_\ell+\delta_{k\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_k-6\hat{R}_i\hat{R}_k\hat{R}_\ell)[3(\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m)-15\hat{R}_j\hat{R}_m\hat{R}_n]+$$

$$[3(\delta_{i\ell}\hat{R}_\ell+\delta_{\ell\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_\ell)-15\hat{R}_i\hat{R}_\ell\hat{R}_\ell][3(\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m)-15\hat{R}_j\hat{R}_m\hat{R}_n]$$

$$- [3(\delta_{i\ell}\hat{R}_\ell+\delta_{\ell\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_\ell)-15\hat{R}_i\hat{R}_\ell\hat{R}_\ell](2\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m-6\hat{R}_j\hat{R}_m\hat{R}_n)$$

$$f_{ijk\ell mn} = 0$$

$$g_{ijk\ell mn} = [3(\delta_{i\ell}\hat{R}_\ell+\delta_{\ell\ell}\hat{R}_i+\delta_{i\ell}\hat{R}_\ell)-15\hat{R}_i\hat{R}_\ell\hat{R}_\ell][3(\delta_{jm}\hat{R}_n+\delta_{mn}\hat{R}_j+\delta_{jn}\hat{R}_m)-15\hat{R}_j\hat{R}_m\hat{R}_n]$$

$$(4.A.7)$$

In Section 4.8, one of the products required is

$$\bar{f}_{ij}(kR)l_{k\ell mn}(kR) =$$

$$\left[\frac{h_{ijk\ell mn}}{k^2R^2} + \frac{i_{ijk\ell mn}}{k^3R^3} + \frac{j_{ijk\ell mn}}{k^4R^4} + \frac{k_{ijk\ell mn}}{k^5R^5} + \frac{l_{ijk\ell mn}}{k^6R^6} + \frac{m_{ijk\ell mn}}{k^7R^7} + \frac{n_{ijk\ell mn}}{k^8R^8}\right]$$

where

$$h_{ijk\ell mn} = \alpha_{ij}\alpha_{k\ell}\hat{R}_m\hat{R}_n$$

$$i_{ijk\ell mn} = -i\alpha_{ij}(\delta_{k\ell}\delta_{mn}-4\delta_{k\ell}\hat{R}_m\hat{R}_n-\delta_{km}\hat{R}_\ell\hat{R}_n-\delta_{kn}\hat{R}_\ell\hat{R}_m-\delta_{\ell m}\hat{R}_k\hat{R}_n-\delta_{\ell n}\hat{R}_k\hat{R}_m$$

$$-\delta_{mn}\hat{R}_k\hat{R}_\ell+ 10\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n) -i\beta_{ij}\alpha_{k\ell}\hat{R}_m\hat{R}_n$$

$$j_{ijk\ell mn} = -\alpha_{ij}[6(\delta_{km}\hat{R}_\ell\hat{R}_n+\delta_{kn}\hat{R}_\ell\hat{R}_m+\delta_{\ell m}\hat{R}_k\hat{R}_n+\delta_{\ell n}\hat{R}_k\hat{R}_m+\delta_{mn}\hat{R}_k\hat{R}_\ell)+9\delta_{k\ell}\hat{R}_m\hat{R}_n-$$

$$2\delta_{k\ell}\delta_{mn}-\delta_{km}\delta_{\ell n}-\delta_{\ell m}\delta_{kn}-45\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n]-\beta_{ij}(\delta_{k\ell}\delta_{mn}-4\delta_{k\ell}\hat{R}_m\hat{R}_n-\delta_{km}\hat{R}_\ell\hat{R}_n$$

$$-\delta_{kn}\hat{R}_\ell\hat{R}_m-\delta_{\ell m}\hat{R}_k\hat{R}_n-\delta_{\ell n}\hat{R}_k\hat{R}_m-\delta_{mn}\hat{R}_k\hat{R}_\ell+10\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n)-\beta_{ij}\alpha_{k\ell}\hat{R}_m\hat{R}_n$$

$$k_{ijk\ell mn} = i\alpha_{ij}[3(\delta_{k\ell}\delta_{mn}+\delta_{km}\delta_{\ell n}+\delta_{\ell m}\delta_{kn})+105\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n+15(\delta_{k\ell}\hat{R}_m\hat{R}_n+\delta_{km}\hat{R}_\ell\hat{R}_n$$

$$+\delta_{kn}\hat{R}_\ell\hat{R}_m+\delta_{\ell m}\hat{R}_k\hat{R}_n+\delta_{\ell n}\hat{R}_k\hat{R}_m+\delta_{mn}\hat{R}_k\hat{R}_\ell)]+i\beta_{ij}[6(\delta_{km}\hat{R}_\ell\hat{R}_n+\delta_{kn}\hat{R}_\ell\hat{R}_m+$$

$$\delta_{\ell m}\hat{R}_k\hat{R}_n+\delta_{\ell n}\hat{R}_k\hat{R}_m+\delta_{mn}\hat{R}_k\hat{R}_\ell)+9\delta_{k\ell}\hat{R}_m\hat{R}_n-2\delta_{k\ell}\delta_{mn}-\delta_{km}\delta_{\ell n}-\delta_{\ell m}\delta_{kn}-$$

$$45\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n] +i\beta_{ij}[\delta_{k\ell}\delta_{mn}-4\delta_{k\ell}\hat{R}_m\hat{R}_n-\delta_{km}\hat{R}_\ell\hat{R}_n-\delta_{kn}\hat{R}_\ell\hat{R}_m-\delta_{\ell m}\hat{R}_k\hat{R}_n-$$

$$\delta_{\ell n}\hat{R}_k\hat{R}_m-\delta_{mn}\hat{R}_k\hat{R}_\ell+10\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n]$$

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$$l_{ij\ell\ell mn} = (\beta_{ij} - \alpha_{ij})[3(\delta_{\ell\ell}\delta_{mn} + \delta_{\ell m}\delta_{\ell n} + \delta_{\ell m}\delta_{\ell n}) + 105\hat{R}_{\ell}\hat{R}_{\ell}\hat{R}_{m}\hat{R}_{n} - 15(\delta_{\ell\ell}\hat{R}_{m}\hat{R}_{n} +$$

$$\delta_{\ell m}\hat{R}_{\ell}\hat{R}_{n} + \delta_{\ell n}\hat{R}_{\ell}\hat{R}_{m} + \delta_{\ell m}\hat{R}_{\ell}\hat{R}_{n} + \delta_{\ell n}\hat{R}_{\ell}\hat{R}_{m} + \delta_{mn}\hat{R}_{\ell}\hat{R}_{\ell})] +$$

$$\beta_{ij}[6(\delta_{\ell m}\hat{R}_{\ell}\hat{R}_{n} + \delta_{\ell n}\hat{R}_{\ell}\hat{R}_{m} + \delta_{\ell m}\hat{R}_{\ell}\hat{R}_{n} + \delta_{\ell n}\hat{R}_{\ell}\hat{R}_{m} + \delta_{mn}\hat{R}_{\ell}\hat{R}_{\ell}) + 9\delta_{\ell\ell}\hat{R}_{m}\hat{R}_{n} -$$

$$2\delta_{\ell\ell}\delta_{mn} - \delta_{\ell m}\delta_{\ell n} - \delta_{\ell m}\delta_{\ell n} - 45\hat{R}_{\ell}\hat{R}_{\ell}\hat{R}_{m}\hat{R}_{n}]$$

$$m_{ij\ell\ell mn} = 0$$

$$n_{ij\ell\ell mn} = \beta_{ij}[3(\delta_{\ell\ell}\delta_{mn} + \delta_{\ell m}\delta_{\ell n} + \delta_{\ell m}\delta_{\ell n}) + 105\hat{R}_{\ell}\hat{R}_{\ell}\hat{R}_{m}\hat{R}_{n} - 15(\delta_{\ell\ell}\hat{R}_{m}\hat{R}_{n} +$$

$$+ \delta_{\ell m}\hat{R}_{\ell}\hat{R}_{n} + \delta_{\ell n}\hat{R}_{\ell}\hat{R}_{m} + \delta_{\ell m}\hat{R}_{\ell}\hat{R}_{n} + \delta_{\ell n}\hat{R}_{\ell}\hat{R}_{m} + \delta_{mn}\hat{R}_{\ell}\hat{R}_{\ell})]. \qquad (4.A.8)$$

Since

$$\bar{f}_{ij}(kR)l_{\ell\ell mn}(kR) + \bar{l}_{\ell\ell mn}(kR)f_{ij}(kR) = 2(h_{ij\ell\ell mn} + j_{ij\ell\ell mn} + l_{ij\ell\ell mn} + n_{ij\ell\ell mn})$$

and

$$h_{ij\ell}(kR)\bar{h}_{\ell mn}(kR) + \bar{h}_{ij\ell}(kR)h_{\ell mn}(kR) = 2(a_{ij\ell\ell mn} + c_{ij\ell\ell mn} + e_{ij\ell\ell mn} + g_{ij\ell\ell mn}),$$

the tensors written in (4.8.6) are defined as

$$p_{ij\ell\ell mn} = 2(a_{ij\ell\ell mn} + h_{ij\ell\ell mn})$$

$$r_{ij\ell\ell mn} = 2(c_{ij\ell\ell mn} + j_{ij\ell\ell mn})$$

$$t_{ij\ell\ell mn} = 2(e_{ij\ell\ell mn} + l_{ij\ell\ell mn})$$

$$v_{ij\ell\ell mn} = 2(g_{ij\ell\ell mn} + n_{ij\ell\ell mn})$$

$$q_{ij\ell\ell mn} = s_{ij\ell\ell mn} = u_{ij\ell\ell mn} = 0. \qquad (4.A.9)$$

Also required in Section 4.8 is

$$f_{ij}(iuR)1_{k\ell mn}(iuR) =$$

$$\left[\frac{H_{ijk\ell mn}}{u^2R^2} + \frac{I_{ijk\ell mn}}{u^3R^3} + \frac{J_{ijk\ell mn}}{u^4R^4} + \frac{K_{ijk\ell mn}}{u^5R^5} + \frac{L_{ijk\ell mn}}{u^6R^6} + \frac{M_{ijk\ell mn}}{u^7R^7} + \frac{N_{ijk\ell mn}}{u^8R^8}\right]$$

where

$$H_{ijk\ell mn} = -\alpha_{ij}\alpha_{k\ell}\hat{R}_m\hat{R}_n$$

$$I_{ijk\ell mn} = \alpha_{ij}(\delta_{k\ell}\delta_{mn} - 4\delta_{k\ell}\hat{R}_m\hat{R}_n + 10\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n - \delta_{km}\hat{R}_\ell\hat{R}_n - \delta_{kn}\hat{R}_\ell\hat{R}_m - \delta_{\ell m}\hat{R}_k\hat{R}_n -$$
$$\delta_{\ell n}\hat{R}_k\hat{R}_m - \delta_{mn}\hat{R}_k\hat{R}_\ell) - \beta_{ij}\alpha_{k\ell}\hat{R}_m\hat{R}_n$$

$$J_{ijk\ell mn} = \alpha_{ij}[-6(\delta_{km}\hat{R}_\ell\hat{R}_n + \delta_{kn}\hat{R}_\ell\hat{R}_m + \delta_{\ell m}\hat{R}_k\hat{R}_n + \delta_{\ell n}\hat{R}_k\hat{R}_m + \delta_{mn}\hat{R}_k\hat{R}_\ell) - 9\delta_{k\ell}\hat{R}_m\hat{R}_n +$$
$$2\delta_{k\ell}\delta_{mn} + \delta_{km}\delta_{\ell n} + 2\delta_{kn}\delta_{\ell m} + 45\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n] + \beta_{ij}[\delta_{k\ell}\delta_{mn} - 4\delta_{k\ell}\hat{R}_m\hat{R}_n +$$
$$10\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n - \delta_{km}\hat{R}_\ell\hat{R}_n - \delta_{kn}\hat{R}_\ell\hat{R}_m - \delta_{\ell m}\hat{R}_k\hat{R}_n - \delta_{\ell n}\hat{R}_k\hat{R}_m - \delta_{mn}\hat{R}_k\hat{R}_\ell] - \beta_{ij}\alpha_{k\ell}\hat{R}_m\hat{R}_n$$

$$K_{ijk\ell mn} = \alpha_{ij}[3(\delta_{k\ell}\delta_{mn} + \delta_{km}\delta_{\ell n} + \delta_{\ell m}\delta_{kn}) - 15(\delta_{k\ell}\hat{R}_m\hat{R}_n + \delta_{km}\hat{R}_\ell\hat{R}_n + \delta_{kn}\hat{R}_\ell\hat{R}_m +$$
$$\delta_{\ell m}\hat{R}_k\hat{R}_n + \delta_{\ell n}\hat{R}_k\hat{R}_m + \delta_{mn}\hat{R}_k\hat{R}_\ell) + 105\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n] + \beta_{ij}[-6(\delta_{km}\hat{R}_\ell\hat{R}_n + \delta_{kn}\hat{R}_\ell\hat{R}_m +$$
$$\delta_{\ell m}\hat{R}_k\hat{R}_n + \delta_{\ell n}\hat{R}_k\hat{R}_m + \delta_{mn}\hat{R}_k\hat{R}_\ell) - 9\delta_{k\ell}\hat{R}_m\hat{R}_n + 2\delta_{k\ell}\delta_{mn} + \delta_{km}\delta_{\ell n} + \delta_{kn}\delta_{\ell m} + 45\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n] +$$
$$\beta_{ij}[\delta_{k\ell}\delta_{mn} - 4\delta_{k\ell}\hat{R}_m\hat{R}_n + 10\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n - \delta_{km}\hat{R}_\ell\hat{R}_n - \delta_{kn}\hat{R}_\ell\hat{R}_m - \delta_{\ell m}\hat{R}_k\hat{R}_n -$$
$$\delta_{\ell n}\hat{R}_k\hat{R}_m - \delta_{mn}\hat{R}_k\hat{R}_\ell]$$

$$L_{ijk\ell mn} = (\alpha_{ij}+\beta_{ij})[3(\delta_{k\ell}\delta_{mn} + \delta_{km}\delta_{\ell n} + \delta_{\ell m}\delta_{kn}) + 105\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n - 15(\delta_{k\ell}\hat{R}_m\hat{R}_n +$$
$$\delta_{km}\hat{R}_\ell\hat{R}_n + \delta_{kn}\hat{R}_\ell\hat{R}_m + \delta_{\ell m}\hat{R}_k\hat{R}_n + \delta_{\ell n}\hat{R}_k\hat{R}_m + \delta_{mn}\hat{R}_k\hat{R}_\ell)] + \beta_{ij}[-6(\delta_{km}\hat{R}_\ell\hat{R}_n + \delta_{kn}\hat{R}_\ell\hat{R}_m +$$
$$\delta_{\ell m}\hat{R}_k\hat{R}_n + \delta_{mn}\hat{R}_k\hat{R}_\ell + \delta_{\ell n}\hat{R}_k\hat{R}_m) - 9\delta_{k\ell}\hat{R}_m\hat{R}_n + 2\delta_{k\ell}\delta_{mn} + \delta_{km}\delta_{\ell n} + \delta_{kn}\delta_{\ell m} + 45\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n]$$

$$M_{ijk\ell mn} = 2\beta_{ij}[3(\delta_{k\ell}\delta_{mn} + \delta_{km}\delta_{\ell n} + \delta_{kn}\delta_{\ell m}) + 105\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n - 15(\delta_{k\ell}\hat{R}_m\hat{R}_n +$$
$$\delta_{km}\hat{R}_\ell\hat{R}_n + \delta_{kn}\hat{R}_\ell\hat{R}_m + \delta_{\ell m}\hat{R}_k\hat{R}_n + \delta_{\ell n}\hat{R}_k\hat{R}_m + \delta_{mn}\hat{R}_k\hat{R}_\ell)]$$

$$N_{ijk\ell mn} = \beta_{ij}[3(\delta_{k\ell}\delta_{mn} + \delta_{km}\delta_{\ell n} + \delta_{kn}\delta_{\ell m}) + 105\hat{R}_k\hat{R}_\ell\hat{R}_m\hat{R}_n - 15(\delta_{k\ell}\hat{R}_m\hat{R}_n +$$
$$\delta_{km}\hat{R}_\ell\hat{R}_n + \delta_{kn}\hat{R}_\ell\hat{R}_m + \delta_{\ell m}\hat{R}_k\hat{R}_n + \delta_{\ell n}\hat{R}_k\hat{R}_m + \delta_{mn}\hat{R}_k\hat{R}_\ell)].\qquad (4.A.10)$$

The tensors used in (4.8.7) take on the definitions

$$P_{ijk\ell mn} = A_{ijk\ell mn} + H_{ijk\ell mn}$$

$$Q_{ijk\ell mn} = B_{ijk\ell mn} + I_{ijk\ell mn}$$

$$R_{ijk\ell mn} = C_{ijk\ell mn} + J_{ijk\ell mn}$$

$$S_{ijk\ell mn} = D_{ijk\ell mn} + K_{ijk\ell mn}$$

$$T_{ijk\ell mn} = E_{ijk\ell mn} + L_{ijk\ell mn}$$

$$U_{ijk\ell mn} = F_{ijk\ell mn} + M_{ijk\ell mn}$$

$$V_{ijk\ell mn} = G_{ijk\ell mn} + N_{ijk\ell mn} \ . \tag{4.A.11}$$

In Section 4.9, the required products are

$$\bar{g}_{ij}(kR)h_{k\ell m}(kR) - g_{ij}(kR)\bar{h}_{k\ell m}(kR) =$$

$$\left[\frac{g_{ijk\ell m}}{k^2 R^2} + \frac{h_{ijk\ell m}}{k^3 R^3} + \frac{i_{ijk\ell m}}{k^4 R^4} + \frac{j_{ijk\ell m}}{k^5 R^5} + \frac{k_{ijk\ell m}}{k^6 R^6} \right]$$

where

$$g_{ijk\ell m} = -2i\varepsilon_{ij\partial}\alpha_{k\ell}\hat{R}_{\partial}\hat{R}_m$$

$$h_{ijk\ell m} = 0$$

$$i_{ijk\ell m} = 2i\varepsilon_{ij\partial}\hat{R}_{\partial}[3(\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_{\ell} + \delta_{\ell m}\hat{R}_k) - 15\hat{R}_k\hat{R}_{\ell}\hat{R}_m] -$$

$$\qquad [(2\delta_{k\ell}\hat{R}_m + \delta_{\ell m}\hat{R}_k + \delta_{km}\hat{R}_{\ell}) - 6\hat{R}_k\hat{R}_{\ell}\hat{R}_m]$$

$$j_{ijk\ell m} = 0$$

$$k_{ijk\ell m} = 2i\varepsilon_{ij\partial}\hat{R}_{\partial}[3(\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_{\ell} + \delta_{\ell m}\hat{R}_k) - 15\hat{R}_k\hat{R}_{\ell}\hat{R}_m] \tag{4.A.12}$$

and

$$g_{ij}(iuR)h_{k\ell m}(iuR) = \left[\frac{G_{ijk\ell m}}{u^2 R^2} + \frac{H_{ijk\ell m}}{u^3 R^3} + \frac{I_{ijk\ell m}}{u^4 R^4} + \frac{J_{ijk\ell m}}{u^5 R^5} + \frac{K_{ijk\ell m}}{u^6 R^6} \right]$$

where

$$G_{ijk\ell m} = i\varepsilon_{ij\partial}\alpha_{k\ell}\hat{R}_{\partial}\hat{R}_m$$

$$H_{ijk\ell m} = i\varepsilon_{ij\delta}\hat{R}_\delta[\{(2\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k) - 6\hat{R}_k\hat{R}_\ell\hat{R}_m\} + \alpha_{k\ell}\hat{R}_m]$$

$$I_{ijk\ell m} = i\varepsilon_{ij\delta}\hat{R}_\delta[\{3(\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k) - 15\hat{R}_k\hat{R}_\ell\hat{R}_m\} +$$

$$\{(2\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k) - 6\hat{R}_k\hat{R}_\ell\hat{R}_m\}]$$

$$J_{ijk\ell m} = 2i\varepsilon_{ij\delta}\hat{R}_\delta[3(\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k) - 15\hat{R}_k\hat{R}_\ell\hat{R}_m]$$

$$K_{ijk\ell m} = i\varepsilon_{ij\delta}\hat{R}_\delta[3(\delta_{k\ell}\hat{R}_m + \delta_{km}\hat{R}_\ell + \delta_{\ell m}\hat{R}_k) - 15\hat{R}_k\hat{R}_\ell\hat{R}_m]. \tag{4.A.13}$$

In Section 4.10, one of the terms needed is

$$j_{ijk}(kR)\bar{f}_{\ell m}(kR) + \bar{j}_{ijk}(kR)f_{\ell m}(kR) =$$

$$\left[\frac{l_{ijk\ell m}}{k^2 R^2} + \frac{m_{ijk\ell m}}{k^3 R^3} + \frac{n_{ijk\ell m}}{k^4 R^4} + \frac{o_{ijk\ell m}}{k^5 R^5} + \frac{p_{ijk\ell m}}{k^6 R^6}\right]$$

where

$$l_{ijk\ell m} = -2\varepsilon_{ij\delta}\alpha_{\ell m}\hat{R}_\delta\hat{R}_k$$

$$m_{ijk\ell m} = 0$$

$$n_{ijk\ell m} = 2\varepsilon_{ij\delta}(\beta_{\ell m}\hat{R}_\delta\hat{R}_k + \beta_{\delta k}\beta_{\ell m} - \beta_{\delta k}\alpha_{\ell m})$$

$$o_{ijk\ell m} = 0$$

$$p_{ijk\ell m} = 2\varepsilon_{ij\delta}\beta_{\delta k}\beta_{\ell m} \tag{4.A.14}$$

so that the geometrical part of (4.10.4), as written in (4.10.5), can be expressed as

$$\bar{h}_{k\ell m}(kR)g_{ij}(kR) - \bar{g}_{ij}(kR)h_{k\ell m}(kR) - i[\bar{f}_{\ell m}(kR)j_{ijk}(kR) + \bar{j}_{ijk}(kR)f_{\ell m}(kR)] =$$

$$\left[\frac{q_{ijk\ell m}}{k^2 R^2} + \frac{r_{ijk\ell m}}{k^3 R^3} + \frac{s_{ijk\ell m}}{k^4 R^4} + \frac{t_{ijk\ell m}}{k^5 R^5} + \frac{u_{ijk\ell m}}{k^6 R^6}\right]$$

where

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$$q_{ijk\ell m} = g_{ijk\ell m} + il_{ijk\ell m}$$

$$r_{ijk\ell m} = h_{ijk\ell m} + im_{ijk\ell m} = 0$$

$$s_{ijk\ell m} = i_{ijk\ell m} + in_{ijk\ell m}$$

$$t_{ijk\ell m} = j_{ijk\ell m} + io_{ijk\ell m} = 0$$

$$u_{ijk\ell m} = k_{ijk\ell m} + ip_{ijk\ell m}. \tag{4.A.15}$$

Also required in Section 4.10 is the product

$$ij_{ijk}(iuR)f_{\ell m}(iuR) = \left[\frac{L_{ijk\ell m}}{u^2R^2} + \frac{M_{ijk\ell m}}{u^3R^3} + \frac{N_{ijk\ell m}}{u^4R^4} + \frac{O_{ijk\ell m}}{u^5R^5} + \frac{P_{ijk\ell m}}{u^6R^6} \right]$$

where

$$L_{ijk\ell m} = i\varepsilon_{ij\sigma}\alpha_{\ell m}\hat{R}_\sigma\hat{R}_k$$

$$M_{ijk\ell m} = i\varepsilon_{ij\sigma}(\beta_{\ell m}\hat{R}_\sigma\hat{R}_k - \alpha_{\ell m}\beta_{\sigma k})$$

$$N_{ijk\ell m} = i\varepsilon_{ij\sigma}(-\beta_{\ell m}\hat{R}_\sigma\hat{R}_k - \beta_{\sigma k}\beta_{\ell m} - \beta_{\sigma k}\alpha_{\ell m})$$

$$O_{ijk\ell m} = -2i\varepsilon_{ij\sigma}\beta_{\sigma k}\beta_{\ell m}$$

$$P_{ijk\ell m} = -i\varepsilon_{ij\sigma}\beta_{\sigma k}\beta_{\ell m} \tag{4.A.16}$$

so that the geometrical part of (4.10.6) is given by

$$ij_{ijk}(iuR)f_{\ell m}(iuR) + g_{ij}(iuR)h_{k\ell m}(iuR) =$$

$$\left[\frac{Q_{ijk\ell m}}{u^2R^2} + \frac{R_{ijk\ell m}}{u^3R^3} + \frac{S_{ijk\ell m}}{u^4R^4} + \frac{T_{ijk\ell m}}{u^5R^5} + \frac{U_{ijk\ell m}}{u^6R^6} \right] ,$$

$$Q_{ijk\ell m} = G_{ijk\ell m} + L_{ijk\ell m}$$

$$R_{ijk\ell m} = H_{ijk\ell m} + M_{ijk\ell m}$$

$$S_{ijk\ell m} = I_{ijk\ell m} + N_{ijk\ell m}$$

$$T_{ijk\ell m} = J_{ijk\ell m} + O_{ijk\ell m}$$

$$U_{ijk\ell m} = K_{ijk\ell m} + P_{ijk\ell m} . \tag{4.A.17}$$

CHAPTER 5

MOLECULE INDUCED CIRCULARLY POLARISED LUMINESCENCE

5.1 INTRODUCTION

Circularly polarised luminescence [60] is defined as the difference in rates of spontaneous emission of left- and right-handed circularly polarised light from a chiral molecular species in an isotropic medium. A closely related phenomenon is molecule induced circularly polarised luminescence which is the differential circular emission rate arising from chirality induced in an achiral molecule through intermolecular interaction with a chiral molecule.

Circularly polarised emission spectroscopy is increasingly used in the determination of molecular stereochemistry and electronic structure with circularly polarised luminescence observables reflecting the chirality of molecular emitting states and providing configurational and conformational structure information. This complements techniques used to probe naturally optically active systems in the ground state such as optical rotation, optical rotatory dispersion, circular dichroism and circular intensity differential scattering, each of which also has a firm basis in theory, ranging from early semi-classical treatments given by Rosenfeld [61] and Condon [62], to fully quantum field descriptions by Barron and Buckingham [63], by Power and Thirunamachandran [64] and by Atkins and Barron [65]. Riehl and Richardson [66] have given the general quantum electrodynamical theory of circularly polarised emission and magnetic circularly polarised emission, the latter being the emission analogue of magnetic circular dichroism [67].

In addition to natural optical activity, there is a related class of phenomena in which an achiral molecule acquires optical activity

through interaction with a chiral molecule. A well known example is molecule induced circular dichroism [68], whose theoretical derivation was given by Craig et al [69] . This theory was presented using QED in the Schrödinger picture where the time dependence is contained entirely within the state function for the radiation-matter system. Intermolecular interaction involved the exchange of a virtual photon, expressed in terms of retarded potentials. An equivalent formulation based on the Heisenberg picture, where the time dependence is contained entirely within the operators, was later presented by Power and Thirunamachandran [70]. In this viewpoint, the coupling of the transition moment of the achiral species to the electromagnetic fields produced by the chiral molecule was examined.

In this Chapter, the theory of molecule induced circularly polarised luminescence is developed using both the Schrödinger and Heisenberg pictures of QED. Chirality in the achiral molecule A is induced dynamically by the coupling of virtual transitions in the chiral molecule C to those of molecule A, with the result that a real photon of circular polarisation is emitted spontaneously. The essential feature which enables the phenomenon to be observed is that luminescence occurs at a frequency characteristic of a transition in the achiral molecule, the chiral species being transparent at that frequency. QED provides a suitable framework for the study of emission phenomena; the radiation field is quantised and forms part of the dynamical system, in contrast to semi-classical theory, which fails to correctly account for spontaneous emission. In both the Schrödinger and Heisenberg pictures, the multipolar form of QED is best suited for the study of molecule induced circularly polarised luminescence. Molecules couple with the electromagnetic field solely through electric and magnetic multipole moments mediated by the exchange of photons.

The theory is first outlined within the Schrödinger picture and used to determine the matrix element for molecule induced circularly polarised emission. The theory is then presented using the Heisenberg formalism and the matrix element calculated is shown to be identical to that obtained using the Schrödinger approach. Either of the two matrix elements can then be used to determine the differential emission rate. The results are applicable whether A and C are held fixed with respect to the intermolecular join corresponding to the fully locked in case, or are allowed to rotate as a single entity relative to the wavevector of the emergent ray, or are permitted to be completely randomly oriented. The dependence of the rate expression on intermolecular separation is examined after each stage of averaging. The two methods are compared and contrasted to gain insight into the nature of radiation-molecule interactions in QED.

5.2 EVALUATION OF MATRIX ELEMENT IN THE SCHRODINGER PICTURE

The total Hamiltonian for the system of molecules interacting with the electromagnetic field in multipolar framework is given by (1.2.30). Since molecule induced circularly polarised emission is a one photon process, only the terms linear in the electromagnetic field appearing in the interaction Hamiltonian (1.2.33) can contribute. The last term of (1.2.33), being quadratic in $\vec{b}(\vec{r})$ is ignored to this order of approximation. The interaction Hamiltonian to dipole approximation may then be written as

$$H_{INT} \simeq -\varepsilon_0^{-1}\vec{\mu}(A).\vec{d}^\perp(\vec{R}_A)-\varepsilon_0^{-1}\vec{\mu}(C).\vec{d}^\perp(\vec{R}_C)-\vec{m}(C).\vec{b}(\vec{R}_C). \qquad (5.2.1)$$

Strictly the electric quadrupole interaction term, being of the same order as $-\vec{m}.\vec{b}$, must also be included in (5.2.1). However, the contribution from this term to the differential rate is zero for randomly oriented molecules, and is thus omitted.

The transitions in C are both electric and magnetic dipole allowed whereas that in A is only electric dipole allowed. Let the emitted photon of left- or right-circular polarisation be of mode $(\vec{k}, L/R)$ corresponding to an electric dipole allowed transition of the achiral molecule A. The energy levels are assumed to be non-degenerate and their wavefunctions are chosen to be real. The extension to the degenerate case is straightforward. Let the energy levels of the chiral molecule be $|E_n\rangle$. The transition rate corresponding to the transition $|E_0^A, E_0^C\rangle \longleftarrow$ $|E_m^A, E_0^C\rangle$ in the achiral molecule, with no overall change in the state of the chiral molecule, is given by the Fermi golden rule (1.2.57). The initial and final states for the process are specified as

$$|i\rangle = |E_m^A, E_0^C; 0(\vec{k}, L/R)\rangle \qquad\qquad (5.2.2)$$

$$|f\rangle = |E_0^A, E_0^C; 1(\vec{k}, L/R)\rangle \qquad\qquad (5.2.3)$$

corresponding to A in the mth excited state initially, in the ground state with one circularly polarised photon finally, and with C remaining unchanged in the ground state overall.

The calculation of the probability amplitude M_{fi} in the Schrödinger picture is facilitated by the use of time-ordered graphs. The leading contribution to M_{fi} for the transition $|final\rangle \longleftarrow |initial\rangle$ is of first order corresponding to the graph in Fig.5.1., which shows spontaneous emission by A, from which

$$M_{fi}^{(1)(L/R)} = i\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\bar{e}_i^{(L/R)}(\vec{k})\mu_i^{0m}(A) \tag{5.2.4}$$

choosing A to be situated at the origin of the molecular coordinate frame. To first order there is no effect arising from the chiral nature of C, the transition rate based on (5.2.4) being identical for photons of a definite helicity. Higher order contributions include the interaction between A and C via the exchange of virtual photons. The leading contribution taking account of such interaction is of third order corresponding to one-photon exchange. This is described completely by six graphs, one of which is shown in Fig.5.2.

The third order process involves virtual excitation to the states $|E_n\rangle$ of the chiral molecule and the exchange of a virtual photon between C and A. The total contribution to the third order matrix element is obtained by considering all possible time-ordered sequences and is calculated using conventional time-dependent perturbation theory. Diagrams in which the virtual photon propagates from A to C contribute (5.2.5)

$$i\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\sum_{\vec{p},\lambda}\left(\frac{\hbar cp}{2\varepsilon_0 V}\right)\mu_\ell^{0m}(A)\frac{e^{i(\vec{p}-\vec{k})\cdot\vec{R}}}{(\hbar cp-\hbar ck)}\times$$

$$\left[\frac{1}{c}\bar{e}_i^{(L/R)}(\vec{k})e_j^{(\lambda)}(\vec{p})\bar{e}_\ell^{(\lambda)}(\vec{p})\sum_n\left\{\frac{\mu_i^{0n}\mu_j^{n0}}{E_{no}-\hbar ck}+\frac{\mu_j^{0n}\mu_i^{n0}}{E_{no}+\hbar ck}\right\}+\right.$$

$$\frac{1}{c}\bar{e}_i^{(L/R)}(\vec{k})b_j^{(\lambda)}(\vec{p})\bar{e}_\ell^{(\lambda)}(\vec{p})\sum_n\left\{\frac{\mu_i^{0n}m_j^{n0}}{E_{no}-\hbar ck}+\frac{m_j^{0n}\mu_i^{n0}}{E_{no}+\hbar ck}\right\}+$$

$$\left.\frac{1}{c}\bar{b}_i^{(L/R)}(\vec{k})e_j^{(\lambda)}(\vec{p})\bar{e}_\ell^{(\lambda)}(\vec{p})\sum_n\left\{\frac{\mu_j^{0n}m_i^{n0}}{E_{no}+\hbar ck}+\frac{m_i^{0n}\mu_j^{n0}}{E_{no}-\hbar ck}\right\}\right] \tag{5.2.5}$$

to the matrix element in which the photon of wavevector $\vec{k}$ is circularly polarised and is associated with the real photon emission. The virtual photon wavevector $\vec{p}$ and polarisation index λ are both summed, along with
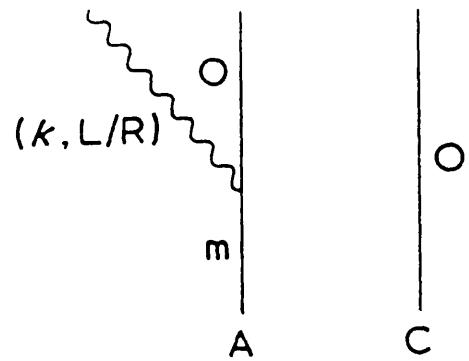
Fig. 1. First order graph for luminescence.
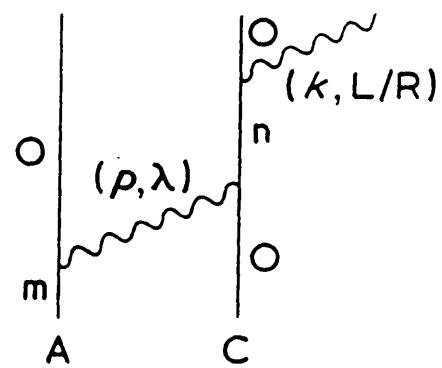
Fig. 2. Typical third order graph for luminescence.

all the allowed virtual states. Use has also been made of the fact that for real wavefunctions, $\vec{\mu}^{n0} = \vec{\mu}^{0n}$ and $\vec{m}^{n0} = -\vec{m}^{0n}$. The polarisation sums in expression (5.2.5) may be performed with the aid of (2.2.19) and (2.2.20), and by use of the identity [6]

$$\vec{b}^{(L/R)}(\vec{k}) = \mp i \vec{e}^{(L/R)}(\vec{k}).$$

(5.2.6)

The molecular terms within the square brackets of (5.2.5) correspond to the electric dipole polarisability $\alpha_{ij}(\omega)$ and the mixed electric dipole-magnetic dipole analogue $G_{ij}(\omega)$, whose definitions were given by (4.2.2) and (4.3.2). $\alpha_{ij}(\omega)$ is the same for a chiral molecule and its enantiomer. $G_{ij}(\omega)$ is of opposite sign for a chiral molecule and its enantiomer since the magnetic dipole matrix element does not change sign under inversion, in contrast to the electric dipole matrix element. Expression (5.2.5) may now be rewritten as

$$i\left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2} \bar{e}_i^{(L/R)}(\vec{k}) \mu_{\ell}^{0m}(A) \sum_{\vec{p}}\left(\frac{\hbar c p}{2\varepsilon_0 V}\right)\frac{e^{-i(\vec{k}-\vec{p}).\vec{R}}}{(\hbar c p - \hbar c k)} \times$$
$$\left[(\delta_{j\ell}-\hat{p}_j\hat{p}_\ell)[\alpha_{ij}(\omega)\mp\frac{i}{c}G_{ji}(\omega)] + \frac{1}{c}\varepsilon_{j\ell\ell'}\hat{p}_{\ell'}G_{ij}(\omega)\right]$$

(5.2.7)

where the upper and lower signs refer to L and R respectively. The contribution from the other three time-ordered graphs where the virtual photon travels from C to A is

$$i\left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2} \bar{e}_i^{(L/R)}(\vec{k}) \mu_{\ell}^{0m}(A) \sum_{\vec{p}}\left(\frac{\hbar c p}{2\varepsilon_0 V}\right)\frac{e^{-i(\vec{k}+\vec{p}).\vec{R}}}{(\hbar c p + \hbar c k)} \times$$
$$\left[(\delta_{j\ell}-\hat{p}_j\hat{p}_\ell)[\alpha_{ij}(\omega)\mp\frac{i}{c}G_{ji}(\omega)] + \frac{1}{c}\varepsilon_{j\ell\ell'}\hat{p}_{\ell'}G_{ij}(\omega)\right].$$

(5.2.8)

Adding expressions (5.2.7) and (5.2.8) and converting the $\vec{p}$-sum to an

integral using (2.2.21) results in the following for the total third order matrix element

$$
M_{fi}^{(3)(L/R)} = -i\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \bar{e}_i^{(L/R)}(\vec{k})\mu_\ell^{0m}(A)e^{-i\vec{k}\cdot\vec{R}}\left[\frac{1}{2\varepsilon_0}[\alpha_{ij}(\omega)\mp\frac{i}{c}G_{ji}(\omega)]\right.
$$

$$
\times\int\frac{p^2}{(k^2-p^2)}(\delta_{j\ell}-\hat{p}_j\hat{p}_\ell)(e^{i\vec{p}\cdot\vec{R}}+e^{-i\vec{p}\cdot\vec{R}})\frac{d^3\vec{p}}{(2\pi)^3}
$$

$$
\left.+\frac{1}{2\varepsilon_0 c}[k\varepsilon_{j\ell\ell'}G_{ij}(\omega)]\int\frac{p_\ell}{(k^2-p^2)}(e^{i\vec{p}\cdot\vec{R}}-e^{-i\vec{p}\cdot\vec{R}})\frac{d^3\vec{p}}{(2\pi)^3}\right]. \tag{5.2.9}
$$

The integrals appearing in (5.2.9) occur in the study of intermolecular interactions [6]. The relevant integrals are

$$
\frac{1}{2\varepsilon_0}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\int\frac{1}{p}\left(\frac{e^{i\vec{p}\cdot\vec{R}}}{p-k}+\frac{e^{-i\vec{p}\cdot\vec{R}}}{p+k}\right)\frac{d^3\vec{p}}{(2\pi)^3}
$$

$$
= \frac{1}{4\pi\varepsilon_0 R^3}[\beta_{ij}(1-ikR)-\alpha_{ij}k^2R^2]e^{ikR} = V_{ij}(k,\vec{R}) \tag{5.2.10}
$$

and

$$
\frac{ik}{2\varepsilon_0 c}\varepsilon_{ij\ell}\nabla_\ell\int\frac{1}{p}\left(\frac{e^{i\vec{p}\cdot\vec{R}}}{p-k}+\frac{e^{-i\vec{p}\cdot\vec{R}}}{p+k}\right)\frac{d^3\vec{p}}{(2\pi)^3}
$$

$$
= \frac{\varepsilon_{ij\ell}k\hat{R}_\ell}{4\pi\varepsilon_0 cR^2}[1-ikR]e^{ikR} = U_{ij}(k,\vec{R}) \tag{5.2.11}
$$

with the dyadics α_{ij} and β_{ij} defined by (4.3.7). $V_{ij}(k,\vec{R})$ arises from the matrix element representing the resonance coupling between two systems, one in the ground state and the other in excited state and is known as the retarded electric dipole-electric dipole interaction tensor; $U_{ij}(k,\vec{R})$ is the electric dipole-magnetic dipole analogue for chiral systems in which both electric and magnetic interaction terms contributing to intermolecular coupling are included. This enables

(5.2.9) to be written as

$$M_{fi}^{(3)(L/R)} = -i\left(\frac{\hbar c k}{2\varepsilon_0 V}\right)^{1/2} \bar{e}_i^{(L/R)}(\vec{k})\mu_\ell^{0m} e^{-i\vec{k}\cdot\vec{R}} \times$$

$$[(\alpha_{ij}(\omega)\mp\frac{i}{c}G_{ji}(\omega))(V_{j\ell})-iG_{ij}(\omega)U_{j\ell}].$$

$$(5.2.12)$$

Before proceeding to calculate the difference in emission rates it is shown how the matrix element above may be evaluated in the Heisenberg picture. This provides additional insight into chiral-achiral interactions.

5.3 EVALUATION OF MATRIX ELEMENT IN THE HEISENBERG PICTURE

In this Section the matrix element for molecule induced circularly polarised luminescence is obtained using the Heisenberg picture and the result is shown to be identical to that obtained with the Schrödinger method in the previous Section.

As has been shown thus far in this thesis, intermolecular interactions in the Heisenberg framework are calculated directly from the Maxwell fields derived in Chapter 2. In the present problem, the emission rates are determined from the coupling of the electric dipole moment of the achiral molecule to the source fields of the chiral molecule.

The total Hamiltonian is now given by (2.2.7) leading to the derivation of the fields as described in the second Chapter. Only the electric displacement vector field in the vicinity of the chiral molecule as given by (2.2.47) is needed in this calculation since the electric dipole of A can only couple to the electric displacement

radiation field of the chiral molecule. For the application to molecule induced emission in which the chiral molecule remains in its ground electronic state overall, it is necessary for the fermion operators of the quadratic field, representing the electronic state of the chiral molecule, to be set to the lowest level E_0. Further, those terms in (2.2.47) exhibiting a sinusoidal time-variation when at near resonance, where they are almost stationary, may be ignored. This enables the second order displacement field to be written in terms of molecular polarisabilities as in expression (5.3.1)

$$d_i^{(2)}(\vec{r},t) = \frac{i}{4\pi}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V\varepsilon_0}\right)^{1/2}\left\{e^{i\vec{k}\cdot\vec{R}}\alpha(0)\left[\left[e_\ell\alpha_{j\ell}(\omega)+\frac{1}{c}b_\ell G_{j\ell}(\omega)\right](-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\right.\right.$$

$$\left.\left.+\frac{1}{c}\left[e_\ell G_{\ell j}(\omega)\right](ik\varepsilon_{ij\ell}\nabla_\ell)\right]\frac{e^{ik((r-R)-ct)}}{r-R} + \text{H.C.}\right\}.$$

$$(5.3.1)$$

If it is assumed that the transition $0 \leftarrow m$ of A is electric dipole allowed, the leading contribution to the coupling is

$$H_{INT}^A = -\varepsilon_0^{-1}\vec{\mu}(A)\cdot\vec{d}^\perp(\vec{R}_A).$$

$$(5.3.2)$$

The matrix element is then given by

$$M_{fi}^{(L/R)} = \langle 1(\vec{k},L/R);E_0^C,E_0^A|-\varepsilon_0^{-1}\vec{\mu}(A)\cdot\vec{d}^\perp(\vec{R}_A,t)|E_m^A,E_0^C;0(\vec{k},L/R)\rangle$$

$$(5.3.3)$$

where use is made of the power series expansion of the field of molecule A. As $\vec{d}^{(0)}$ and $\vec{d}^{(2)}$ depend linearly on the photon creation and annihilation operators, both contribute to the matrix element. $\vec{d}^{(1)}$ however, does not change the photon number and so does not contribute to (5.3.3). Using the expression for the free field (2.2.15) and (5.3.1),

$$M_{fi}^{(1)(L/R)} = -i\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \mu_{\dot{\iota}}^{0m}(A)\bar{e}_{\dot{\iota}}^{(L/R)}(\vec{k})e^{i\vec{k}\cdot\vec{R}_A}$$

(5.3.4)

and

$$M_{fi}^{(3)(L/R)} = -i\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \mu_{\dot{\iota}}^{0m}(A)e^{i\vec{k}\cdot\vec{R}_C}\left[[\bar{e}_{\ell}^{(L/R)}\alpha_{j\ell}(\omega)+\frac{1}{c}b_{\ell}^{(L/R)}G_{j\ell}(\omega)]\times\right.$$

$$\left.(-\nabla^2\delta_{\dot{\iota}\dot{\jmath}}+\nabla_{\dot{\iota}}\nabla_{\dot{\jmath}})\frac{e^{ik(R_A-R_C)}}{R_A-R_C} + \frac{1}{c}\bar{e}_{\ell}^{(L/R)}G_{\ell j}(\omega)(ik\varepsilon_{\dot{\iota}\dot{\jmath}\ell}\nabla_\ell)\frac{e^{ik(R_A-R_C)}}{R_A-R_C}\right]$$

(5.3.5)

which on addition gives for the total matrix element

$$M_{fi}^{(L/R)} = -i\mu_{\dot{\iota}}^{0m}(A)\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}e^{i\vec{k}\cdot\vec{R}_A}\left\{\bar{e}_{\dot{\iota}}^{(L/R)}(\vec{k})+e^{-i\vec{k}\cdot\vec{R}}\left[[\bar{e}_{\ell}^{(L/R)}\alpha_{j\ell}(\omega)\right.\right.$$

$$\left.\left.+\frac{1}{c}b_{\ell}^{(L/R)}G_{j\ell}(\omega)](-\nabla^2\delta_{\dot{\iota}\dot{\jmath}}+\nabla_{\dot{\iota}}\nabla_{\dot{\jmath}})\frac{e^{ikR}}{R} + \frac{1}{c}\bar{e}_{\ell}^{(L/R)}G_{\ell j}(\omega)(ik\varepsilon_{\dot{\iota}\dot{\jmath}\ell}\nabla_\ell)\frac{e^{ikR}}{R}\right]\right\}$$

(5.3.6)

correct up to third order in the transition moments, with $\vec{R} = \vec{R}_A-\vec{R}_C$. By noting that the geometrical tensors $V_{\dot{\iota}\dot{\jmath}}(k,\vec{R})$ and $U_{\dot{\iota}\dot{\jmath}}(k,\vec{R})$ given earlier in the expressions (5.2.10) and (5.2.11), can also be obtained from the relations

$$V_{\dot{\iota}\dot{\jmath}}(k,\vec{R}) = \frac{i}{4\pi\varepsilon_0}(-\nabla^2\delta_{\dot{\iota}\dot{\jmath}}+\nabla_{\dot{\iota}}\nabla_{\dot{\jmath}})\frac{e^{ikR}}{kR}$$

(5.3.7)

and

$$U_{\dot{\iota}\dot{\jmath}}(k,\vec{R}) = -\frac{k\varepsilon_{\dot{\iota}\dot{\jmath}\ell}}{4\pi\varepsilon_0 c}\nabla_\ell\frac{e^{ikR}}{R},$$

(5.3.8)

and with use of the relation (5.2.6), it is seen that the matrix element (5.3.6) is now identical to that obtained by the addition of (5.2.4) and (5.2.12) in the Schrödinger picture.

5.4 EVALUATION OF DIFFERENTIAL EMISSION RATE

Either of the matrix elements calculated in the previous two Sections can now be used to calculate the differential emission rate for molecule induced circularly polarised luminescence. The difference in emission rate between left- and right-circularly polarised light is found using the Fermi rule

$$\Gamma^{(L/R)} = \frac{2\pi}{\hbar} |M_{fi}^{(1)(L/R)} + M_{fi}^{(3)(L/R)}|^2 \rho . \tag{5.4.1}$$

Taken by itself the third order term, like the first order term on its own, does not give rise to a difference in the rates of luminescence. The first order amplitude when combined with the third order contribution however, results in an interference term which depends on the handedness of C and leads to different emission rates for left- and right-circularly polarised radiation. The leading contribution comes from the first order-third order cross term

$$\Gamma^L - \Gamma^R = \frac{2\pi\rho}{\hbar} \left[M_{fi}^{(1)(L)} \bar{M}_{fi}^{(3)(L)} + \bar{M}_{fi}^{(1)(L)} M_{fi}^{(3)(L)} - M_{fi}^{(1)(R)} \bar{M}_{fi}^{(3)(R)} - \bar{M}_{fi}^{(1)(R)} M_{fi}^{(3)(R)} \right]$$

$$\tag{5.4.2}$$

where the overbar indicates the conjugate complex quantity. With the aid of the first and third order matrix elements (5.2.4) and (5.2.12) the difference in emission rate occurring within an element of solid angle

dΩ around the direction of propagation of the emergent ray is

$$d\Gamma^L - d\Gamma^R = -i\frac{\pi k}{\varepsilon_0 V}\rho\ \mu_\ell^{0m}\mu_i^{0m}\left[(\delta_{ij}-\hat{k}_i\hat{k}_j)G_{mj}(\omega)(ReV_{m\ell})(e^{i\vec{k}\cdot\vec{R}} + e^{-i\vec{k}\cdot\vec{R}})\right.$$

$$\left.+c\varepsilon_{ijn}\hat{k}_n[\alpha_{jm}(\omega)(ReV_{m\ell})-iG_{jm}(\omega)(ReU_{m\ell})](e^{i\vec{k}\cdot\vec{R}} - e^{-i\vec{k}\cdot\vec{R}})\right] \qquad (5.4.3)$$

where Re denotes the real part and where use has been made of the identity

$$e_\mu^{(L/R)}(\vec{k})\bar{e}_\nu^{(L/R)}(\vec{k}) = \frac{1}{2}\left[(\delta_{\mu\nu}-\hat{k}_\mu\hat{k}_\nu) \mp i\varepsilon_{\mu\nu\omega}\hat{k}_\omega\right]. \qquad (5.4.4)$$

The differential rate (5.4.3) applies when the orientations of A and C are held fixed relative to $\vec{R}$ with $\vec{R}$ itself fixed relative to the direction of propagation $\hat{k}_i$. On substituting (5.4.5) for the density of states

$$\rho = \frac{k^2 V d\Omega}{(2\pi)^3 \hbar c} \qquad (5.4.5)$$

and performing a tumbling average, that is, averaging under the assumption that all directions of $\vec{R}$ are equally probable, the molecule induced differential spontaneous emiss.,ion rate is

$$\langle\Gamma^L\rangle - \langle\Gamma^R\rangle = \left(\frac{-i\omega^3}{\pi\varepsilon_0\hbar c^4}\right)\mu_\ell^{0m}\mu_i^{m0}\left\{\left[\alpha_{ij}\frac{sinkR}{kR} + \beta_{ij}\left(\frac{coskR}{k^2R^2} - \frac{sinkR}{k^3R^3}\right)\right]G_{mj}(\omega)(ReV_{m\ell})\right.$$

$$\left.-ic\varepsilon_{ijn}\hat{R}_n\left(\frac{coskR}{kR} - \frac{sinkR}{k^2R^2}\right)[\alpha_{jm}(\omega)(ReV_{m\ell})-iG_{jm}(\omega)(ReU_{m\ell})]\right\}. \qquad (5.4.6)$$

The rate is a modulation of a power law by sinusoidal terms depending on the wavelength k^{-1} and products of various molecular structure factors expressed as transition dipole moments. When kR is small, the limiting

behaviour of the rate is found to be

$$\frac{-i\omega^3}{12\pi^2\epsilon_0^2\hbar c^4 R^3}\,\mu_\ell^{0m}\mu_i^{m0}\beta_{m\ell}[2G_{mi}(\omega) + ic\epsilon_{ijn}R_n k\alpha_{jm}(\omega)]\tag{5.4.7}$$

whose leading term has an R^{-3} dependence on intermolecular separation. The result is not independent of k as is usually the case in the near zone limit $kR \ll 1$. If experiments are carried out in the fluid phase a further average of (5.4.6) is needed. This involves performing a rotational average over relative orientations A-C in a given pair. Further, for a system in thermal equilibrium the average should be weighted by a Boltzmann factor as in

$$\langle\langle\Gamma^L\rangle-\langle\Gamma^R\rangle\rangle = \frac{\iint\langle\Gamma^L\rangle-\langle\Gamma^R\rangle\exp(-V_{AC}(\vec{R},\Omega,\Omega')/kT)d\Omega d\Omega'}{\iint\exp(-V_{AC}(\vec{R},\Omega,\Omega')/kT)d\Omega d\Omega'}\tag{5.4.8}$$

where $V_{AC}(\vec{R},\Omega,\Omega')$ is the intermolecular potential, a function of the separation $\vec{R}$ and of sets of Eulerian angles for the two molecules.

The random unweighted average is computed, corresponding to the leading term in the expansion of (5.4.8) being independent of V_{AC} in the limit $kT \gg V_{AC}$. Using the standard method [41] results in

$$\langle\langle\Gamma^L\rangle-\langle\Gamma^R\rangle\rangle = \frac{i\omega^3}{36\pi^2\epsilon_0^2\hbar c^4 R^3}|\vec{\mu}^{0m}|^2 G_{\lambda\lambda}(\omega)\left\{\sin2kR\left(\frac{1}{kR}-\frac{3}{k^3R^3}\right) + \frac{6\cos2kR}{k^2R^2}\right\}.\tag{5.4.9}$$

The asymptotic behaviour of (5.4.9) for small kR gives

$$\frac{8ik^5}{135\pi^2\epsilon_0^2\hbar cR}\,|\vec{\mu}^{0m}|^2 G_{\lambda\lambda}(\omega)\tag{5.4.10}$$

as the leading contribution, exhibiting R^{-1} separation dependence.

The differential emission rate for molecule induced circularly polarised luminescence for a chiral-achiral pair has been derived using the Schrödinger and Heisenberg pictures within the framework of QED. Discriminatory effects occur since chirality is induced in the achiral molecule via intermolecular coupling with the chiral molecule. Despite differences in the calculational procedure, the results obtained from the two methods have been shown to be identical. The Schrödinger treatment employs perturbation theory in the calculation of the matrix element, interpreted in terms of the interference of transition amplitudes. The picture is one where intermolecular coupling is viewed as the exchange of a virtual photon, expressed in terms of the retarded potentials. In the Heisenberg representation, the calculation is more direct; the matrix element representing the coupling of the dipole moment of the achiral molecule to the causal source fields of the chiral species is determined.

The differential transition rate in the region where the intermolecular separation is much smaller than the reduced wavelength of the radiation depends on the inverse separation due to the inclusion of the magnetic dipole coupling term in addition to the electric dipole interaction.

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