THE APPLICATION OF QUANTUM ELECTRODYNAMICS TO INTERMOLECULAR INTERACTIONS

by

Jonathan Kingsley JENKINS

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Sir Christopher Ingold Laboratories,
University College London.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

ABSTRACT

Molecular quantum electrodynamics describes the interaction of molecules with radiation. This theory in its multipolar form is applied to intermolecular interactions; coupling proceeds through the radiation field and is mediated by an exchange of photons. The basic theory is outlined in Chapter 1 and the conventional transformation from the minimal-coupling to the multipolar Hamiltonian is generalized to include non-neutral systems and translational motion. The equivalence of the multipolar and minimal-coupling forms is demonstrated by comparison of results obtained for two-photon absorption and scattering by chiral molecules.

Chapter 4 examines the dispersion interaction between neutral molecules; all interactions occur via the field and are fully retarded. The standard result in terms of electric-dipole polarizabilities is supplemented by those obtained through interaction of higher-order molecular multipole moments with the field; electric-quadrupole and magnetic-dipole interactions are included. The results are valid at all separations large enough to neglect electron exchange and apply to molecules with specific orientations. Rotationally-averaged expressions are presented also, as are results obtained in the near- and far-zones. Where appropriate results have been expressed in terms of pure electric and mixed electric-magnetic polarizability tensors.

The Hamiltonian developed in Chapter 2 is applied in Chapter 5 to the calculation of the dispersion interaction between a molecule and an ion at rest; supplementing the energy shifts calculated in

Chapter 4 are non-retarded terms arising from charge-multipole interactions. All terms up to a cut-off point of an R^{-6} dependence on separation are taken into account and the minimal-coupling treatment of this interaction is contrasted.

In the final chapter the theory is modified in order to determine the interaction of a free electron with a neutral molecule. A new transformation to the minimal-coupling Lagrangian is used where only the molecular terms are transformed; the dynamics of the free electron are described within the minimal-coupling formalism while the multipolar nature of the molecular interactions is preserved.

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CHAPTER 1

INTRODUCTION

Quantum electrodynamics (QED) has an established platform among the modern theories of physics. It is the theory which describes how matter interacts with the electromagnetic field. Its identifying feature and fundamental principle is its treatment of the radiation field in a fully quantized manner; the collection of particles and the radiation field compose the dynamical system. Both conceptually and in its predictive capacity QED has superseded semi-classical radiation theories; it accounts for effects for which the latter cannot and provides excellent agreement with experiment.

Although it is a modern theory its development may be traced back to 1927, the famous paper by Dirac [1] in which quantization of the field was discussed. The particles arising from the quantization are photons, the procedure itself known as second quantization. This framework is particularly suited to problems in theoretical chemistry and chemical physics since in this description of the radiation field the number of photons need not be conserved; processes such as absorption, emission and scattering are ideally accounted for in terms of interactions of photons with atoms or molecules. Fluctuations of the field, allowed for in this formalism, directly lead to the derivation, with excellent agreement with experiment, of the Einstein A coefficient in spontaneous emission, the Lamb shift and the magnetic moment of the electron, effects for which semi-classical theories have no account. Such cases were instrumental in the adoption of QED as the theory for elucidating the interactions of light with matter. Schwinger's compilation [2] is a valuable source of early papers in

QED.

Molecular quantum electrodynamics is the structured non-relativistic limit of QED and it is the form of the theory used here. The particles in interaction with the field are electrons and nuclei; the number of such particles is assumed to be fixed and they are assumed to be moving at low speeds (and hence with constant masses) so that they may be grouped together to form atoms and molecules. Certain approximations are invoked where appropriate, such as the neglect of the motion of nuclei compared with that of the electrons and the neglect of recoil following absorption or emission of a photon. Other than those mentioned, the theory has also been successfully applied to problems in optical activity (such as optical rotation and circular dichroism), intermolecular interactions and more recently non-linear optics (for instance second harmonic generation, Hyper-Raman scattering and CARS), an area which is becoming of increasing interest with the continuing improvement of laser sources.

Various aspects of the form of the theory and its applications may be found in accounts by Power [3], Loudon [4] and Moss [5], reviews by Woolley [6] and others [7-9], and in recent texts by Healy [10] and Craig and Thirunamachandran [11].

In the discussion of the interactions between molecules the coupling may be considered as identical to the electron-photon interactions discussed in other optical effects. That is, molecule-molecule interactions proceed via the field, which mediates photon exchange. In this thesis quantum electrodynamics is used to discuss such interactions. As a preliminary to these discussions it is useful to outline some of the relevant features of the theory.

1.1 Basic Theory

This section gives an outline of the formulation of the quantum electrodynamical Hamiltonian from its classical origins. For simplicity let us consider a system of particles with a total net charge of zero interacting with the electromagnetic field in the Coulomb gauge. If the charge and position of a particle α are given by e_α and $\mathbf{q}_\alpha$ respectively then the total system is described classically by the Lagrangian function L given by

$$L = 1/2\sum_{\alpha} m_\alpha \dot{\mathbf{q}}_\alpha^2 - V + \frac{\epsilon_0}{2}\int\left\{\dot{\mathbf{a}}(\mathbf{r})^2 - c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r} + \int \mathbf{j}^\perp(\mathbf{r})\cdot\mathbf{a}(\mathbf{r})d^3\mathbf{r} \tag{1.1.1}$$

where $\mathbf{j}^\perp(\mathbf{r})$ is the transverse component of the current density, and where the positions of the moving charges are defined with the use of the Dirac delta function so that

$$\mathbf{j}(\mathbf{r}) = \sum_{\alpha} e_\alpha \dot{\mathbf{q}}_\alpha \delta(\mathbf{r}-\mathbf{q}_\alpha) \ . \tag{1.1.2}$$

V is the Coulombic potential energy summed over all pairs of charges.

The Lagrangian for the coupled system, given by (1.1.1), is a function of the particle coordinates and velocities and a functional of the transverse vector potential $\mathbf{a}(\mathbf{r})$ of the field and its corresponding velocity. The vector potential is related to the electric and magnetic field vectors $\mathbf{e}(\mathbf{r})$ and $\mathbf{b}(\mathbf{r})$ by the relations

$$\mathbf{b}(\mathbf{r}) = \mathit{curl}\,\mathbf{a}(\mathbf{r}) \tag{1.1.3}$$

$$\mathbf{e}^\perp(\mathbf{r}) = -\dot{\mathbf{a}}(\mathbf{r}) \tag{1.1.4}$$

The Lagrangian function is fundamental to classical mechanics. Its origin lies in the calculus of variation; Hamilton's principle of variation, which minimises the action integral, leads to Lagrange's equations, a solution of which is the Lagrangian.[1] It is not a unique solution, however, and as we shall see there is some flexibility in the explicit choice of Lagrangian.

The first two terms of (1.1.1) are particle terms and they are followed by a field term and an interaction term. The standard texts develop the formalism through consideration of separate particle and field systems before considering interaction. In the absence of interaction the dynamical variables of one system do not affect the other; the two systems have equations of motion that are not coupled to one another and move independently. When the particles and field interact the equations of motion of both particle and field are coupled; the particles have their motions affected by the fields, of which they (as charges and currents) are taken to be the sources. Hence the Lorentz force (1.1.5) appears, representing the force of the field on the particles and in turn the equations of motion for the field are Maxwell's equations with sources (1.1.6).

$$m_\alpha \ddot{\underset{\sim}{q}}_{i\alpha} = -\frac{\partial V}{\partial \underset{\sim}{q}_{i\alpha}} + e_\alpha\left(\underset{\sim}{e}_i^{\perp}(\underset{\sim}{q}_\alpha) + [\dot{\underset{\sim}{q}}_\alpha \times \underset{\sim}{b}(\underset{\sim}{q}_\alpha)]_i\right) \tag{1.1.5}$$

$$\begin{aligned} \underset{\sim}{\nabla}.\underset{\sim}{e} &= \frac{\rho}{\varepsilon_0} \\ \underset{\sim}{\nabla}.\underset{\sim}{b} &= 0 \\ \underset{\sim}{\nabla} \times \underset{\sim}{e} &= \frac{-\partial \underset{\sim}{b}}{\partial t} \\ c^2\, \underset{\sim}{\nabla} \times \underset{\sim}{b} &= \frac{\partial \underset{\sim}{e}}{\partial t} + \frac{1}{\varepsilon_0}\underset{\sim}{j} \end{aligned} \tag{1.1.6}$$

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[1] These steps have been referred to in order to ensure continuity in the formulation. For a fuller account the reader is referred to texts. See for example [12-16].

The choice of the Coulomb gauge, and hence $e^{\perp} = -\partial \underset{\sim}{a}/\partial t$, allows (1.1.5) to be written with the transverse electric field in the second term. The subscript i may be any of the Cartesian components. Throughout the thesis the standard summation convention is used so that a repeated Latin suffix (in script font) always implies a sum.

The Lagrangian (1.1.1) may be shown to lead to these equations through the use of Lagrange's equations.

An alternative representation to (1.1.1) was proposed by Hamilton, in which a new function was defined from the Lagrangian. In Hamilton's formalism the function H, which is called the Hamiltonian, is defined by

$$H = \sum_{\alpha} \underset{\sim}{p}_{\alpha} \cdot \dot{\underset{\sim}{q}}_{\alpha} + \int \underset{\sim}{\Pi} . \dot{\underset{\sim}{a}}(\underset{\sim}{r}) d^3 \underset{\sim}{r} - L \qquad (1.1.7)$$

where $\underset{\sim}{p}_{\alpha}$ and $\underset{\sim}{\Pi}(\underset{\sim}{r})$ are the momenta canonically conjugate to $\underset{\sim}{q}_{\alpha}$ and $\underset{\sim}{a}(\underset{\sim}{r})$ respectively. Their definitions are given below.

$$\underset{\sim}{p}_{\alpha} = \frac{\partial L}{\partial \dot{\underset{\sim}{q}}_{\alpha}} \quad ; \quad \underset{\sim}{\Pi}(\underset{\sim}{r}) = \frac{\partial \mathcal{L}}{\partial \dot{\underset{\sim}{a}}} , \qquad (1.1.8)$$

where $\mathcal{L}$ is the density functional of the Lagrangian (1.1.1). It should be noted that the canonical and kinetic momenta are not necessarily identical: it is the canonical momentum which is required.

For a conservative system the Hamiltonian is the total energy of the system, the sum of the kinetic and potential terms ie H = T + V. In the canonical formalism the Hamiltonian should be written in terms of the 'canonical variables'. These are the coordinates and canonical momenta for field and particle. Hence the coordinate 'velocities' for field and particle must be eliminated in their favour.

The Lagrangian function (1.1.1) is known as the minimal-coupling

Lagrangian, or L_{min}. If the charges are grouped together to form electrically neutral assemblages, ie atoms and molecules denoted by the label ζ, then the resulting Hamiltonian from the use of (1.1.7) is consequently known as the minimal-coupling Hamiltonian, or H_{min};

$$H_{min} = \sum_{\zeta} H_{mol}(\zeta) + H_{rad} + \sum_{\zeta} H_{int}(\zeta) + V_{inter}, \qquad (1.1.9)$$

with

$$H_{mol}(\zeta) = \sum_{\alpha} \frac{1}{2m_\alpha} \mathbf{p}_\alpha^2(\zeta) + V(\zeta) \qquad (1.1.10)$$

$$H_{rad} = \frac{1}{2}\int\left\{\frac{\mathbf{\Pi}^2(\mathbf{r})}{\epsilon_0} + \epsilon_0 c^2(\mathbf{\nabla}\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r} \qquad (1.1.11)$$

$$H_{int}(\zeta) = -\sum_{\alpha}\left(\frac{e_\alpha}{m_\alpha}\right)\mathbf{p}_\alpha(\zeta)\cdot\mathbf{a}(\mathbf{q}_\alpha(\zeta)) + \sum_{\alpha}\left(\frac{e_\alpha^2}{2m_\alpha}\right)\mathbf{a}^2(\mathbf{q}_\alpha(\zeta)) \qquad (1.1.12)$$

and

$$V_{inter} = \sum_{\zeta<\zeta'} V(\zeta,\zeta') \qquad (1.1.13)$$

The Hamiltonian (1.1.9) is a classical function. Its quantum mechanical analogue is written down directly by interpreting the canonical variables as operators subject to the commutation restrictions

$$\left[q_{i(\alpha)}(\zeta), q_{j(\beta)}(\zeta')\right] = i\hbar\delta_{ij}\delta_{\alpha\beta}\delta_{\zeta\zeta'}\ , \qquad (1.1.14)$$

and

$$\left[a_i(\mathbf{r}), \Pi_j(\mathbf{r}')\right] = i\hbar\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{r}')\ . \qquad (1.1.15)$$

where $\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{r}')$ is the transverse delta function [17] defined by

$$\delta^{\perp}_{ij}(\mathbf{r}-\mathbf{r}') = (1/2\pi)^3\int(\delta_{ij}-\hat{k}_i\hat{k}_j)e^{i\mathbf{k}.(\mathbf{r}-\mathbf{r}')}d^3\mathbf{k} \tag{1.1.16}$$

The interaction terms are given in (1.1.12). The first-order term shows the interaction of the particle momentum with the vector potential; the second-order term is quadratic in the vector potential. Note also that the potential term V appears explicitly and is partitioned into intra- and intermolecular parts.

For many applications of the quantum electrodynamical theory to problems in quantum optics and theoretical chemistry, however, it is more convenient to employ the multipolar Hamiltonian in which the interaction is described in terms of the electric displacement and magnetic fields rather than the potentials and coupling of the field is with molecular multipoles rather than the canonical momentum.

If the chosen Lagrangian has been shown to lead to the correct equations of motion then a new and equivalent Lagrangian may be obtained [18-19,11] by the transformation

$$L_{mult} = L_{min} - \frac{d}{dt}\int\mathbf{p}^{\perp}(\mathbf{r}).\mathbf{a}(\mathbf{r})d^3\mathbf{r} \tag{1.1.17}$$

where $\mathbf{p}(\mathbf{r})$, the electric polarization field [20-23], is a function of the particle coordinates. L_{mult} must then also be a suitable choice. The two action integrals arising from L_{mult} and L_{min} differ by a quantity which gives zero on variation and so the form of the equations of motion is unchanged. Thus the Lagrangian is defined only to within the addition of any function of the particle coordinates and time.

The resulting Lagrangian is given by

$$L_{\mathrm{mult}} = 1/2\sum_{\alpha} m_{\alpha}\dot{\mathbf{q}}_{\alpha}^{2} + \frac{\varepsilon_0}{2}\int\left\{\dot{\mathbf{a}}(\mathbf{r})^2 - c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r}$$

$$+\int\{\nabla\times\mathbf{M}(\mathbf{r})\}.\mathbf{a}(\mathbf{r})d^3\mathbf{r} - \int\mathbf{p}^{\perp}(\mathbf{r}).\dot{\mathbf{a}}(\mathbf{r})d^3\mathbf{r} - V \qquad (1.1.18)$$

where $\mathbf{p}(\mathbf{r})$ amd $\mathbf{M}(\mathbf{r})$, the magnetization field, are defined by

$$\mathbf{p}(\mathbf{r}) = \sum_{\alpha} e_{\alpha}(\mathbf{q}_{\alpha}-\mathbf{R})\int_0^1 \delta(\mathbf{r}-\mathbf{R}-\lambda(\mathbf{q}_{\alpha}-\mathbf{R}))d\lambda \ ,$$

$$(1.1.19)$$

and

$$\mathbf{M}(\mathbf{r}) = \sum_{\alpha} e_{\alpha}\left\{(\mathbf{q}_{\alpha}-\mathbf{R})\times\dot{\mathbf{q}}_{\alpha}\right\}\int_0^1 \lambda\delta(\mathbf{r}-\mathbf{R}-\lambda(\mathbf{q}_{\alpha}-\mathbf{R}))d\lambda.$$

$$(1.1.20)$$

The use of polarization and magnetization fields allows the total charge density associated with each assemblage to be divided into 'true' (ionic or free electronic) and polarization charge densities, and the total current density into true, polarization and magnetization current densities. The charge density is given by

$$\rho(\mathbf{r}) = \sum_{\alpha} e_{\alpha}\delta(\mathbf{r}-\mathbf{q}_{\alpha}) \qquad (1.1.21)$$

$$= \rho^{\mathrm{true}}(\mathbf{r}) - \nabla\cdot\mathbf{p}(\mathbf{r}) \qquad (1.1.22)$$

with

$$\rho^{\mathrm{true}}(\mathbf{r}) = \sum_{\alpha} e_{\alpha}\delta(\mathbf{r}-\mathbf{R}) \ , \qquad (1.1.23)$$

and (1.1.2) may be rewritten as

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_{\mathrm{ionic}}(\mathbf{r}) + \dot{\mathbf{p}}(\mathbf{r}) + \nabla\times\mathbf{M}(\mathbf{r}) \qquad (1.1.24)$$

Clearly $\rho^{\mathrm{true}}(\mathbf{r})$ and $\mathbf{j}_{\mathrm{ionic}}(\mathbf{r})$ vanish if there are no net or free charges, as in this case. Of course, the partitioning of the total charge and current densities into true and bound contributions necessitates the introduction of the reference vector $\mathbf{R}$, relative to which motion of the composite particles is to be defined. This vector may be chosen, for example, as the centre of mass, a local chromophore centre or an inversion centre.

L_{mult} is known as the multipolar Lagrangian. The multipolar Hamiltonian is formed in the usual way and is given by

$$H_{mult} = \sum_{\zeta} H_{mol}(\zeta) + H_{rad} + \sum_{\zeta} H_{int}(\zeta) + H_{self} \qquad (1.1.25)$$

with $H_{mol}(\zeta)$ unchanged from (1.1.10),

$$H_{rad} = \frac{1}{2}\int\left\{\frac{\mathbf{d}^{\perp 2}(\mathbf{r})}{\varepsilon_0} + \varepsilon_0 c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r} \qquad (1.1.26)$$

$$H_{self} = \frac{1}{2\varepsilon_0}\int \sum_{\zeta}|\mathbf{p}^{\perp}(\zeta;\mathbf{r})|^2 d^3\mathbf{r} \qquad (1.1.27)$$

and the interaction terms now given by

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

$$+\frac{1}{2}\iint O_{ij}(\zeta;\mathbf{r},\mathbf{r}')b_i(\mathbf{r})b_j(\mathbf{r}')d^3\mathbf{r}d^3\mathbf{r}' \ . \qquad (1.1.28)$$

Note that the definitions of $\mathbf{p}(\mathbf{r})$ and $\mathbf{M}(\mathbf{r})$ have been modified; we write

$$\mathbf{p}(\mathbf{r}) = \sum_{\zeta} \mathbf{p}(\zeta;\mathbf{r}) \ ; \ \mathbf{M}(\mathbf{r}) = \sum_{\zeta} \mathbf{M}(\zeta;\mathbf{r}) \qquad (1.1.29)$$

where we have partitioned the contribution to each field from the individual molecules, which are labelled ζ. In (1.1.28) $\mathbf{d}(\mathbf{r})$ is the electric displacement field, $\mathbf{m}(\mathbf{r})$ the magnetization and $O_{ij}(\mathbf{r},\mathbf{r}')$ the diamagnetizaton field. These new fields are defined below.

The first term of (1.1.28) contains the interaction of the electric multipole series with the field. The electric displacement field is defined by

$$\underset{\sim}{d}(\underset{\sim}{r}) = -\varepsilon_0\dot{\underset{\sim}{a}}(\underset{\sim}{r}) + \underset{\sim}{p}(\underset{\sim}{r}) \tag{1.1.30}$$

and its transverse component appears in the interaction and radiation terms. The interaction of the magnetic multipole series with the magnetic field $\underset{\sim}{b}(\underset{\sim}{r})$ is given by the second term of (1.1.28). The magnetization is defined as

$$\underset{\sim}{m}(\underset{\sim}{r}) = \sum_{\zeta} \underset{\sim}{m}(\zeta;\underset{\sim}{r}) \tag{1.1.31}$$

with

$$\underset{\sim}{m}(\zeta;\underset{\sim}{r}) = \frac{1}{2}\sum_{\alpha(\zeta)} \frac{1}{m_\alpha}\left\{\underset{\sim}{n}_\alpha(\zeta;\underset{\sim}{r})\times\underset{\sim}{p}_\alpha(\zeta) - \underset{\sim}{p}_\alpha(\zeta)\times\underset{\sim}{n}_\alpha(\zeta;\underset{\sim}{r})\right\} \tag{1.1.32}$$

In (1.1.32) the vector field $\underset{\sim}{n}(\zeta;\underset{\sim}{r})$ for a molecule ζ is given by

$$\underset{\sim}{n}(\zeta;\underset{\sim}{r}) = \sum_{\alpha(\zeta)} \underset{\sim}{n}_\alpha(\zeta;\underset{\sim}{r}) = \sum_{\alpha(\zeta)} e_\alpha(\underset{\sim}{q}_\alpha-\underset{\sim}{R}_\zeta)\int_0^1 \lambda\delta(\underset{\sim}{r}-\underset{\sim}{R}_\zeta-\lambda(\underset{\sim}{q}_\alpha-\underset{\sim}{R}_\zeta))d\lambda\ , \tag{1.1.33}$$

where the label ζ of $\underset{\sim}{q}_\alpha$ is implicit. The diamagnetization interaction (the final term of (1.1.28)) contains terms which are second-order in the magnetic field. Its field definition below includes the use of the auxiliary vector field defined above. We have

$$O_{ij}(\underset{\sim}{r},\underset{\sim}{r}') = \sum_{\zeta} O_{ij}(\zeta;\underset{\sim}{r},\underset{\sim}{r}') \tag{1.1.34}$$

$$O_{ij}(\zeta;\underset{\sim}{r},\underset{\sim}{r}') = \varepsilon_{ik\ell}\varepsilon_{jm\ell}\sum_{\alpha(\zeta)} \frac{1}{m_\alpha} n_{k(\alpha)}(\zeta;\underset{\sim}{r})\, n_{m(\alpha)}(\zeta;\underset{\sim}{r}') \tag{1.1.35}$$

H_{self} is composed of only the transverse electric polarization field associated with each molecule and as such is a self-energy correction term which does not contribute to radiative processes (and so may usually be ignored). Note that it only contains one-centre terms; it will be shown in Chapter 2 that it is the cross terms of the transverse polarization product which exactly cancel the intermolecular potential term, a consequence of the highly localized nature of the total molecular polarization fields. Thus no such potential term appears explicitly in the Hamiltonian and all interactions proceed via coupling of the electric and magnetic moments with the transverse fields; they are then fully retarded, with propagation at the speed of light.

The quantization of the field supplements the quantized particle collection in the description of the total system. In this procedure the mode expansion for the classical radiation field confined to a box of volume *V* subject to periodic boundary conditions is equivalent to a sum of harmonic oscillators. Quantization of these oscillators allows the free field Hamiltonian to be written as

$$H_{rad} = \sum_{\underset{\sim}{k},\lambda} \left\{ a^{\dagger(\lambda)}(\underset{\sim}{k}) a^{(\lambda)}(\underset{\sim}{k}) + 1/2 \right\} \hbar ck \qquad (1.1.36)$$

Photons are then the particles associated with the quanta of energy, introduced by the quantization of the field and $a^{\dagger(\lambda)}(\underset{\sim}{k})$ and $a^{(\lambda)}(\underset{\sim}{k})$ are the creation and annihilation operators respectively for a photon of wavevector $\underset{\sim}{k}$ and polarization $\underset{\sim}{e}^{(\lambda)}(\underset{\sim}{k})$, similar to the ladder operators in harmonic oscillator theory. These operators are subject to the commutation relationships

$$\left[a^{(\lambda)}(\underset{\sim}{k}),a^{(\lambda')}(\underset{\sim}{k}')\right] = 0 = \left[a^{\dagger(\lambda)}(\underset{\sim}{k}),a^{\dagger(\lambda')}(\underset{\sim}{k}')\right] \tag{1.1.37}$$

$$\left[a^{(\lambda)}(\underset{\sim}{k}),a^{\dagger(\lambda')}(\underset{\sim}{k}')\right] = \delta_{\lambda\lambda'}\delta_{\underset{\sim}{k}\underset{\sim}{k}'} \tag{1.1.38}$$

The quantum analogues of the classical mode expansions are given by

$$\underset{\sim}{a}(\underset{\sim}{r}) = \sum_{\underset{\sim}{k},\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\left\{\underset{\sim}{e}^{(\lambda)}(\underset{\sim}{k})a^{(\lambda)}(\underset{\sim}{k})e^{i\underset{\sim}{k}.\underset{\sim}{r}} + \bar{\underset{\sim}{e}}^{(\lambda)}(\underset{\sim}{k})a^{\dagger(\lambda)}(\underset{\sim}{k})e^{-i\underset{\sim}{k}.\underset{\sim}{r}}\right\} \tag{1.1.39}$$

$$\underset{\sim}{d}^{\perp}(\underset{\sim}{r}) = i\sum_{\underset{\sim}{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left\{\underset{\sim}{e}^{(\lambda)}(\underset{\sim}{k})a^{(\lambda)}(\underset{\sim}{k})e^{i\underset{\sim}{k}.\underset{\sim}{r}} - \bar{\underset{\sim}{e}}^{(\lambda)}(\underset{\sim}{k})a^{\dagger(\lambda)}(\underset{\sim}{k})e^{-i\underset{\sim}{k}.\underset{\sim}{r}}\right\} \tag{1.1.40}$$

$$\underset{\sim}{b}(\underset{\sim}{r}) = i\sum_{\underset{\sim}{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}\left\{\underset{\sim}{b}^{(\lambda)}(\underset{\sim}{k})a^{(\lambda)}(\underset{\sim}{k})e^{i\underset{\sim}{k}.\underset{\sim}{r}} - \bar{\underset{\sim}{b}}^{(\lambda)}(\underset{\sim}{k})a^{\dagger(\lambda)}(\underset{\sim}{k})e^{-i\underset{\sim}{k}.\underset{\sim}{r}}\right\} \tag{1.1.41}$$

with the magnetic polarization vector defined by

$$\underset{\sim}{b}^{(\lambda)}(\underset{\sim}{k}) = \underset{\sim}{\hat{k}} \times \underset{\sim}{e}^{(\lambda)}(\underset{\sim}{k}) \; ; \tag{1.1.42}$$

it is these expansions which must be substituted into the terms in the minimal-coupling and multipolar Hamiltonians. In (1.1.39-41) an overbar denotes the complex conjugate and a dagger the adjoint.

The addition to the classical Lagrangian of the total time derivative of a function of the particle coordinates and the field allows a number of possible equivalent Lagrangian s to be written down, which in turn suggests a number of possible Hamiltonians for the combined system. These Hamiltonians are similarly said to be equivalent and are related by canonical transformation. It is possible to write

$$H_{new} = e^{-iS} H_{min} e^{iS} , \qquad (1.1.43)$$

where (1.1.43) is such a transformation. The multipolar form of the Hamiltonian is generated by the choice

$$S = 1/\hbar \int \mathbf{p}^{\perp}(\mathbf{r}) . \mathbf{a}(\mathbf{r}) d^3\mathbf{r} . \qquad (1.1.44)$$

The operators representing the canonical variables in the new form are related to those in the minimal-coupling form by a similar transformation. In fact the coordinate operators are invariant under such a change; only the momenta change, such that the field momentum is proportional to the transverse electric displacement field rather than the transverse electric field. We have

$$P_{min(\alpha)} = m_{\alpha}\dot{\mathbf{q}}_{\alpha} + e_{\alpha}\mathbf{a}(\mathbf{q}_{\alpha}) \qquad (1.1.45)$$

$$P_{mult(\alpha)} = m_{\alpha}\dot{\mathbf{q}}_{\alpha} - \int \mathbf{n}_{\alpha}(\zeta;\mathbf{r}) \times \mathbf{b}(\mathbf{r}) d^3\mathbf{r} , \qquad (1.1.46)$$

$$\Pi_{min}(\mathbf{r}) = \varepsilon_0 \dot{\mathbf{a}}(\mathbf{r}) = -\varepsilon_0 \mathbf{e}^{\perp}(\mathbf{r}) \qquad (1.1.47)$$

$$\Pi_{mult}(\mathbf{r}) = \varepsilon_0 \dot{\mathbf{a}}(\mathbf{r}) - \mathbf{p}^{\perp}(\mathbf{r}) \qquad (1.1.48)$$

$$= -\mathbf{d}^{\perp}(\mathbf{r}) . \qquad (1.1.49)$$

The new canonical variables are similarly Hermitian operators which satisfy the canonical commutation relations and since they are Schrödinger operators they are not functions of time. Note the relationship between the magnetization field $\mathbf{M}(\mathbf{r})$ and the magnetization $\mathbf{m}(\mathbf{r})$. The former is defined in terms of velocities and the latter is the quantum mechanical operator, defined in terms of the canonical momenta.

In the expression for $\mathbf{m}(\mathbf{r})$ the order in which the non-commuting operators occur is significant and is prescribed by the unitary transformation. This is a fundamental part of the canonical formalism and should be stressed. The minimal-coupling Hamiltonian (1.1.9) is written in Hermitian form, the order of the operators $\mathbf{p}_\alpha$ and $\mathbf{a}(\mathbf{q}_\alpha)$ immaterial since they commute, a consequence of the choice of the Coulomb gauge. Transformation of this Hamiltonian gives the multipolar Hamiltonian, which automatically appears in Hermitian form.

Symmetrization is a necessary requirement in the construction of Hermitian operators in quantum mechanics. For example, if we proceed by the earlier method of the addition of a total time derivative to the Lagrangian and the Lagrangian is not written in a symmetrized form beforehand, the resulting Hamiltonian will not in general be Hermitian. Promotion of the canonical variables to operators in a Hermitian form in the Hamiltonian, subject to the appropriate commutation relations, is called canonical quantization.

Let us now expand the multipolar interaction terms and write them in their more familiar and usable form in terms of molecular multipoles. This follows from the Taylor series expansion about $(\mathbf{r}-\mathbf{R}_\zeta)$ of the delta functions appearing in $\mathbf{p}(\zeta;\mathbf{r})$, $\mathbf{m}(\zeta;\mathbf{r})$, $\mathbf{n}_\alpha(\zeta;\mathbf{r})$ and $O_{ij}(\zeta;\mathbf{r},\mathbf{r}')$. The multipole expansions give

$$p_i(\zeta;\mathbf{r}) = (\mu_i(\zeta) - Q_{ij}(\zeta)\nabla_j + \ldots)\delta(\mathbf{r}-\mathbf{R}_\zeta) \tag{1.1.50}$$

$$m_i(\zeta;\mathbf{r}) = (m_i(\zeta) - m_{ij}(\zeta)\nabla_j + \ldots)\delta(\mathbf{r}-\mathbf{R}_\zeta) \tag{1.1.51}$$

and the first term of the diamagnetization interaction may be written for the molecule ζ as

$$H_{dia}(\zeta) = \sum_{\alpha} \frac{e_{\alpha}^{2}}{8m_{\alpha}} \left\{ (\underset{\sim}{q}_{\alpha} - \underset{\sim}{R}_{\zeta}) \times \underset{\sim}{b}(\underset{\sim}{R}_{\zeta}) \right\}^{2} . \tag{1.1.52}$$

In (1.1.50) $\mu_{i}(\zeta)$ and $Q_{ij}(\zeta)$ are the components of the electric dipole and electric quadrupole moments respectively of molecule ζ, given by

$$\mu_{i}(\zeta) = \sum_{\alpha} e_{\alpha(\zeta)} (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta})_{i} \tag{1.1.53}$$

$$Q_{ij}(\zeta) = (1/2) \sum_{\alpha} e_{\alpha(\zeta)} (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta})_{i} (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta})_{j} . \tag{1.1.54}$$

The magnetic dipole and quadrupole moments appearing in (1.1.51) are given by

$$m_{i}(\zeta) = \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \left\{ (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta}) \times \underset{\sim}{p}_{\alpha} \right\}_{i} \tag{1.1.55}$$

$$m_{ij}(\zeta) = \sum_{\alpha} \frac{e_{\alpha}}{6m_{\alpha}} \left[\left\{ (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta}) \times \underset{\sim}{p}_{\alpha} \right\}_{i} (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta})_{j} + (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta})_{j} \left\{ (\underset{\sim}{q}_{\alpha(\zeta)} - \underset{\sim}{R}_{\zeta}) \times \underset{\sim}{p}_{\alpha} \right\}_{i} \right] \tag{1.1.56}$$

Using the multipole expansions (1.1.50) and (1.1.51) we may write down the interaction Hamiltonian by integrating over the volume $d^{3}\underset{\sim}{r}$ in the first two terms of (1.1.28), using the definitions (1.1.53-55) for the molecular multipole moments. This gives

$$H_{int}(\zeta) = -\varepsilon_0^{-1}\boldsymbol{\mu}(\zeta)\cdot\mathbf{d}^{\perp}(\mathbf{R}_{\zeta}) - \varepsilon_0^{-1}Q_{ij}(\zeta)\nabla_j d_i^{\perp}(\mathbf{R}_{\zeta}) - \mathbf{m}(\zeta)\cdot\mathbf{b}(\mathbf{R}_{\zeta})$$

$$+ \sum_{\alpha}\frac{e_{\alpha}^2}{8m_{\alpha}}\left\{(\mathbf{q}_{\alpha}-\mathbf{R}_{\zeta})\times\mathbf{b}(\mathbf{R}_{\zeta})\right\}^2 . \qquad (1.1.57)$$

The expression is given up to the electric quadrupole interaction for the polarization field and includes all terms of comparable magnitude. Hence the magnetic dipole interaction and the first term of the diamagnetic interaction appear in (1.1.57). Terms of higher order than these are not required for the present work although such interactions may readily be incorporated from the multipole expansions.

In (1.1.57) the first two interaction terms are linear in $\mathbf{d}(\mathbf{r})$ and the third in $\mathbf{b}(\mathbf{r})$. These terms have non-vanishing first-order matrix elements, corresponding to absorption or emission of a single photon with each interaction. The final term is second-order in the magnetic field; consequently its first-order matrix element corresponds to creation or annihilation of two photons or creation/annihilation simultaneously.

In both the minimal-coupling (1.1.9) and multipolar (1.1.25) forms the Hamiltonian has been partitioned into two parts; we have

$$H = H_0 + H_{int} \qquad (1.1.58)$$

with

$$H_0 = \sum_{\zeta} H_{mol}(\zeta) + H_{rad} \qquad (1.1.59)$$

$$H_{int} = \sum_{\zeta} H_{int}(\zeta) + V_{inter}, \qquad (1.1.60)$$

except that the term V_{inter} does not appear in (1.1.25), as noted. In general H_{int} is small compared with H_0 and it is possible to employ perturbation theory to describe the interactions between the molecules and the radiation field. The base states for the calculations are the eigenstates of H_0 which are the products of the eigenstates of the unperturbed molecular and radiation field Hamiltonians. The interactions between molecules are described by stationary perturbation theory; H_{int} causes shifts of the eigenvalues of H_0 given as a series expansion in H_{int}. The shift in energy of a non-degenerate state $|i\rangle$ of H_0 is given by

$$\Delta E_i = \langle i|H_{int}|i\rangle$$

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

$$-\sum_{III}\sum_{II}\sum_{I}\frac{\langle i|H_{int}|III\rangle\langle III|H_{int}|II\rangle\langle II|H_{int}|I\rangle\langle I|H_{int}|i\rangle}{(E_{III}-E_i)(E_{II}-E_i)(E_I-E_i)} + \dots \tag{1.1.61}$$

In (1.1.61) the summations are over the intermediate states of the unperturbed system; the state $|i\rangle$ is excluded from the summation.

In time-dependent perturbation theory, H_{int} gives rise to transitions between the unperturbed states. If the states of the system before and after the interaction are given by $|i\rangle$ and $|f\rangle$ respectively then the rate of transition between these states is given by the Fermi golden rule

$$\Gamma = 2\pi/\hbar|M_{fi}|^2\rho \tag{1.1.62}$$

subject to the overall conservation of energy and that either $|i\rangle$ or $|f\rangle$ belongs to a continuum spectrum with density of states per unit energy interval ρ. The time-scale considered must be greater than the period $\hbar/E_{fi}$ of the molecular transition but short enough to ensure a small transition probability. The matrix element of the transition is then given by

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

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

$$- \sum_{III}\sum_{II}\sum_{I} \frac{\langle f|H_{int}|III\rangle\langle III|H_{int}|II\rangle\langle II|H_{int}|I\rangle\langle I|H_{int}|i\rangle}{(E_{III}-E_i)(E_{II}-E_i)(E_I-E_i)} + \dots \tag{1.1.63}$$

1.2 Applications

From its classical origins the previous section outlined the construction of the multipolar Hamiltonian, commonly used in non-relativistic molecular quantum electrodynamics. This Hamiltonian is used to solve problems in areas of spectroscopy, laser physics and intermolecular forces, and applies to systems which are comprised of atoms or neutral molecules which have no net velocity. In the following chapter the formulation leading to the multipolar Hamiltonian is given in more detail but for a more general case. The transformation from minimal-coupling Lagrangian includes a relaxation on the restriction of electrical neutrality and allows for translational motion of the molecules and ions by considering the motions of the centres of mass.

An application of quantum electrodynamics discussed in Chapter 3 contrasts the use of the multipolar and minimal-coupling Hamiltonians in their accounts of phenomena such as two-photon absorption, Rayleigh and Raman scattering. Although the partitioning of the multipolar Hamiltonian into unperturbed and interaction parts differs from the corresponding partitioning of the minimal-coupling Hamiltonian and depends on the transformation chosen, the matrix elements for processes on the energy shell are the same in each case. The equivalence of their forms is not only demonstrated, but facilitated with the derivation of some new sum rules. These topics are useful in illustrating how the methods of QED are applied and serve to highlight some important points encountered.

In Chapter 4 the interaction between neutral molecules in their ground states, the so-called dispersion interaction, is discussed. Previous works are extended by the inclusion of higher-order interaction terms; the electric quadrupole, the magnetic dipole and the diamagnetic interactions; and by obtaining results for molecules at any separation outside electronic overlap and with an arbitrary relative orientation. Results are presented for the interactions of molecules with large or small separations in the fluid state.

Using the new form of the multipolar Hamiltonian derived in Chapter 2 a discussion of the dispersion interaction between a molecule and an ion follows next. The discerning feature of this calculation is the presence of non-retarded potential terms which supplement the molecular multipole interactions. The minimal-coupling form of this interaction is presented as a contrast.

The concluding chapter extends this work by calculating the interaction of a free electron with a neutral molecule. Since the interactions of a free electron are best described within the minimal-coupling framework of QED, the transformation of Chapter 2 is deemed inappropriate. A modification of the theory to retain this form of interaction for the electron is necessary and a new type of transformation is used so that the multipolar description of the molecular interactions is preserved. The new Hamiltonian is then applied to the calculation of the energy shift between the electron and the molecule.

CHAPTER 2

THE MULTIPOLAR HAMILTONIAN FOR NON-NEUTRAL SYSTEMS ALLOWING FOR TRANSLATIONAL MOTION

2.1 Introduction

This chapter describes how a general multipolar Hamiltonian may be obtained from the minimal-coupling Lagrangian, the classical starting point. Unlike in previous studies, which were mostly confined to neutral systems at rest, no constraints are imposed here on the motion or electrical neutrality of the atoms, molecules or ions under study. As noted in the preceding chapter (and to be explained shortly in the text) the characteristic feature of the multipolar Hamiltonian for neutral systems is the absence of an explicit intermolecular potential term, which is a direct consequence of the highly localized nature of the polarization fields. In Chapter 1 the derivation was outlined for the neutral case. Here the theory is developed more thoroughly but for the more general case, and outlines how Maxwell's equations, through the introduction of the vector and scalar potentials, may lead to the minimal-coupling Lagrangian, from which the subsequent Hamiltonian is constructed. Of those described in Chapter 1 the method of transformation chosen is via the addition of a total time derivative of a function of the particle coordinates and field to the minimal-coupling Lagrangian.

Some new features arise from the theory when net charges and translational motion are considered. A complete elimination of the intermolecular electrostatic terms is now not possible [24] and the simplification of the treatment in Section 1.1 is lost. In order to allow for translational motion we must consider motion of the molecular centre, about which the molecular multipole moments have been defined. The Röntgen current appears as a contribution to the magnetization current and terms dependent on this motion then appear in the Hamiltonian. The Lagrangian must also include a term which represents motion of the net charges and it is the presence of this term which makes it impossible to completely eliminate the vector potential from the final multipolar Hamiltonian.

Translational motion of two-particle systems has been previously considered by Lamb [25] and Healy [22] and the effect of allowing for centres of mass motion on the Hamiltonian within a semi-classical framework has been examined by Yang *et al* [26]. Lam [27] has presented a less comprehensive account of the complete multipolar Hamiltonian.

The new Hamiltonian is used in Chapter 5 to study the ion-molecule dispersion interaction, supplementing the neutral interaction determined in Chapter 4, and in Chapter 6 the theory is modified to account for the interaction of free electrons with atoms.

2.2 The Coulomb Gauge Lagrangian

The equations of motion for the coupled system of the electromagnetic field and charged particles are given in terms of the electric and magnetic field vectors by the Maxwell-Lorentz equations (1.1.5/6). We may write these equations in an alternative form by introducing the electromagnetic potentials [28-30]; this serves to facilitate the subsequent quantization of the electromagnetic field. Now since the magnetic field is divergence-free (1.1.6) we may define the vector potential $\underset{\sim}{a}(\underset{\sim}{r})$ by

$$\underset{\sim}{b}(\underset{\sim}{r}) = \mathit{curl}\,\underset{\sim}{a}(\underset{\sim}{r}) \qquad (2.2.1)$$

since any vector which is divergence-free may be expressed as the *curl* of a new vector. Combining the second and third equations of (1.1.6) leads to

$$\mathit{curl}\left[\underset{\sim}{e}(\underset{\sim}{r}) + \dot{\underset{\sim}{a}}(\underset{\sim}{r})\right] = 0 \tag{2.2.2}$$

and we may define the scalar potential $\Phi(\underset{\sim}{r})$ such that

$$\underset{\sim}{e}(\underset{\sim}{r}) + \dot{\underset{\sim}{a}}(\underset{\sim}{r}) = -\underset{\sim}{\nabla}\Phi(\underset{\sim}{r}) \ . \tag{2.2.3}$$

This is possible since a vector whose *curl* is zero may be defined as the gradient of a new scalar function. The equations (2.2.1) and (2.2.3) define the electromagnetic potentials. However, the electromagnetic fields $\underset{\sim}{e}(\underset{\sim}{r})$ and $\underset{\sim}{b}(\underset{\sim}{r})$ do not uniquely determine the vector and scalar potentials; there is a family of possible $(\underset{\sim}{a},\Phi)$ pairs as the equations are unaltered by the substitutions

$$\left.\begin{array}{l} \underset{\sim}{a}(\underset{\sim}{r}) \Rightarrow \underset{\sim}{a}(\underset{\sim}{r}) + \underset{\sim}{\nabla}\chi \\ \Phi(\underset{\sim}{r}) \Rightarrow \Phi(\underset{\sim}{r}) - \dfrac{\partial\chi}{\partial t} \end{array}\right\} , \tag{2.2.4}$$

as is evident from (2.2.3), where χ is called the gauge function. The particular choice of χ, ie the choice of gauge, may be such as to be convenient to the area of study. When QED is applied to problems in chemical physics it is convenient [3] to employ the known solutions of the particles-only Schrödinger equations as bases for a perturbation theory of the coupled system including the quantized field (the equations of which not being exactly solvable). This requires there to be an explicit Coulomb potential term in the Hamiltonian. The choice of χ given by

$$\nabla^2\chi = -\underset{\sim}{\nabla}.\underset{\sim}{a}(\underset{\sim}{r}) \tag{2.2.5}$$

leads to the so-called Coulomb gauge which is defined by

$$\underset{\sim}{\nabla}.\underset{\sim}{a} = 0 \quad . \tag{2.2.6}$$

The electric field $\underset{\sim}{e}(\underset{\sim}{r})$ given by (2.2.3) is split [3,22] into its longitudinal and transverse parts. Thus

$$\underset{\sim}{e}^{\perp}(\underset{\sim}{r}) = -\dot{\underset{\sim}{a}}(\underset{\sim}{r}) \quad ; \quad \underset{\sim}{e}''(\underset{\sim}{r}) = -\underset{\sim}{\nabla}\phi(\underset{\sim}{r}) \ . \tag{2.2.7}$$

The electrostatic field due to the charged particles is given by $\underset{\sim}{e}''(\underset{\sim}{r})$ and the radiation field $\underset{\sim}{e}^{\perp}(\underset{\sim}{r})$ is described by the transverse vector potential. The photons involved in radiative processes which arise from quantization of the field are thus known as transverse photons. The new equations of motion in terms of the potentials are obtained from the remaining Maxwell equations and are given by

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\underset{\sim}{a}(\underset{\sim}{r}) = -\frac{1}{\varepsilon_0 c^2}\underset{\sim}{j}^{\perp}(\underset{\sim}{r}) \tag{2.2.8}$$

$$\nabla^2\phi = -\rho/\varepsilon_0 \tag{2.2.9}$$

If we now apply the variational principles of classical mechanics we obtain Lagrange's equations. As discussed in Chapter 1 the solution of these equations is the Lagrangian function: its new requirement, however, is that it must lead to the new equations of motion (2.2.8/9). A suitable choice of such a function in terms of the electromagnetic potentials is given by

$$L = 1/2\sum_{\alpha} m_\alpha \dot{\underset{\sim}{q}}_\alpha^2 + \frac{\varepsilon_0}{2}\int\left\{\underset{\sim}{e}^2(\underset{\sim}{r}) - c^2\underset{\sim}{b}^2(\underset{\sim}{r})\right\}d^3\underset{\sim}{r} + \int\underset{\sim}{j}^{\perp}(\underset{\sim}{r}).\underset{\sim}{a}(\underset{\sim}{r})d^3\underset{\sim}{r} - \int\rho(\underset{\sim}{r})\phi(\underset{\sim}{r})d^3\underset{\sim}{r} \tag{2.2.10}$$

which is known as the Coulomb gauge Lagrangian. In (2.2.10) the charge density is given by

$$\rho \;=\; \sum_{\alpha} e_{\alpha}\, \delta(\underset{\sim}{r}-\underset{\sim}{q}_{\alpha}) \;. \tag{2.2.11}$$

The Lagrangian (2.2.10) gives a starting point from which we derive the quantum mechanical Hamiltonian.

2.3 Elimination of the scalar potential

By introducing the electrostatic potentials and choosing the Coulomb gauge, the Lagrangian leads to the equations of motion (2.2.8) and (2.2.9), rather than Maxwell's equations, although the two are equivalent; the source-free Maxwell equations are of course implicit in the definition of the potentials. Note though that the scalar potential $\Phi(\underset{\sim}{r})$ is a function of the particle coordinates and should not be treated as a dynamical variable; it is not described by a wave equation of the form of (2.2.8). Rather, the solution of (2.2.9) gives the scalar potential as

$$\Phi(\underset{\sim}{r}) \;=\; (4\pi\varepsilon_0)^{-1}\sum_{\alpha} \frac{e_{\alpha}}{|\underset{\sim}{r}-\underset{\sim}{q}_{\alpha}|} \;. \tag{2.3.1}$$

Hence in this case the scalar potential is simply the Coulomb potential of the system of charges. We may therefore choose to eliminate $\Phi(\underset{\sim}{r})$ from the Lagrangian in favour of the electrostatic potential energy V, which is our first aim and which we can do because of its relationship with the longitudinal component of the electric field. That is, expanding the field term of (2.2.10) using (2.2.7) and integrating by parts gives

$$(\varepsilon_0/2)\int|\underset{\sim}{\nabla}\Phi(\underset{\sim}{r})|^2 d^3\underset{\sim}{r} \;=\; \tfrac{1}{2}\int\rho(\underset{\sim}{r})\Phi(\underset{\sim}{r})d^3\underset{\sim}{r} \tag{2.3.2}$$

which may be combined with the last term of (2.2.10) to give

$$-\frac{1}{2}\int\rho(\mathbf{r})\Phi(\mathbf{r})d^3\mathbf{r} \quad = \quad -V_{\mathrm{Total}} \tag{2.3.3}$$

with the potential energy term V given by

$$V_{\mathrm{Total}} \quad = \quad (8\pi\varepsilon_0)^{-1}\sum_{\alpha}\sum_{\beta}\frac{e_\alpha e_\beta}{|\mathbf{q}_\alpha-\mathbf{q}_\beta|} \; . \tag{2.3.4}$$

Strictly we should write the Lagrangian in terms of the vector potential $\mathbf{a}(\mathbf{r})$ and its derivative rather than the field vectors. This is straightforward but we note that the cross term from the expansion of $\mathbf{e}^2(\mathbf{r})$ vanishes in this gauge. That is

$$\int\dot{\mathbf{a}}(\mathbf{r}).\nabla\Phi(\mathbf{r})d^3\mathbf{r} \quad = \quad 0 \; , \tag{2.3.5}$$

since $\mathbf{a}(\mathbf{r})$ is entirely transverse and $\nabla\Phi(\mathbf{r})$ longitudinal. Thus the Lagrangian is given directly by

$$L \quad = \quad 1/2\sum_{\alpha} m_\alpha\dot{\mathbf{q}}_\alpha^2 + \frac{\varepsilon_0}{2}\int\left\{\dot{\mathbf{a}}(\mathbf{r})^2-c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r} + \int\mathbf{j}^{\perp}(\mathbf{r}).\mathbf{a}(\mathbf{r})d^3\mathbf{r} - V \; . \tag{2.3.6}$$

with $\mathbf{j}(\mathbf{r})$ given by (1.1.2). We have thus generated the minimal-coupling Lagrangian (1.1.1), starting from an arbitrary gauge, from which the minimal-coupling Hamiltonian will include an explicit electrostatic interaction term, as shown in Chapter 1. In contrast to the previous works outlined in Chapter 1, however, in the sections which follow we make no assumptions regarding the velocities or net charges of the molecules, and proceed instead with the development of the complete multipolar Hamiltonian.

2.4 An equivalent Lagrangian

The multipolar Lagrangian is obtained from (2.3.6) by performing a transformation of the kind described in Chapter 1. In order to do this the total charge and current densities must be partitioned in terms of true and bound contributions, which in turn requires the definition of a molecular centre, about which motion of the composite particles is defined. $\mathbf{R}_\zeta$ is suitably chosen as the position vector of the centre of mass [22-26]. The charge density is given by (1.1.22) but the current density now contains additional terms compared with that used in Section 1.1; the complete current density is used for the first time here in the development of the multipolar Hamiltonian. The current density may be expressed as a sum of true, polarization, magnetization and Röntgen current densities [29,24,31-32]. The ionic convective current (which includes a free electronic contribution) is denoted by $\mathbf{j}_{\text{ionic}}$. Now if the magnetic multipole moments are defined relative to $\mathbf{R}_\zeta$, then the total magnetization field will contain a term which depends explicitly on the motion of this centre. This term is called the Röntgen current [31,29], and it represents the magnetization of the moving assemblage relative to the inertial frame. The polarization and magnetization fields, on the other hand, are those relative to the molecular frame and are likewise additive over the assemblages, as defined by (1.1.29). j_{Rontgen} and $\mathbf{j}_{\text{ionic}}$ are defined below. Hence it is possible to write

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_{\text{ionic}}(\mathbf{r}) + \dot{\mathbf{p}}(\mathbf{r}) + \nabla\times\mathbf{M}(\mathbf{r}) + \mathbf{j}_{\text{Rontgen}} \tag{2.4.1}$$

with the definitions

$$\mathbf{j}_{\text{ionic}}(\mathbf{r}) = \sum_{\zeta} Q_{\zeta}\dot{\mathbf{R}}_{\zeta}\delta(\mathbf{r}-\mathbf{R}_{\zeta}) \tag{2.4.2}$$

and

$$\mathbf{j}_{\text{Rontgen}} = \sum_{\zeta} \boldsymbol{\nabla}\times\left(\mathbf{p}(\zeta;\mathbf{r})\times\dot{\mathbf{R}}_{\zeta}\right) . \tag{2.4.3}$$

The fields $\mathbf{p}(\mathbf{r})$ and $\mathbf{M}(\mathbf{r})$ are redefined shortly.

Let us write down a new Lagrangian given by (2.4.4), which we know must be equivalent to (2.3.6). This is the same transformation that was given by (1.1.17) for neutral systems. We have

$$L_{\text{new}} = L_{\text{min}} - \frac{d}{dt}\int \mathbf{p}^{\perp}(\mathbf{r}).\mathbf{a}(\mathbf{r})d^{3}\mathbf{r} . \tag{2.4.4}$$

However, before we write down L_{new} in full we make a distinction between the labels associated with electrons and those with nuclei. In Section 1.1 α represented a general particle label; the coordinates $\mathbf{q}_{\alpha}$ were therefore regarded as generalised coordinates so that the Lagrangian function $L = L(\mathbf{q}_{\alpha},\dot{\mathbf{q}}_{\alpha},t)$ was sufficient to describe the state of the system. If we instead define the electron labels $\alpha(\zeta)$ and the nuclear labels $a(\zeta)$, for an assemblage ζ, then the transverse polarization and magnetization fields are given by

$$\begin{aligned} p_{i}^{\perp}(\zeta;\mathbf{r}) = {} & -e\sum_{\alpha} (\mathbf{q}_{\alpha}-\mathbf{R}_{\zeta})_{j}\int_{0}^{1}\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{R}_{\zeta}-\lambda(\mathbf{q}_{\alpha}-\mathbf{R}_{\zeta}))d\lambda \\ & +e\sum_{a} Z_{a}(\mathbf{q}_{a}-\mathbf{R}_{\zeta})_{j}\int_{0}^{1}\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{R}_{\zeta}-\lambda(\mathbf{q}_{a}-\mathbf{R}_{\zeta}))d\lambda \end{aligned} \tag{2.4.5}$$

and

$$\begin{aligned} M_{i}^{\perp}(\zeta;\mathbf{r}) = {} & -e\sum_{\alpha}\left\{(\mathbf{q}_{\alpha}-\mathbf{R}_{\zeta})\times(\dot{\mathbf{q}}_{\alpha}-\dot{\mathbf{R}}_{\zeta})\right\}_{j}\int_{0}^{1}\lambda\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{R}_{\zeta}-\lambda(\mathbf{q}_{\alpha}-\mathbf{R}_{\zeta}))d\lambda. \\ & +e\sum_{a} Z_{a}\left\{(\mathbf{q}_{a}-\mathbf{R}_{\zeta})\times(\dot{\mathbf{q}}_{a}-\dot{\mathbf{R}}_{\zeta})\right\}_{j}\int_{0}^{1}\lambda\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{R}_{\zeta}-\lambda(\mathbf{q}_{a}-\mathbf{R}_{\zeta}))d\lambda. \end{aligned} \tag{2.4.6}$$

respectively, where Z_a is the atomic number of nucleus a. The transverse part of the total polarization field is defined above since it is the transverse current density which appears in the minimal-coupling Lagrangian; $\nabla\times\mathbf{M}(\mathbf{r})$ is transverse in any case, as is j_{Rontgen}. The new Lagrangian in terms of these variables is given by (2.4.7).

$$L = L_{\mathrm{part}} + L_{\mathrm{rad}} + L_{\mathrm{int}} \tag{2.4.7}$$

$$L_{\mathrm{part}} = (m_e/2)\sum_{\zeta}\sum_{\alpha} \dot{\mathbf{q}}^2_{\alpha(\zeta)} + (1/2)\sum_{\zeta}\sum_{a} m_a(\zeta)\dot{\mathbf{q}}^2_{a(\zeta)} \tag{2.4.8}$$

$$L_{\mathrm{rad}} = + \frac{\varepsilon_0}{2}\int\left\{\dot{\mathbf{a}}(\mathbf{r})^2 - c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r} \tag{2.4.9}$$

$$\begin{aligned} L_{\mathrm{int}} = & -\int\mathbf{p}^{\perp}(\mathbf{r}).\dot{\mathbf{a}}(\mathbf{r})d^3\mathbf{r} + \sum_{\zeta} Q_{\zeta}\dot{\mathbf{R}}_{\zeta}.\mathbf{a}(\mathbf{R}_{\zeta}) - V \\ & + \int\left\{\nabla\times\mathbf{M}(\mathbf{r})\right\}.\mathbf{a}(\mathbf{r})d^3\mathbf{r} + \sum_{\zeta}\int\left\{\nabla\times\left[\mathbf{p}(\zeta;\mathbf{r})\times\dot{\mathbf{R}}_{\zeta}\right]\right\}.\mathbf{a}(\mathbf{r})d^3\mathbf{r} \end{aligned} \tag{2.4.10}$$

with V given by (2.3.4). (2.4.10) shows that the inclusion of $\mathbf{j}_{\mathrm{ionic}}(\mathbf{r})$ and $\mathbf{j}_{\mathrm{Rontgen}}$ in (2.4.1) has modified the Lagrangian. Comparing L_{int} with (1.1.18) we see that there are two new interaction terms; these will lead to additional terms in the final Hamiltonian.

The vector $\mathbf{R}_{\zeta}$, which is included in the definitions of the ionic current and the polarizations and which we have chosen to be the centre of mass of the molecule/ion ζ, is treated as a dynamical variable; $\mathbf{R}_{\zeta}$ and its canonical momentum $\mathbf{P}_{\zeta}$ form a canonical pair. It is a good approximation to equate $\mathbf{R}_{\zeta}$ with the centre of mass of the nuclei, since the mass of the electron is small compared with the masses of the nuclei ie $m_e \ll m_a$. Thus we may write

$$M_\zeta \simeq \sum_{a(\zeta)} m_a(\zeta) \tag{2.4.11}$$

and

$$\underset{\sim}{R}_\zeta \simeq \sum_{a(\zeta)} (m_a(\zeta) q_a(\zeta)/M_\zeta) \; . \tag{2.4.12}$$

The terms of the Lagrangian (2.4.7), however, are written with sums over the general nuclear coordinate a(ζ); by introducing a set of orthogonal coordinates for each molecule, it is possible to write down the multipolar Lagrangian in a form which separates the centres of mass motion from the internal nuclear and electronic motions.

q_a

For each assemblage we define a set of mass-weighted orthogonal coordinates $Q_{r(\zeta)}$ [33], given by the linear transformation

$$Q_{r(\zeta)} = \sum_{a(\zeta)} m_a^{1/2} l_{r(\zeta),i(a)} q_{i(a)} \; , \qquad r = 1,2,\ldots 3N \tag{2.4.13}$$

where N is the number of nuclei in assemblage ζ. In (2.4.13) the contribution of the coordinate $\underset{\sim}{q}_{(a)}$ along the direction i to the mode $Q_{r(\zeta)}$ is proportional to $l_{r(\zeta),i(a)}$. l is then a real, unitary 3N × 3N matrix, with matrix elements $l_{r(\zeta),i(a)}$. The transformation is orthogonal. That is, the inverse of the transformation may be written as

$$q_{i(a)} = m_a^{-1/2} \sum_{r(\zeta)}^{3N} l_{r(\zeta),i(a)} Q_{r(\zeta)} \; , \tag{2.4.14}$$

and the sum of the squares of the nuclear coordinates is given by the sum of the squares of the modes,

$$1/2 \sum_{a(\zeta)} m_a(\zeta)\dot{\underset{\sim}{q}}_a^{2} = 1/2 \sum_{r(\zeta)}^{3N-3} \dot{Q}_{r(\zeta)}^{2} + 1/2M_\zeta \dot{R}_\zeta^{2}$$

(2.4.15)

from which translational motion has been separated by defining for each molecule the matrix elements

$$l_{3N-2,x(a)} = l_{3N-1,y(a)} = l_{3N,z(a)} = (m_a/M)^{1/2}.$$

(2.4.16)

(2.4.16) ensures that the final three modes for each molecule describe translational motion along the Cartesian axes x, y and z ie

$$Q_{3N-2} = M^{1/2}R_x \quad ; \quad Q_{3N-2} = M^{1/2}R_y \quad ; \quad Q_{3N} = M^{1/2}R_z \; .$$

(2.4.17)

Using this transformation the Lagrangian may be written in its multipolar form, with translational motion separated from rotational and vibrational motion.

Introducing the vector fields $\underset{\sim}{n}_\alpha(\zeta;\underset{\sim}{r})$ and $\underset{\sim}{n}_a(\zeta;\underset{\sim}{r})$ for molecule ζ,

$$\underset{\sim}{n}_\alpha(\zeta;\underset{\sim}{r}) = -e(\underset{\sim}{q}_\alpha-\underset{\sim}{R}_\zeta)\int_0^1 \lambda\delta(\underset{\sim}{r}-\underset{\sim}{R}_\zeta-\lambda(\underset{\sim}{q}_\alpha-\underset{\sim}{R}_\zeta))d\lambda,$$

(2.4.18)

$$\underset{\sim}{n}_a(\zeta;\underset{\sim}{r}) = eZ_a(\underset{\sim}{q}_a-\underset{\sim}{R}_\zeta)\int_0^1 \lambda\delta(\underset{\sim}{r}-\underset{\sim}{R}_\zeta-\lambda(\underset{\sim}{q}_a-\underset{\sim}{R}_\zeta))d\lambda,$$

(2.4.19)

the multipolar Lagrangian becomes

$$L_{mult} = \sum_\zeta L_{part}(\zeta) + L_{rad} + \sum_\zeta L_{int}(\zeta) - V$$

(2.4.20)

with

$$L_{\mathrm{part}}(\zeta) = (m_e/2)\sum_{\alpha} \dot{\mathbf{q}}^2_{\alpha(\zeta)} + (1/2)\sum_{r(\zeta)}^{3N-3} \dot{Q}^2_{r(\zeta)} + (1/2)M_\zeta \dot{R}^2_\zeta \tag{2.4.21}$$

$$L_{\mathrm{rad}} = +\frac{\epsilon_0}{2}\int\left\{\dot{\mathbf{a}}(\mathbf{r})^2 - c^2\mathbf{b}^2(\mathbf{r})\right\}d^3\mathbf{r} \tag{2.4.22}$$

$$\begin{aligned} L_{\mathrm{int}}(\zeta) = & -\int \mathbf{p}^{\perp}(\zeta;\mathbf{r}).\dot{\mathbf{a}}(\mathbf{r})d^3\mathbf{r} - \sum_{\alpha}\dot{\mathbf{q}}_{\alpha(\zeta)}\cdot\int \mathbf{n}_\alpha(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} \\ & - V - \sum_{\alpha}\sum_{r(\zeta)}^{3N-3} m_a^{-1/2}\, l_{r(\zeta),i(a)}\dot{Q}_{r(\zeta)}\left\{\int \mathbf{n}_a(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r}\right\}_i \\ & - \dot{\mathbf{R}}_\zeta.\left\{\int \mathbf{p}(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - \sum_{\alpha}\int \mathbf{n}_\alpha(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - Q_\zeta\mathbf{a}(\mathbf{R}_\zeta)\right\} \end{aligned} \tag{2.4.23}$$

Written in this form (2.4.23) allows easy determination of the canonical momenta. The final term depends directly on translational motion of the molecule and in contrast to the Lagrangian for neutral systems (2.4.23) contains a term which is linear in the vector potential. The canonical momentum of the molecule will therefore be coupled to the vector potential.

The centre of mass and the normal modes associated with the nuclei for each assemblage, together with the electron coordinates, now form a complete set of linearly independent particle coordinates for the Lagrangian while the variables of the radiation field remain unaltered. Note that the electromagnetic field is described by a density functional since it varies continuously in space. Hence the terms which appear in (2.4.22) and (2.4.23) are of the form

$$L = \int \mathcal{L} d^3\mathbf{r} \tag{2.4.24}$$

where $\mathcal{L}$ is the Lagrangian density.

The canonical momenta are next obtained from (2.4.20) before finally constructing the multipolar Hamiltonian in Section 2.7.

2.5 The canonical momenta

Having written down the Lagrangian in its multipolar form, we now determine the momenta conjugate to the canonical coordinates in order to construct the multipolar Hamiltonian. The four pairs of canonical variables are now given by $(\mathbf{q}_\alpha,\mathbf{p}_\alpha)$ for the electrons, $(Q_{r(\zeta)},p_{r(\zeta)})$ for the normal modes, $(\mathbf{R}_\zeta,\mathbf{P}_\zeta)$ for molecular translational motion and $(\mathbf{a}(\mathbf{r}),\mathbf{\Pi}(\mathbf{r}))$ for the electromagnetic field. The canonical momenta are defined, analogously to the momentum of the generalized coordinate α in (1.1.8), by the expressions below. We have

$$\mathbf{p}(\alpha) = \partial L_{\text{mult}}/\dot{\mathbf{q}}(\alpha) , \qquad (2.5.1)$$

$$p_{r(\zeta)} = \partial L_{\text{mult}}/\dot{Q}_{r(\zeta)} , \qquad (2.5.2)$$

$$\mathbf{P}_\zeta = \partial L_{\text{mult}}/\dot{\mathbf{R}}_\zeta , \qquad (2.5.3)$$

and

$$\mathbf{\Pi}(\mathbf{r}) = \partial \mathcal{L}_{\text{mult}}/\dot{\mathbf{a}}(\mathbf{r}) . \qquad (2.5.4)$$

Hence, using (2.4.20), we may write down the momenta directly as

$$\mathbf{p}(\alpha) = m_e\dot{\mathbf{q}}(\alpha) - \int \mathbf{n}_\alpha(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} \qquad (2.5.5)$$

$$p_{r(\zeta)} = \dot{Q}_{r(\zeta)} - \Lambda_{r(\zeta)} \qquad (2.5.6)$$

$$\mathbf{P}_\zeta = M_\zeta\dot{\mathbf{R}}_\zeta - \left\{\int \mathbf{p}(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - \int \sum_\alpha \mathbf{n}_\alpha(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - Q_\zeta \mathbf{a}(\mathbf{R}_\zeta)\right\} \qquad (2.5.7)$$

and

$$\mathbf{\Pi}(\mathbf{r}) = \varepsilon_0\dot{\mathbf{a}}(\mathbf{r}) - \mathbf{p}^{\perp}(\mathbf{r}) \tag{2.5.8}$$

where $\Lambda_{r(\zeta)}$ in (2.5.6) is given by the sum

$$\Lambda_{r(\zeta)} = \sum_{a(\zeta)} m_a^{-1/2} l_{r(\zeta),i(a)} \left\{ \int \mathbf{n}_a(\zeta;\mathbf{r}) \times \mathbf{b}(\mathbf{r})d^3\mathbf{r} \right\}_i \tag{2.5.9}$$

In (2.5.9) r may take the value r = 1,2,..,3N-3.

The field and electron canonical momenta (2.5.8) and (2.5.5) are the same as those in the basic theory. New features here are the momenta associated with the mode r and with the molecule itself; (2.5.7) arises directly from the new interaction terms.

Construction of the Hamiltonian using (2.5.5-8) is the final task. However, in anticipation of the form of this function, it is convenient to examine now, some of the terms of the Lagrangian individually. In particular we shall see how the Lagrangian (and hence the Hamiltonian) may be written down in a form which excludes the potential energy term V_{inter}.

2.6 The electrostatic potential

The multipolar Lagrangian (2.4.20) contains the electrostatic potential term V, given earlier by the expression (2.3.4) in terms of the general coordinates α and β representing all particles. It was shown earlier (Section 2.3) that this term is preserved in the formulation of the minimal-coupling Hamiltonian from the minimal-coupling Lagrangian (2.3.6). It is shown in this section how this term may be partitioned into inter- and intramolecular parts and how the multipolar formalism leads to the complete elimination of the intermolecular contribution for neutral systems, giving the results of

Chapter 1. Further, the residue terms associated with charge-charge and/or charge-multipole interactions for systems containing net charges following incomplete cancellation of the intermolecular potential term are determined here.

Adopting the notation of Section 2.4 (but excluding the normal modes for simplicity), (2.3.4) may be rewritten with sums explicitly over electrons and nuclei. Summing over all molecules gives a potential energy total of

$$V_{\mathrm{Total}} = V_{\mathrm{intra}} + V_{\mathrm{inter}} \tag{2.6.1}$$

where the intramolecular contribution to V_{Total} is given by

$$V_{\mathrm{intra}} = \sum_{\zeta} V(\zeta) , \tag{2.6.2}$$

where for molecule ζ we write

$$V(\zeta) = (e^2/4\pi\varepsilon_0)\left\{ \sum_{\alpha<\beta} \frac{1}{|\underset{\sim}{q}_\alpha - \underset{\sim}{q}_\beta|} - \sum_{\alpha,a} \frac{Z_a}{|\underset{\sim}{q}_\alpha - \underset{\sim}{q}_a|} + \sum_{a<b} \frac{Z_a Z_b}{|\underset{\sim}{q}_a - \underset{\sim}{q}_b|} \right\} . \tag{2.6.3}$$

In (2.6.3) α and β are electron labels implicit to ζ and a and b denote the nuclei. Nucleus a has a charge of eZ_a. This term is usually treated as part of the molecular Hamiltonian, once it is formed, and is common to both the minimal-coupling and multipolar forms.

The intermolecular term is similarly given by

$$V_{\mathrm{inter}} = \sum_{\zeta<\zeta'} V(\zeta,\zeta') \tag{2.6.4}$$

with

$$V(\zeta,\zeta') = (e^2/4\pi\varepsilon_0)\left\{ \sum_{\alpha,\beta}\frac{1}{|\underset{\sim}{q}_{\alpha(\zeta)}-\underset{\sim}{q}_{\beta(\zeta')}|} - \sum_{\alpha,b}\frac{Z_{b(\zeta')}}{|\underset{\sim}{q}_{\alpha(\zeta)}-\underset{\sim}{q}_{b(\zeta')}|} - \sum_{a,\beta}\frac{Z_{a(\zeta)}}{|\underset{\sim}{q}_{a(\zeta)}-\underset{\sim}{q}_{\beta(\zeta')}|} + \sum_{a,b}\frac{Z_{a(\zeta)}Z_{b(\zeta')}}{|\underset{\sim}{q}_{a(\zeta)}-\underset{\sim}{q}_{b(\zeta')}|}\right\}. \qquad (2.6.5)$$

Here the pairs (α,a) and (β,b) are associated with molecules ζ and ζ' respectively. (2.6.5) includes the electrostatic intermolecular interactions between all particle pairs in the system.

Let us consider the Lagrangian (2.4.20) further. When constructing the multipolar Hamiltonian from this expression it will be necessary to substitute for the coordinate 'velocities', obtained by rearranging the equations (2.5.5-8), so that each term is written in terms of the canonical variables, the coordinates and momenta. Now when we substitute for $\dot{\underset{\sim}{a}}(\underset{\sim}{r})$ in (2.4.23) using

$$\dot{\underset{\sim}{a}}(\underset{\sim}{r}) = (1/\varepsilon_0)\left(\underset{\sim}{\Pi}(\underset{\sim}{r}) + \underset{\sim}{p}^{\perp}(\underset{\sim}{r})\right) \qquad (2.6.6)$$

we obtain the term

$$(1/2\varepsilon_0)\int|\underset{\sim}{p}^{\perp}(\underset{\sim}{r})|^2 d^3\underset{\sim}{r} \qquad (2.6.7)$$

which is independent of the electromagnetic field. In (2.6.6) $\underset{\sim}{p}^{\perp}(\underset{\sim}{r})$ is the transverse polarization field summed for all molecules. Expanding the modulus square allows us to write this term as

$$(1/2\varepsilon_0)\int\sum_{\zeta}|\underset{\sim}{p}^{\perp}(\zeta;\underset{\sim}{r})|^2 d^3\underset{\sim}{r} + (1/\varepsilon_0)\int\sum_{\zeta<\zeta'}\underset{\sim}{p}^{\perp}(\zeta;\underset{\sim}{r}).\underset{\sim}{p}^{\perp}(\zeta';\underset{\sim}{r})d^3\underset{\sim}{r} \qquad (2.6.8)$$

where the transverse polarization product has now been decomposed into one- and two-centre parts. The one-centre term of (2.6.8) may be set aside for now and regained later as a self-energy term in the Hamiltonian. The two-centre term may be treated by considering the intermolecular polarization product

$$(1/\varepsilon_0)\int \sum_{\zeta<\zeta'} \underset{\sim}{p}(\zeta;\underset{\sim}{r})\cdot\underset{\sim}{p}(\zeta';\underset{\sim}{r})d^3\underset{\sim}{r}\ . \tag{2.6.9}$$

The polarization fields in (2.6.9) are local; where the charge distributions of the molecules ζ and ζ' do not overlap this product vanishes and the above integral goes to zero. The transverse and longitudinal polarization products then become equal and opposite. That is

$$(1/\varepsilon_0)\int \sum_{\zeta<\zeta'} \underset{\sim}{p}^{\perp}(\zeta;\underset{\sim}{r})\cdot\underset{\sim}{p}^{\perp}(\zeta';\underset{\sim}{r})d^3\underset{\sim}{r} = -(1/\varepsilon_0)\int \sum_{\zeta<\zeta'} \underset{\sim}{p}^{\shortparallel}(\zeta;\underset{\sim}{r})\cdot\underset{\sim}{p}^{\shortparallel}(\zeta';\underset{\sim}{r})d^3\underset{\sim}{r} \tag{2.6.10}$$

since the cross terms are identically zero. The longitudinal polarization field given by

$$\begin{aligned} p_i^{\shortparallel}(\zeta;\underset{\sim}{r}) = &-e\sum_{\alpha} (\underset{\sim}{q}_{\alpha}-\underset{\sim}{R}_{\zeta})_j\int_0^1 \delta_{ij}^{\shortparallel}(\underset{\sim}{r}-\underset{\sim}{R}_{\zeta}-\lambda(\underset{\sim}{q}_{\alpha}-\underset{\sim}{R}_{\zeta}))d\lambda \\ &+e\sum_{\alpha} Z_a(\underset{\sim}{q}_a-\underset{\sim}{R}_{\zeta})_j\int_0^1 \delta_{ij}^{\shortparallel}(\underset{\sim}{r}-\underset{\sim}{R}_{\zeta}-\lambda(\underset{\sim}{q}_a-\underset{\sim}{R}_{\zeta}))d\lambda \end{aligned} \tag{2.6.11}$$

may be substituted into the right-hand side of (2.6.10) and for a system of neutral molecules this term cancels the intermolecular potential energy term [11]. Since we are considering a collection of ions and molecules, however, such will not be the case and we are required to determine the new result. After a straightforward but lengthy manipulation of the resulting terms it is possible to write an identity of the form

$$(1/\varepsilon_0)\int \sum_{\zeta<\zeta'} \mathbf{p}''(\zeta;\mathbf{r})\cdot\mathbf{p}''(\zeta';\mathbf{r})d^3\mathbf{r} \quad = \quad V_{\mathrm{inter}} - W_{\mathrm{elec}} \ , \qquad , \tag{2.6.12}$$

where V_{inter} is that sum given by (2.6.4) and is the intermolecular potential energy, while W_{elec} is a collection of electrostatic terms which are dependent on the net charges of the molecules. A concise form of these terms is given below. Q_ζ denotes the net charge of molecule ζ at position $\mathbf{R}_\zeta$ and is not to be confused with the mode $Q_{r(\zeta)}$.

$$\begin{aligned} W_{\mathrm{elec}} \quad = \quad (1/4\pi\varepsilon_0)\sum_{\zeta<\zeta'}\Bigg\{ & -\sum_{\alpha}\frac{eQ_{\zeta'}}{|\mathbf{q}_{\alpha(\zeta)}-\mathbf{R}_{\zeta'}|} + \sum_{a}\frac{eQ_{\zeta'}Z_{a(\zeta)}}{|\mathbf{q}_{a(\zeta)}-\mathbf{R}_{(\zeta')}|} \\ & -\frac{Q_\zeta Q_{\zeta'}}{|\mathbf{R}_\zeta-\mathbf{R}_{\zeta'}|} - \sum_{\beta}\frac{eQ_\zeta}{|\mathbf{q}_{\beta(\zeta')}-\mathbf{R}_\zeta|} + \sum_{b}\frac{eQ_\zeta Z_{b(\zeta')}}{|\mathbf{q}_{b(\zeta')}-\mathbf{R}_{(\zeta)}|}\Bigg\} \end{aligned} \tag{2.6.13}$$

Note the minus sign in the definition of W_{elec} given by (2.6.12): the potential energy term is best regarded as the sum of the terms which comprise W_{elec} and the longitudinal intermolecular polarization product. W_{elec} represents the electrostatic coupling of the electrons and nuclei of one aggregate with the net charge of another positioned at its centre of mass. Clearly for neutral systems we have

$$W_{\mathrm{elec}} \ = \ 0 \ , \tag{2.6.14}$$

as before. Thus, as long as the molecules are well separated, the intermolecular Coulomb energies are effectively cancelled by the two-centre terms of the transverse polarization product. The resulting multipolar Hamiltonian, discussed in Chapter 1, then contains no explicit potential terms and all intermolecular interactions proceed, via coupling to the field, through exchange of transverse photons. Note that in the minimal-coupling Hamiltonian, where V_{inter} remains even for neutral systems, the lowest-order electrostatic term given by the expansion of the left hand side of (2.6.12) is the familiar dipole-dipole coupling term

$$V_{\zeta\zeta'} = (4\pi\varepsilon_0)^{-1}\mu_i(\zeta)\mu_j(\zeta')(\delta_{ij}-3\hat{R}_i\hat{R}_j)/R^3 \quad , \tag{2.6.15}$$

where $\underset{\sim}{R}$ is the intermolecular separation vector.

The multipolar Hamiltonian for systems containing ions and molecules includes electrostatic potential energy terms given in total by W_{elec}. However, the form of (2.6.13) is not such that these interactions may be readily determined. We wish to write W_{elec} in a form in which it may easily be used in applications. It is possible to rewrite these terms by performing Taylor expansions about $\underset{\sim}{R}$ with

$$\underset{\sim}{R} = \underset{\sim}{R}_{\zeta'} - \underset{\sim}{R}_{\zeta} \tag{2.6.16}$$

such that

$$(\underset{\sim}{q}_{\alpha}(\zeta)-\underset{\sim}{R}_{\zeta}),\ (\underset{\sim}{q}_{a}(\zeta)-\underset{\sim}{R}_{\zeta}),\ (\underset{\sim}{q}_{\beta}(\zeta')-\underset{\sim}{R}_{\zeta'}),\ (\underset{\sim}{q}_{b}(\zeta')-\underset{\sim}{R}_{\zeta'}) \ll \underset{\sim}{R} \ . \tag{2.6.17}$$

Keeping only terms up to the charge-quadrupole interaction this leads to the result

$$\begin{aligned} W_{\mathrm{elec}} = (1/4\pi\varepsilon_0)\sum_{\zeta<\zeta'}\Big\{ & Q_\zeta Q_{\zeta'}/R + \Big(Q_{\zeta'}\mu_i(\zeta) - Q_\zeta\mu_i(\zeta')\Big)\hat{R}_i/R^2 \\ & - \Big(Q_\zeta Q_{ij}(\zeta') + Q_{\zeta'}Q_{ij}(\zeta)\Big)(\delta_{ij}-3\hat{R}_i\hat{R}_j)/R^3 + \ldots \Big\} \ . \end{aligned} \tag{2.6.18}$$

This result may be verified by an independent route. The intermolecular potential term V_{inter} given by (2.6.4) is defined by the expression

$$V_{\mathrm{inter}} = (1/4\pi\varepsilon_0)\sum_{\zeta<\zeta'}\iint\rho(\zeta;\mathbf{r})\rho(\zeta';\mathbf{r}')\Big/|\mathbf{r}-\mathbf{r}'|\,d^3\mathbf{r}\,d^3\mathbf{r}' \tag{2.6.19}$$

where $\rho(\zeta;\mathbf{r})$ and $\rho(\zeta';\mathbf{r}')$ are the charge distributions of molecules ζ and ζ' given by

$$\rho(\zeta;\mathbf{r}) = \sum_{\alpha} e_{\alpha(\zeta)}\delta(\mathbf{r}-\mathbf{q}_{\alpha(\zeta)}) + \sum_{a} e_{a(\zeta)}\delta(\mathbf{r}-\mathbf{q}_{a(\zeta)}) \tag{2.6.20}$$

$$\rho(\zeta';\mathbf{r}') = \sum_{\beta} e_{\beta(\zeta')}\delta(\mathbf{r}'-\mathbf{q}_{\beta(\zeta')}) + \sum_{b} e_{b(\zeta')}\delta(\mathbf{r}'-\mathbf{q}_{b(\zeta')}) \,. \tag{2.6.21}$$

Alternative definitions of the charge densities in terms of the polarization fields are given, following the definition of (1.1.22), by

$$\rho(\zeta;\mathbf{r}) = \sum_{\alpha} e_{\alpha(\zeta)}\delta(\mathbf{r}-\mathbf{R}_{\zeta}) + \sum_{a} e_{a(\zeta)}\delta(\mathbf{r}-\mathbf{R}_{\zeta}) - \boldsymbol{\nabla}.\mathbf{p}''(\zeta;\mathbf{r}) \tag{2.6.22}$$

$$\rho(\zeta';\mathbf{r}') = \sum_{\beta} e_{\beta(\zeta')}\delta(\mathbf{r}'-\mathbf{R}_{\zeta'}) + \sum_{b} e_{b(\zeta')}\delta(\mathbf{r}'-\mathbf{R}_{\zeta'}) - \boldsymbol{\nabla}'.\mathbf{p}''(\zeta';\mathbf{r}') \,, \tag{2.6.23}$$

written in this form since $\boldsymbol{\nabla}.\mathbf{p}^{\perp}(\mathbf{r}) = 0$. Substituting these expressions in (2.6.19), and integrating by parts, again gives V_{inter} as the sum of W_{elec} and the longitudinal polarization product, but with the former in its multipolar form.

We have determined the electrostatic interaction term between two ions and those between an ion and a neutral molecule, which remain in the new Hamiltonian. In the form (2.6.18) such interactions may be easily determined by application of the methods of QED and the results will appear in terms of molecular properties such as permanent dipole moments or polarizabilities. In contrast to the minimal-coupling Hamiltonian, however, the electrostatic terms here are just charge-multipole series; all multipole-multipole terms have been eliminated. In the following sections W_{elec} is assumed and will not be written out explicitly.

2.7 The multipolar Hamiltonian

The Hamiltonian may be formed directly from the Lagrangian (2.4.20) and is given by

$$H_{mult} = \sum_{\zeta}\sum_{\alpha(\zeta)} \mathbf{p}_{\alpha}\cdot\dot{\mathbf{q}}_{\alpha} + \sum_{\zeta}\sum_{r(\zeta)} \mathbf{p}_{r}\cdot\dot{\mathbf{Q}}_{r} + \sum_{\zeta} \mathbf{P}_{\zeta}\cdot\dot{\mathbf{R}}_{\zeta} + \int\mathbf{\Pi}(\mathbf{r})\cdot\dot{\mathbf{a}}(\mathbf{r})d^{3}\mathbf{r} - L_{mult} \tag{2.7.1}$$

where the third term is included to represent the canonical pair $(\mathbf{R}_{\zeta},\mathbf{P}_{\zeta})$. The Hamiltonian is written in terms of the canonical variables by substituting for the coordinate velocities, obtained by rearranging the equations (2.5.5-8), into (2.7.1). In the previous Section this process was pre-emted by a consideration of three of the terms such that the intermolecular potential energy term was partly eliminated, leaving only those interactions dependent on net charge. Here the remaining terms are considered and the Hamiltonian will be given shortly.

An alternative to (2.7.1) is to consider the Hamiltonian as the sum of two terms; the molecule and field energies E_{mol} and E_{rad}, which are themselves the sum of kinetic and potential energies. Thus we may write

$$H_{mult} = (T+V)_{mol} + (T+V)_{rad} \ . \tag{2.7.2}$$

The two methods of formulation are not dissimilar, however, in that each requires a knowledge of the velocities $\dot{\mathbf{q}}_{\alpha}(\zeta)$, $\dot{\mathbf{a}}(\mathbf{r})$ etc in order to proceed. Where (2.7.2) may have the edge, though, is an assurance that the resulting Hamiltonian appears in Hermitian form, since we take the squares of these velocities. Additional assumptions concerning the symmetry of the variables prior to quantization are then unnecessary and their operator form follows naturally. Should we choose (2.7.1), on the other hand, then it is best to symmetrize each term, beforehand, in which the order of the variables might be important later on. The latter method is that chosen by Healy [22,10].

The Hamiltonian is given by

$$\begin{aligned} H_{\mathrm{mult}} = {} & \sum_{\zeta}\left\{(1/2m_e)\sum_{\alpha(\zeta)}\left[\mathbf{p}_{(\alpha)} + \int \mathbf{n}_{\alpha}(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r}\right]^2 + V(\zeta)\right\} \\ & + \sum_{\zeta}\left\{(1/2M_{\zeta})\left[\mathbf{P}_{\zeta} + \int \mathbf{p}(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - \int\sum_{\alpha}\mathbf{n}_{\alpha}(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - Q_{\zeta}\mathbf{a}(\mathbf{R}_{\zeta})\right]^2\right\} \\ & + (1/2)\sum_{r}\left[p_{r(\zeta)} + \Lambda_{r(\zeta)}\right]^2 + V_{\mathrm{inter}} \\ & + \frac{1}{2}\int\left\{\{\mathbf{\Pi}(\mathbf{r}) + \mathbf{p}^{\perp}(\mathbf{r})\}^2/\varepsilon_0 + \varepsilon_0 c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r} \end{aligned}$$

(2.7.3)

There are no explicit interaction terms in (2.7.3); these appear following expansion of the various terms, the form of which effectively corresponds to the introduction of coupling between the particles and radiation field ie if there was no coupling then each canonical momentum would be identical to its kinetic form. In the first term of (2.7.3) the electron canonical momentum takes its multipolar form. The second term is interesting. The molecular canonical momentum, given by the sum of the momenta of the constituent particles, is minimally coupled to the vector potential at $\mathbf{R}_{\zeta}$ and to the magnetic field. The latter interaction will give rise to additional contributions to the magnetization. V_{inter} is included in the expression above but its partial cancellation is unaffected by this method and W_{elec} is included in the Hamiltonian given below.

A simplification of the Hamiltonian may be achieved by its partition into molecular, field and interaction terms; a new feature compared with the corresponding function for neutral systems is the presence of the intermolecular Coulomb potential term W_{elec}, which it has been shown depends on the net charge(s) of the interacting species. There are also additional interaction terms, both linear and quadratic in the field, which occur as a result of translation. The Hamiltonian is given by

$$H_{mult} = \sum_{\zeta} H_{mol}(\zeta) + H_{rad} + \sum_{\zeta} H^{(1)}_{int}(\zeta) + \sum_{\zeta} H^{(2)}_{int}(\zeta) + H_{self} + W_{elec} \tag{2.7.4}$$

with W_{elec} given by (2.6.17) and

$$H_{mol}(\zeta) = \frac{1}{2m_e} \sum_{\alpha} \mathbf{p}_{\alpha}^2(\zeta) + \mathbf{P}_{\zeta}^2/2M_{\zeta} + (1/2) \sum_{r(\zeta)}^{3N-3} p_r^2(\zeta) + V(\zeta) \tag{2.7.5}$$

$$H_{rad} = \frac{1}{2}\int\left\{\mathbf{d}^{\perp 2}(\mathbf{r})/\varepsilon_0 + \varepsilon_0 c^2 (\boldsymbol{\nabla}\times\mathbf{a}(\mathbf{r}))^2\right\} d^3\mathbf{r} \tag{2.7.6}$$

$$H_{self} = \frac{1}{2\varepsilon_0}\int \sum_{\zeta} |\mathbf{p}^{\perp}(\zeta;\mathbf{r})|^2 d^3\mathbf{r} \tag{2.7.7}$$

$$H^{(1)}_{int}(\zeta) = -\varepsilon_0^{-1}\int \mathbf{p}(\zeta;\mathbf{r}).\mathbf{d}^{\perp}(\mathbf{r}) d^3\mathbf{r} - \int \mathbf{m}(\zeta;\mathbf{r}).\mathbf{b}(\mathbf{r}) d^3\mathbf{r} - (Q_{\zeta}/M_{\zeta})\mathbf{P}_{\zeta}.\mathbf{a}(\mathbf{R}_{\zeta}) \tag{2.7.8}$$

and

$$H^{(2)}_{int}(\zeta) = +(1/2m_e)\sum_{\alpha(\zeta)}\left(\int \mathbf{n}_\alpha(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r}\right)^2 + (1/2)\sum_{r(\zeta)}^{3N-3}\Lambda^2_{r(\zeta)}$$
$$+ (1/2M_\zeta)\left(\int \mathbf{p}(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - \int\sum_{\alpha}\mathbf{n}_\alpha(\zeta;\mathbf{r})\times\mathbf{b}(\mathbf{r})d^3\mathbf{r} - Q_\zeta\mathbf{a}(\mathbf{R}_\zeta)\right)^2 \tag{2.7.9}$$

Note that the molecular Hamiltonian H_{mol} now includes the intramolecular electrostatic term $V(\zeta)$, as described in Section 2.6. The self-energy and radiation terms are unchanged from (1.1.26/27) but for convenience the interactions have been split into terms which are first- and second-order in the field.

The new first-order term gives the interaction between a charged aggregate and the field; the momentum $\mathbf{P}_\zeta$ of the aggregate interacts with the vector potential, which takes a constant value over the extent of the molecule. As noted the term is similar to the minimal-coupling first order interaction (1.1.12) and the inclusion of the vector potential is an important feature of this form of the multipolar Hamiltonian, namely that it cannot be written wholly in terms of the electric displacement vector and magnetic fields.

Although (2.7.8) has been written such that it includes a term representing the interaction of the magnetic field with the magnetization $\mathbf{m}(\mathbf{r})$, we note that the latter quantity differs from the definition given in Chapter 1. $\mathbf{m}(\mathbf{r})$ includes all terms of the appropriate dimension, including those which arise following the inclusion of the Röntgen current in the current density, since this term is itself a magnetization, coupling the translational motion to the electric polarization field. The total magnetization $\mathbf{m}(\mathbf{r})$ is written as the sum of contributions from each molecule/ion,

$$\underset{\sim}{m}(\underset{\sim}{r}) = \sum_{\zeta} \underset{\sim}{m}(\zeta;\underset{\sim}{r}) \ , \tag{2.7.10}$$

where for each molecule we have the sum

$$\underset{\sim}{m}(\zeta;\underset{\sim}{r}) \ = \ \underset{\sim}{m}'(\zeta;\underset{\sim}{r}) + \underset{\sim}{m}''(\zeta;\underset{\sim}{r}) \ . \tag{2.7.11}$$

Consider the definition (1.1.32) for $\underset{\sim}{m}(\underset{\sim}{r})$ given in Chapter 1. The quantity $\underset{\sim}{m}'(\zeta;\underset{\sim}{r})$ in (2.7.11) is given by an analogous definition

$$\begin{aligned}\underset{\sim}{m}'(\zeta;\underset{\sim}{r}) \ = \ &+ (1/2M_\zeta)\left\{\underset{\sim}{p}(\zeta;\underset{\sim}{r})\times\underset{\sim}{P}_\zeta - \underset{\sim}{P}_\zeta\times\underset{\sim}{p}(\zeta;\underset{\sim}{r})\right\} \\ &+ \frac{1}{2}\left\{\sum_{\alpha(\zeta)}\left\{\underset{\sim}{n}_\alpha(\zeta;\underset{\sim}{r})\times\left(\underset{\sim}{p}_\alpha/m_e - \underset{\sim}{P}_\zeta/M_\zeta\right) - \left(\underset{\sim}{p}_\alpha/m_e - \underset{\sim}{P}_\zeta/M_\zeta\right)\times\underset{\sim}{n}_\alpha(\zeta;\underset{\sim}{r})\right\}\right\}\end{aligned} \tag{2.7.12}$$

which is similarly in symmetric form. The two forms differ by the inclusion in (2.7.12) of the terms which rely on centre of mass (translational) motion. The first term above arises directly from the coupling of molecular motion to the polarization field (the Röntgen current) and vanishes if the molecules are at rest. The second term is the equivalent of (1.1.32) and its source is the magnetization field $\underset{\sim}{M}(\underset{\sim}{r})$ which was defined (2.4.6) relative to the moving frame.

The second term of (2.7.11) gives the contribution of relative nuclear motion to the magnetization. Defining $\underset{\sim}{l}_{r,a}$ as that vector whose components $l_{r,i(a)}$ give the contribution of nucleus a to the mode Q_r (Section 2.4), allows the definition

$$\underset{\sim}{m}''(\zeta;\underset{\sim}{r}) = -(1/2)\sum_{r(\zeta)}^{3N-3}\sum_{a(\zeta)} m_a^{-1/2}\left(\underset{\sim}{l}_{r,a}\times\underset{\sim}{n}_a(\zeta;\underset{\sim}{r})p_{r(\zeta)} + p_{r(\zeta)}\underset{\sim}{l}_{r,a}\times\underset{\sim}{n}_a(\zeta;\underset{\sim}{r})\right) \tag{2.7.13}$$

If the molecules are treated as fixed bodies, however, as in many problems, this term may be ignored.

Returning to (2.7.9) we consider finally the quadratic interaction terms. These are not of particular interest here but we note their origin. The first term, only, arises in the neutral Hamiltonian and gives rise to the diamagnetization field. The remainder, for which we could write similar fields, depend on translational motion. As we would expect, the $\underset{\sim}{p}_{\zeta}.\underset{\sim}{a}(\underset{\sim}{R}_{\zeta})$ term in $H^{(1)}_{int}$ is accompanied here by the corresponding term quadratic in the vector potential, in analogy to the minimal-coupling interactions.

(2.7.4) is then the quantum mechanical Hamiltonian for the system and the canonical variables are operators subject to the usual commutation restrictions.

In Chapter 1 the interaction Hamiltonian (1.1.57) in terms of molecular multipole moments was written down with the aid of the multipole expansions (1.1.50/51). The Hamiltonian (2.7.4) may be similarly treated to facilitate its application. For example, the electric dipole and quadrupole moments are redefined below, noting that now each is made up of two terms since the electronic variables have been separated from the nuclear variables. Hence

$$\mu_i(\zeta) = - e\sum_{\alpha} (\underset{\sim}{q}_{\alpha(\zeta)}-\underset{\sim}{R}_{\zeta})_i + e\sum_{a} Z_a(\underset{\sim}{q}_{a(\zeta)}-\underset{\sim}{R}_{\zeta})_i \tag{2.7.14}$$

and

$$2Q_{ij}(\zeta) = - e\sum_{\alpha} (\underset{\sim}{q}_{\alpha(\zeta)}-\underset{\sim}{R}_{\zeta})_i(\underset{\sim}{q}_{\alpha(\zeta)}-\underset{\sim}{R}_{\zeta})_j + e\sum_{a} Z_a(\underset{\sim}{q}_{a(\zeta)}-\underset{\sim}{R}_{\zeta})_i(\underset{\sim}{q}_{a(\zeta)}-\underset{\sim}{R}_{\zeta})_j \tag{2.7.15}$$

The magnetic-dipole moment appropriate for a particular problem may be written down from (2.7.11).

One final point of interest which arises from the formulation of the multipolar Lagrangian and Hamiltonian is the new form of the equations which describe the microscopic field. The minimal-coupling and multipolar Lagrangians (2.3.6) and (2.4.20) differ by a total time derivative given by the transformation (2.4.4). Hence the equations of motion of the field are unaffected by this transformation. These equations, given by (2.2.8) and (2.2.9), are equivalent to (1.1.6) in the Coulomb gauge. However, from (2.4.20) we may derive Maxwell's equations in the form of the atomic field equations [29,34] by defining the auxiliary fields $\mathbf{d}(\mathbf{r})$ and $\mathbf{h}(\mathbf{r})$. Following (1.1.30), we define the electric displacement field as

$$\mathbf{d}(\mathbf{r}) = \varepsilon_0\mathbf{e}(\mathbf{r}) + \mathbf{p}(\mathbf{r}) \; ; \tag{2.7.16}$$

the transverse component of this field then appears in the radiation and interaction Hamiltonians. As noted in Chapter 1, $\mathbf{d}(\mathbf{r})$ is related to the field momentum $\mathbf{\Pi}(\mathbf{r})$ by the relation

$$\mathbf{\Pi}_{\text{mult}}(\mathbf{r}) = -\mathbf{d}^{\perp}(\mathbf{r}) \; . \tag{2.7.17}$$

Now if we recall the division of the charge density into its free-charge and polarization contributions such that

$$\rho(\mathbf{r}) = \rho_{\text{true}}(\mathbf{r}) - \boldsymbol{\nabla}.\mathbf{p}''(\mathbf{r}) \; , \tag{2.7.18}$$

then the first Maxwell equation of (1.1.6), namely

$$\boldsymbol{\nabla}.\mathbf{e}''(r) = \rho(\mathbf{r})/\varepsilon_0 \; , \tag{2.7.19}$$

simply becomes

$$\boldsymbol{\nabla}.\mathbf{d}''(\mathbf{r}) = \rho_{\text{true}}(\mathbf{r}) \; . \tag{2.7.20}$$

So Gauss' law now takes the above form, where the displacement field assumes the true charges as sole sources.

Now let us consider the final equation of (1.1.6), in which the transverse current acts as the source of the electric and magnetic fields ie

$$\nabla\times\mathbf{b}(\mathbf{r}) = (1/c^{2})\dot{\mathbf{e}}^{\perp}(\mathbf{r}) + (1/\varepsilon_{0}c^{2})\mathbf{j}^{\perp}(\mathbf{r}) . \tag{2.7.21}$$

If we combine the magnetization field $\mathbf{M}(\mathbf{r})$ with the magnetic polarization associated with the Röntgen current and define a new vector $\boldsymbol{\mathcal{M}}(\mathbf{r})$, with

$$\boldsymbol{\mathcal{M}}(\mathbf{r}) = \mathbf{M}(\mathbf{r}) + \sum_{\zeta}\left(\mathbf{p}(\zeta;\mathbf{r})\times\dot{\mathbf{R}}_{\zeta}\right) , \tag{2.7.22}$$

then substituting for the transverse current

$$\mathbf{j}^{\perp}(\mathbf{r}) = \mathbf{j}^{\perp}_{ionic}(\mathbf{r}) + \dot{\mathbf{p}}^{\perp}(\mathbf{r}) + \nabla\times\boldsymbol{\mathcal{M}}(\mathbf{r}) \tag{2.7.23}$$

in (2.7.21) and introducing the auxiliary field $\mathbf{h}(\mathbf{r})$, the magnetic field given by

$$\mathbf{h}(\mathbf{r}) = \varepsilon_{0}c^{2}\mathbf{b}(\mathbf{r}) - \boldsymbol{\mathcal{M}}(\mathbf{r}) , \tag{2.7.24}$$

gives

$$\nabla\times\mathbf{h}(\mathbf{r}) = \mathbf{j}^{\perp}_{ionic}(\mathbf{r}) + \dot{\mathbf{d}}^{\perp}(\mathbf{r}) ; \tag{2.7.25}$$

the magnetic field is given by the true currents.

The pair (2.7.20) and (2.7.25), together with the source free equations from (1.1.6), which are satisfied because of the choice of gauge, give a form of the Maxwell-Lorentz equations in the fields $\mathbf{d}(\mathbf{r})$ and $\mathbf{h}(\mathbf{r})$ which is of the same form as the macroscopic relations [28-30]. Thus in this form of the atomic field equations both the electric and the magnetic displacements are related to true sources. In (1.1.6) the fundamental fields $\underset{\sim}{e}(\underset{\sim}{r})$ and $\underset{\sim}{b}(\underset{\sim}{r})$ are made up of true and bound sources, as can be seen from the form of (2.7.16) and (2.7.24).

It has been shown in detail here how the multipolar Hamiltonian may be constructed from its parent Lagrangian function, itself obtained via the addition of a total time derivative to the minimal-coupling form. The alternative method of construction, namely the canonical transformation of the minimal-coupling Hamiltonian, has been discussed by various authors [35-38,21] and the relationship between the corresponding canonical variables in the two forms has been determined. Since the generating function S is a function of the particle and field coordinates, it follows that both $\underset{\sim}{q}_{\alpha}$ and $\underset{\sim}{a}(\underset{\sim}{r})$ are invariant to the transformation; only the conjugate momenta change. The precise origin of the multipolar terms and the cancellation of the minimal-coupling interactions has been described by Power and Thirunamachandran [37] by detailing the effect of the transformation upon each term of the old Hamiltonian.

In previous works the minimal-coupling Hamiltonian has been used where the system includes charged species. The Hamiltonian developed here now allows such interactions to be treated within the multipolar framework of QED and accounts for translational motion of all interacting species. The energy shift between an ion and a neutral molecule, for example, may be considered as the sum of electrostatic contributions and retarded contributions arising from conventional multipolar coupling.

In Chapter 5 the above multipolar Hamiltonian will be applied to determine the contributions to the dispersion interaction arising from ionic charge. These results will then supplement those of the neutral case, which will be determined in Chapter 4. The application of this new interaction Hamiltonian will also be compared with the minimal-coupling treatment of the same problem. In the following chapter the equivalence of the multipolar and minimal-coupling Hamiltonians in the calculation of higher-order matrix elements is demonstrated.

CHAPTER 3

MULTIPOLAR AND MINIMAL-COUPLING EQUIVALENCE: HIGHER-ORDER INTERACTIONS

3.1 Introduction

In the preceding chapters it has been shown that in non-relativistic molecular quantum electrodynamics there is a class of equivalent Hamiltonians which describe a system of radiation and atoms, molecules or ions in interaction. The origins of these Hamiltonians through the Lagrangian function have been discussed and the dynamics of the equations of motion compared. The multipolar and minimal-coupling forms of the Hamiltonian were said to be equivalent, interchangeable by a canonical transformation of the form of (1.1.43). Thus, even though the partitioning of the two Hamiltonians into their molecular, radiation and interaction parts is different, the matrix elements for optical (energy conserving) processes involving real photons must be the same. This issue has been discussed in various publications (see [19,35,20,39] and references within). However, the majority of papers on this issue are mainly confined to discussions of the validity of the transformation and the consequential equivalence of the Hamiltonians; where equivalence has been explicitly demonstrated [37,40], it has been within the electric dipole approximation. In Chapter 4 we shall consider the interaction between chiral molecules using the multipolar Hamiltonian. The equivalence of the two forms of Hamiltonian to the order required to account for such interactions has not been demonstrated explicitly and so it is useful to extend previous demonstrations by making a higher multipole approximation; electric quadrupole and magnetic dipole interactions are included, as such interactions are allowed for chiral molecules in addition to electric dipole coupling.

The two Hamiltonians are analysed here in their accounts of two optical processes; two-photon absorption and scattering. In the former we consider absorption of a photon from each of two different modes. In the calculation of the scattering cross-section the inclusion of the higher-order interaction terms leads to differential effects if the incident photon is circularly polarized [11]; in addition to the general case of differential Raman scattering the special case of differential Rayleigh scattering is also discussed briefly. The conversion of the minimal-coupling matrix elements into multipolar form is effected with the use of sum rules appropriate for each case.

The use of sum rules in the conversion of momentum (or dipole-velocity) matrix elements into the dipole length form of the multipolar formalism (usually written in terms of molecular multipole moments) was introduced by Geltman [40] and is central to such demonstrations. He also showed that in order to make such a verification for two-photon absorption it was necessary to include the term in the minimal-coupling Hamiltonian which is second-order in the vector potential. This is a general conclusion for any two-photon process even though there is no corresponding quadratic term of the same order in the multipolar form. In the present work the derivation of the multipolar result from the minimal-coupling form is extended; new sum rules are derived which facilitate the demonstrations of equivalence. It should be noted, however, that in cases where the molecules occupy intermediate states which are to be summed equivalence does not apply to the individual stages of the interaction involving virtual processes and the sum rules may not always be appropriate. The results must agree, though, where the interactions are on the energy shell.

The comparative use of the two forms of interaction will be discussed following the demonstration of their equivalence which begins with an account of two-photon absorption in section 3.3. It will be suggested that for applications of chemical interest the multipolar form is physically more suitable. We begin, however, with the derivation of a series of sum rules which aid this work and which will be useful in other problems of interest.

3.2 Sum rules for use in QED

The conversion of minimal-coupling matrix elements into their equivalent multipolar form is much simplified by the application of certain sum rules. These sum rules are similar to the Thomas-Kuhn-Reiche sum rule [41-43] used to describe the oscillator strengths of atomic or molecular transitions. The sum rules which are used in this work are derived for the specific cases in question but the results may nevertheless be applied to other processes of interest.

The first sum rule which shall be derived is given by (3.2.1).

$$\sum_r \left(E_{mr} q_i^{mr} q_j^{ro} - E_{ro} q_j^{mr} q_i^{ro} \right) = -(\hbar^2/m)\delta_{ij}\delta_{mo} . \qquad (3.2.1)$$

Let us start by considering the double commutator $[q_j,[q_i,H_{mol}]]$; inserting the commutation relations gives

$$[q_j,[q_i,H_{mol}]] = (i\hbar/m)[q_j,p_i] = -(\hbar^2/m)\delta_{ij} . \qquad (3.2.2)$$

For the molecular transition $|m\rangle \leftarrow |o\rangle$ we may therefore write

$$\langle m|[q_j,[q_i,H_{mol}]]|o\rangle = -(\hbar^2/m)\delta_{ij}\delta_{mo} \tag{3.2.3}$$

Alternatively we expand the commutator into its constituent terms,

$$[q_j,[q_i,H_{mol}] = q_jq_iH_{mol} - q_jH_{mol}q_i - q_iH_{mol}q_j + H_{mol}q_iq_j \; . \tag{3.2.4}$$

With the aid of closure we get

$$\langle m|[q_j,[q_i,H_{mol}]]|o\rangle = \sum_r \left\{E_{mr}q_i^{mr}q_j^{ro} - E_{ro}q_j^{mr}q_i^{ro}\right\}. \tag{3.2.5}$$

Sum rule (3.2.1) follows from a comparison of equations (3.2.3) and (3.2.5).

Next there are a family of identities which are useful when considering two-photon processes involving higher multipole interactions. (3.2.6), where Q is the quadrupole moment, is an example of such an identity but there are many others which may be obtained in a similar manner.

$$\sum_r \left\{\frac{E_{ro}}{E_{ro}-\hbar ck}\mu_i^{mr}Q_{jk}^{ro} - \frac{E_{mr}}{E_{mr}-\hbar ck}Q_{jk}^{mr}\mu_i^{ro}\right\}$$
$$= \sum_r \left\{\frac{\hbar ck}{E_{ro}-\hbar ck}\mu_i^{mr}Q_{jk}^{ro} - \frac{\hbar ck}{E_{mr}-\hbar ck}Q_{jk}^{mr}\mu_i^{ro}\right\} \tag{3.2.6}$$

This particular form is encountered in scattering problems. In Raman scattering, for example, we may write the conservation identity

$$E_{mr}+E_{ro} = \hbar ck - \hbar ck' \; . \tag{3.2.7}$$

Thus

$$(E_{ro} + hck') = -(E_{mr} - \hbar ck) \ . \tag{3.2.8}$$

Now since $[\mu_i, Q_{jk}] = 0$, we may write

$$0 = \sum_r \left\{ \mu_i^{mr} Q_{jk}^{ro} - Q_{jk}^{mr} \, \mu_i^{ro} \right\} \tag{3.2.9}$$

from which

$$0 = \sum_r \left\{ (E_{ro} - hck) \frac{\mu_i^{mr} Q_{jk}^{ro}}{E_{ro} - hck} - (E_{mr} - hck) \frac{Q_{jk}^{mr} \, \mu_i^{ro}}{E_{mr} - hck} \right\} . \tag{3.2.10}$$

The result (3.2.6) follows using (3.2.8).

Another result is useful, where higher order multipoles have been used, in the conversion of minimal-coupling matrix elements into their multipolar equivalent form. In this case the vector potential is allowed to vary over the extent of the molecule; the factor $\exp[i\underset{\sim}{k}.\underset{\sim}{q}]$ of the mode expansion for $\underset{\sim}{a}(\underset{\sim}{r})$ then remains a function of the particle coordinate. A series expansion of this factor gives terms which include matrix elements such as $(e/m)\langle r|p_i q_j|s\rangle$, which are clearly of the same order as a magnetic dipole or electric quadrupole interaction. Thus it will be shown that

$$-(e/m) e_i \hat{k}_j \langle r|p_i q_j|s\rangle \; = \; (\underset{\sim}{\hat{k}} \times \underset{\sim}{e})_k \langle r|m_k|s\rangle + i(e_i \hat{k}_j/\hbar) E_{rs} Q_{ij}^{rs} \ . \tag{3.2.11}$$

Denoting the left hand side of the above expression by I we write

$$I \; = \; -(e/2m) e_i \hat{k}_j \langle r|p_i q_j - p_j q_i|s\rangle \; -(e/2m) e_i \hat{k}_j \langle r|p_i q_j + p_j q_i|s\rangle \ . \tag{3.2.12}$$

The first term of (3.2.12) is clearly the same as the first term of

(3.2.11). Using closure in the second term of (3.2.12) and converting $p_i^{rt} \rightarrow q_i^{rt}$ with

$$-(i\hbar/m)\underset{\sim}{p} = [H_{mol},\underset{\sim}{q}] \tag{3.2.13}$$

gives, since $E_{rt} + E_{ts} = E_{rs}$, the terms

$$I = -e_i\hat{k}_j\varepsilon_{ijk}\langle r|m_k|s\rangle -(ie/2\hbar)e_i\hat{k}_jE_{rs}\langle r|q_iq_j|s\rangle \ , \tag{3.2.14}$$

from which we obtain

$$I = (\hat{\underset{\sim}{k}}\times\underset{\sim}{e})_k m_k^{rs} +i(e_i\hat{k}_j/\hbar)E_{rs}\langle r|Q_{ij}|s\rangle \tag{3.2.15}$$

Hence the result (3.2.11).

One final identity is left to be discussed. The minimal-coupling interaction term $(e^2/m)\underset{\sim}{a}^2(\underset{\sim}{q})$, leads to matrix elements of the form $e_i\hat{k}_k\langle m|(\underset{\sim}{q}-\underset{\sim}{R})_k|o\rangle$. Such terms are used in the demonstration of the equivalence of matrix elements using the two Hamiltonians and it would be of some use to be able to write them directly in their multipolar form. An identity similar to (3.2.5) is

$$\langle m|[Q_{i\ell},[\mu_j,H]]|o\rangle = \sum_r \left(E_{mr}\mu_j^{mr}Q_{i\ell}^{ro} - E_{ro}Q_{i\ell}^{mr}\mu_j^{ro}\right) \tag{3.2.16}$$

The left hand side of this identity may be written as

$$[Q_{i\ell},[\mu_j,H]] = \sum_\alpha\sum_\beta (e_\alpha e_\beta/2)[q_{i(\alpha)}q_{\ell(\alpha)},[q_{j(\beta)},H]] = II \ . \tag{3.2.17}$$

Evaluating the inner commutator gives

$$II = i\hbar \sum_{\alpha} \sum_{\beta} (e_{\alpha} e_{\beta}/2m_{\beta})[q_{i(\alpha)} q_{\ell(\alpha)}, p_{j(\beta)}] \tag{3.2.18}$$

which becomes

$$II = (i\hbar)^2 \sum_{\alpha} (e_{\alpha}^2/2m_{\alpha}) \left(q_{i(\alpha)} \delta_{\ell j} + q_{\ell(\alpha)} \delta_{ij} \right) \tag{3.2.19}$$

Thus, combining this result with (3.2.16) we find that

$$\sum_{r} \left(E_{mr} \mu_j^{mr} Q_{i\ell}^{ro} - E_{ro} Q_{i\ell}^{mr} \mu_j^{ro} \right) = - \sum_{\alpha} (e_{\alpha}^2 \hbar^2/2m_{\alpha}) \left(q_{i(\alpha)}^{mo} \delta_{j\ell} + q_{\ell(\alpha)}^{mo} \delta_{ij} \right) \tag{3.2.20}$$

Similarly we may determine

$$\sum_{r} \left(E_{mr} Q_{i\ell}^{mr} \mu_j^{ro} - E_{ro} \mu_j^{mr} Q_{i\ell}^{ro} \right) = - \sum_{\alpha} (e_{\alpha}^2 \hbar^2/2m_{\alpha}) \left(q_{i(\alpha)}^{mo} \delta_{j\ell} + q_{\ell(\alpha)}^{mo} \delta_{ij} \right) \tag{3.2.21}$$

$$\sum_{r} \left(E_{mr} \mu_j^{mr} m_m^{ro} - E_{ro} m_m^{mr} \mu_j^{ro} \right) = - \sum_{\alpha} (e_{\alpha}^2 \hbar^2/2m_{\alpha}^2) \varepsilon_{mjt} p_{t(\alpha)}^{mo} \tag{3.2.22}$$

and

$$\sum_{r} \left(E_{mr} m_m^{mr} \mu_j^{ro} - E_{ro} \mu_j^{mr} m_m^{ro} \right) = 0 \tag{3.2.23}$$

A suitable combination of the last two expressions allows the energy factors to be eliminated from the sum so that

$$\hbar \sum_{r} \left(\mu_i^{mr} m_j^{ro} - m_j^{mr} \mu_i^{ro} \right) = \sum_{\alpha} \left(e_{\alpha}^2 \hbar^3 \big/ 2E_{mo} m_{\alpha}^2 \right) \varepsilon_{ijn} p_{n(\alpha)}^{mo} \ . \tag{3.2.24}$$

The equations (3.2.20/21) and (3.2.24) may now be added. First consider the quantity [k′(α−iδ) + k(β−iγ)], where we define the Greek quantities by

$$\bar{e}'_i e_j \hat{k}'_k \sum_r \left(E_{mr} Q^{mr}_{ik} \mu^{ro}_j - E_{ro} \mu^{mr}_j Q^{ro}_{ik}\right) = \alpha \tag{3.2.25}$$

$$\bar{e}'_i e_j \hat{k}_k \sum_r \left(E_{mr} \mu^{mr}_i Q^{ro}_{jk} - E_{ro} Q^{mr}_{jk} \mu^{ro}_i\right) = \beta \tag{3.2.26}$$

$$\hbar \bar{e}'_i b_j \sum_r \left(\mu^{mr}_i m^{ro}_j - m^{mr}_j \mu^{ro}_i\right) = \gamma \tag{3.2.27}$$

and

$$\hbar \bar{b}'_i e_j \sum_r \left(m^{mr}_i \mu^{ro}_j - \mu^{mr}_j m^{ro}_i\right) = \delta \tag{3.2.28}$$

With the use of the results (3.2.20/21) and (3.2.24) (and a similar expression for δ) we find

$$[k'(\alpha - i\delta) + k(\beta - i\gamma)] = \sum_\alpha (e^2_\alpha \hbar^2/m_\alpha)\left\{k\bar{e}'_i e_i \hat{k}_j q^{mo}_{j(\alpha)} - k'\bar{e}'_i e_i \hat{k}'_j q^{mo}_{j(\alpha)}\right\}. \tag{3.2.29}$$

This is the required result, since the terms on the right hand side have the form of the matrix elements discussed for the $\underset{\sim}{a}^2(\underset{\sim}{q})$ interaction.

The two sum rules which together compose the above expression are given below. We have

$$\sum_\alpha (ie^2_\alpha/m_\alpha) e_i \hat{k}_k \langle m|(\underset{\sim}{q}_\alpha - \underset{\sim}{R})_k|o\rangle$$

$$= (i/\hbar^2)\hat{k}_k e_j \sum_r \left(E_{ro} \mu^{mr}_i Q^{ro}_{jk} - E_{mr} Q^{mr}_{jk} \mu^{ro}_i\right) + (1/\hbar) b_j \sum_r \left(\mu^{mr}_i m^{ro}_j - m^{mr}_j \mu^{ro}_i\right) \tag{3.2.30}$$

and

$$\sum_{\alpha} (ie_{\alpha}^{2}/m_{\alpha})\bar{e}'_{j}\hat{k}'_{k}\langle m|(\underset{\sim}{q}_{\alpha}-\underset{\sim}{R})_{k}|o\rangle$$

$$= (i/\hbar^{2})\hat{k}'_{k}\bar{e}'_{i} \sum_{r} \left(E_{ro}\mu_{j}^{mr}Q_{ik}^{ro} - E_{mr}Q_{ik}^{mr}\mu_{j}^{ro}\right) + (1/\hbar)\bar{b}'_{i} \sum_{r} \left(\mu_{j}^{mr}m_{i}^{ro} - m_{i}^{mr}\mu_{j}^{ro}\right) \tag{3.2.31}$$

In the following sections the above results, together with (3.2.1), (3.2.6) and (3.2.11) will be applied in the demonstration of the equivalence of the multipolar and minimal-coupling matrix elements for the two-photon processes of absorption, Raman and Rayleigh scattering.

3.3 Two-photon absorption

In this section the multipolar and minimal-coupling Hamiltonians are used to calculate the matrix element for two-photon absorption by a chiral molecule. This requires the electric quadrupole and magnetic dipole interactions to be included in the calculation. The two interaction Hamiltonians are given below and the calculations are aided with the use of time-ordered diagrams. The two results are shown to be identical with the use of sum rules.

The multipolar and minimal-coupling interaction Hamiltonians are

$$H_{int}(\mathrm{mult}) = -\varepsilon_{0}^{-1}\underset{\sim}{\mu}.\underset{\sim}{d}^{\perp}(\underset{\sim}{R}) - \underset{\sim}{m}.\underset{\sim}{b}(\underset{\sim}{R}) - \varepsilon_{0}^{-1}Q_{ij}\nabla_{j}d_{i}^{\perp}(\underset{\sim}{R}) \tag{3.3.1}$$

$$H_{int}(\mathrm{min}) = -\sum_{\alpha} (e_{\alpha}/m_{\alpha})p_{i(\alpha)}a_{i}(\underset{\sim}{q}_{\alpha}) + \sum_{\alpha} (e_{\alpha}^{2}/2m_{\alpha})a_{i}(\underset{\sim}{q}_{\alpha})a_{i}(\underset{\sim}{q}_{\alpha}) \tag{3.3.2}$$

where Q_{ij} is the component of the electric quadrupole tensor and $\underset{\sim}{m}$ is the magnetic dipole moment operator.

Consider the case of absorption by a molecule of one photon from each of two monochromatic beams with modes $(\underset{\sim}{k},\lambda)$ and $(\underset{\sim}{k}',\lambda')$ (the case of absorption of two photons from the same mode has been considered in other works [40,44,37]). This may be represented by the time-ordered graphs [45-11] shown in Fig 3.1. In the initial state the molecule is assumed to be in state $|o\rangle$ with energy E_o and the modes $(\underset{\sim}{k},\lambda)$ and $(\underset{\sim}{k}',\lambda')$ occupy the number states $|n\rangle$ and $|n'\rangle$ respectively with energies $n\hbar ck$ and $n'\hbar ck'$. The final state has one less photon in each mode, with the molecule excited to state $|m\rangle$ with energy E_m. The intermediate state contains the molecule in a typical state $|r\rangle$ and a photon has been annihilated from one of the modes.

Fig 3.1 shows the pure electric dipole contribution to two-photon absorption, the interactions at the vertices given by the first term of (3.3.1). Since each of the interactions is linear in the field the matrix element M_{fi} for this process is given by the second-order perturbation result

$$M_{fi} \quad = \quad -\sum_{I} \frac{\langle f|H_{int}|I\rangle\langle I|H_{int}|i\rangle}{(E_I-E_i)} , \tag{3.3.3}$$

where the initial, intermediate and final states are given by

$$|i\rangle \quad = \quad |n(\underset{\sim}{k},\lambda),n'(\underset{\sim}{k}',\lambda');o\rangle \tag{3.3.4}$$

$$|f\rangle \quad = \quad |(n-1)(\underset{\sim}{k},\lambda),(n'-1)(\underset{\sim}{k}',\lambda');m\rangle \tag{3.3.5}$$

$$|I\rangle \quad = \quad \left.\begin{array}{l} |(n-1)(\underset{\sim}{k},\lambda),n'(\underset{\sim}{k}',\lambda');r\rangle \\ |n(\underset{\sim}{k},\lambda),(n'-1)(\underset{\sim}{k}',\lambda');r\rangle \end{array}\right\} . \tag{3.3.6}$$

Using the mode expansion (1.1.40) for $\underset{\sim}{d}^{\perp}(\underset{\sim}{R})$, from (3.3.3) we directly obtain the result

$$M_{fi}^{(1)} = \left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left(\frac{n'\hbar ck'}{2\varepsilon_0 V}\right)^{1/2} e'_i e_j \sum_r \left\{\frac{\mu_i^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} + \frac{\mu_j^{mr}\mu_i^{ro}}{E_{ro}-\hbar ck'}\right\} e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}} \tag{3.3.7}$$

in which the $(\underset{\sim}{k},\lambda)$ and $(\underset{\sim}{k}',\lambda')$ dependences are assumed in e_j and e'_i respectively, and μ_i^{mr}, μ_j^{ro} etc are dipole transition moments.

Let us consider contributions from the remaining terms of (3.3.1). Graphs of the form of Fig 3.1 may be drawn, as in Figs 3.2/3.3 on the following pages, with interactions via magnetic dipole and electric quadrupole coupling; the study is confined to cases where one of the interactions remains via electric dipole coupling. In this way we are considering terms up to an order where the diamagnetic coupling is neglected.

From Fig 3.2 we obtain the magnetic-dipole contribution

$$\begin{aligned} M_{fi}^{(2)} = {} & \left(\frac{\hbar}{2\varepsilon_0 V}\right)(nn'kk')^{1/2} b'_i e_j \sum_r \left\{\frac{m_i^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} + \frac{\mu_j^{mr} m_i^{ro}}{E_{ro}-\hbar ck'}\right\} e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}} \\ & + \left(\frac{\hbar}{2\varepsilon_0 V}\right)(nn'kk')^{1/2} e'_i b_j \sum_r \left\{\frac{\mu_i^{mr} m_j^{ro}}{E_{ro}-\hbar ck} + \frac{m_j^{mr}\mu_i^{ro}}{E_{ro}-\hbar ck'}\right\} e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}} \end{aligned} \tag{3.3.8}$$

Similarly from Fig 3.3 we obtain the electric quadrupole result as

$$\begin{aligned} M_{fi}^{(3)} = {} & i\left(\frac{\hbar c}{2\varepsilon_0 V}\right)(nn'kk')^{1/2} k_\ell e'_i e_j \sum_r \left\{\frac{Q_{i\ell}^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} + \frac{\mu_j^{mr} Q_{i\ell}^{ro}}{E_{ro}-\hbar ck'}\right\} e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}} \\ & + i\left(\frac{\hbar c}{2\varepsilon_0 V}\right)(nn'kk')^{1/2} k_\ell e'_i e_j \sum_r \left\{\frac{\mu_i^{mr} Q_{j\ell}^{ro}}{E_{ro}-\hbar ck} + \frac{Q_{j\ell}^{mr}\mu_i^{ro}}{E_{ro}-\hbar ck'}\right\} e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}. \end{aligned} \tag{3.3.9}$$

The total matrix element is the sum of the terms (3.3.7-9) and is

FIG 3.1 : TIME-ORDERED GRAPHS FOR TWO-PHOTON ABSORPTION:
PURE ELECTRIC DIPOLE CONTRIBUTION

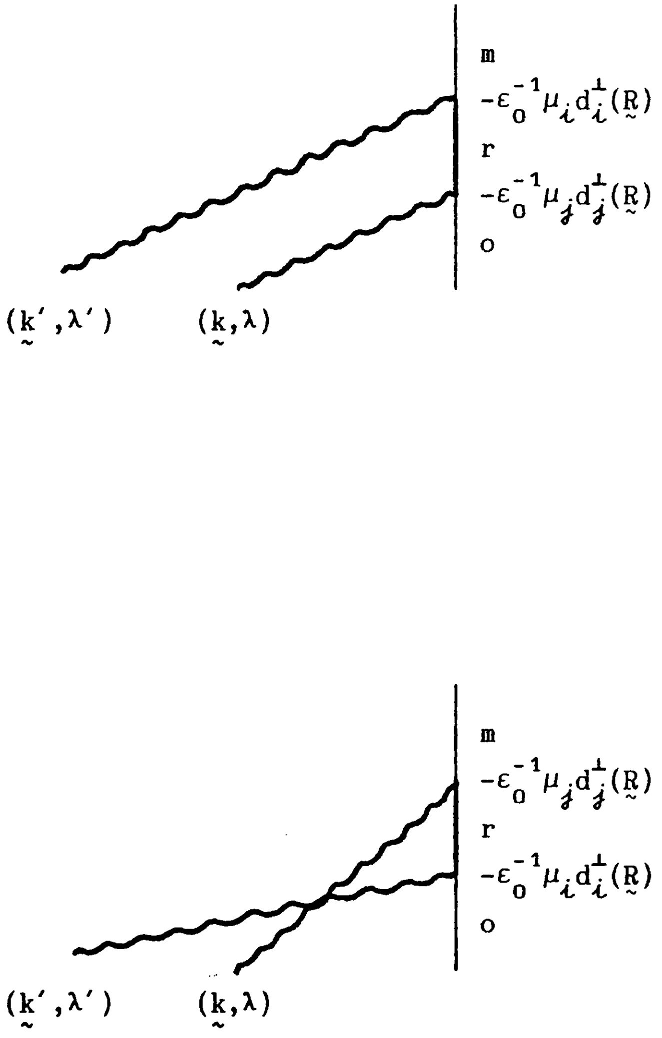


FIG 3.2 : TIME-ORDERED GRAPHS FOR TWO-PHOTON ABSORPTION: INCLUSION OF MAGNETIC DIPOLE INTERACTIONS

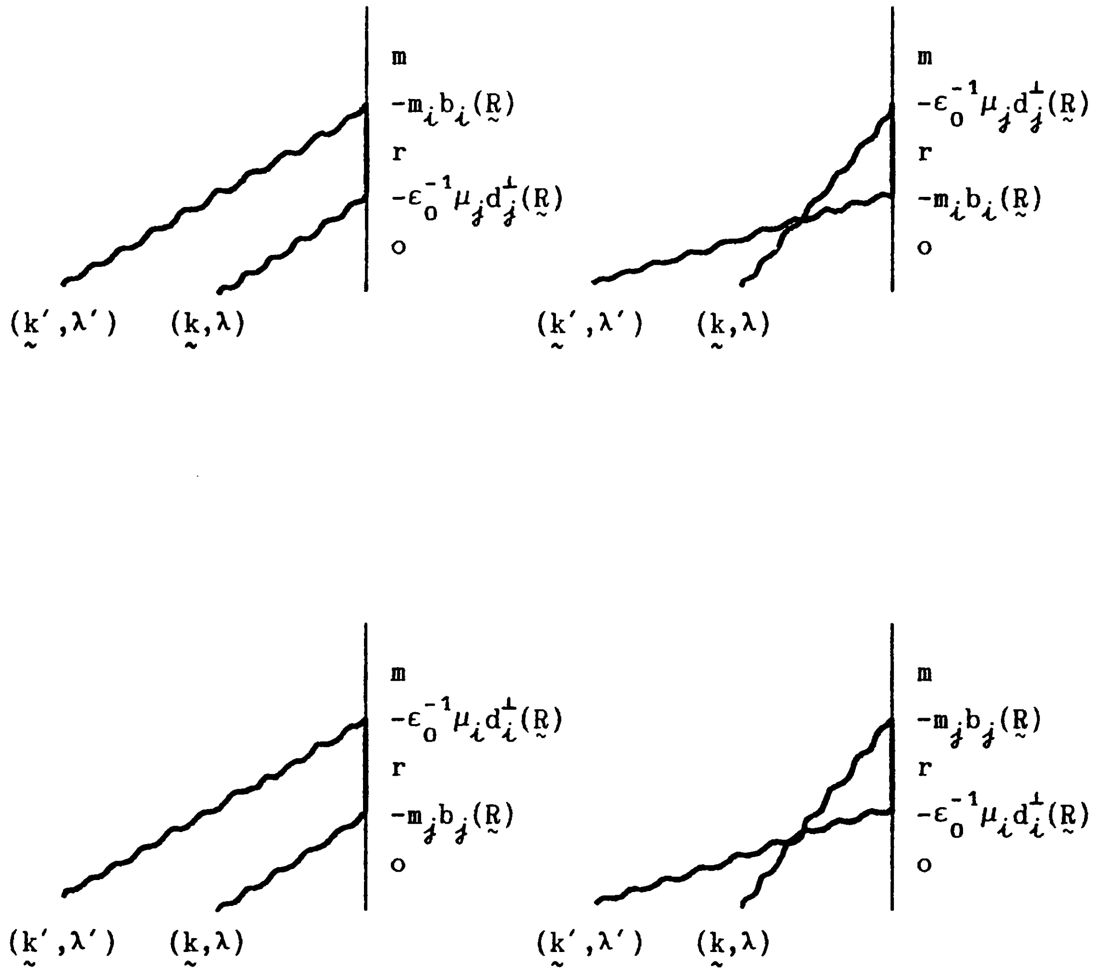
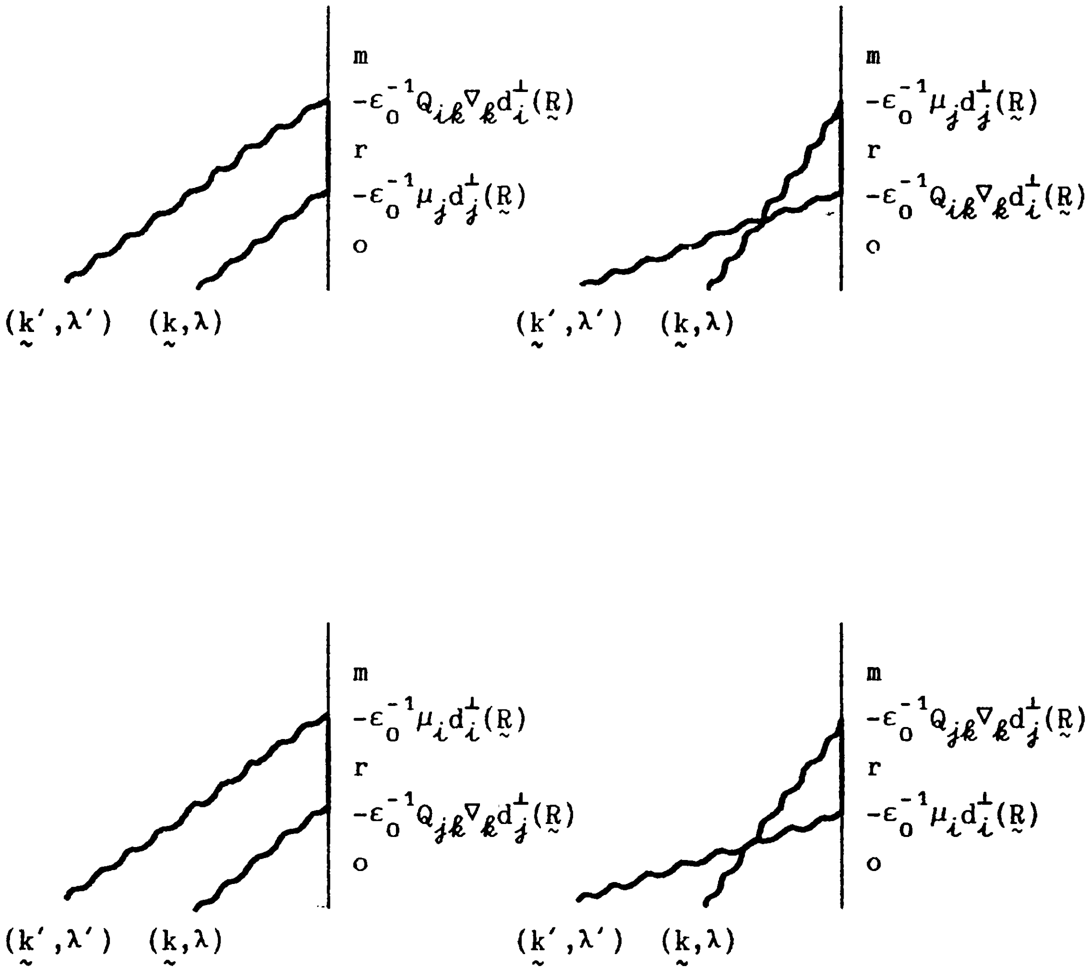


FIG 3.3 : TIME-ORDERED GRAPHS FOR TWO-PHOTON ABSORPTION:
INCLUSION OF ELECTRIC QUADRUPOLE INTERACTIONS



given by (3.3.10). The result is written in terms of the molecular polarizabilities which are defined in Table 3.3.1. $\alpha_{ij}^{mo}(\omega,\omega')$ is the frequency-dependent transition dipole polarizability and $G_{ij}^{mo}(\omega,\omega')$ and $A_{ijk}^{mo}(\omega,\omega')$ are the mixed analogues involving magnetic dipole and electric quadrupole moments.

Thus the matrix element for two-photon absorption in the multipolar framework is given by

$$
\begin{aligned}
M_{fi}(\mathrm{Total}) = \left(\frac{\hbar}{2\varepsilon_0 V}\right)(nn'kk')^{1/2} e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}} \Big\{ & c e_i^{(\lambda')}(\underset{\sim}{k}') e_j^{(\lambda)}(\underset{\sim}{k}) \alpha_{ij}^{mo}(\omega,\omega') \\
& + e_i^{(\lambda')}(\underset{\sim}{k}') b_j^{(\lambda)}(\underset{\sim}{k}) G_{ij}^{mo}(\omega,\omega') + b_i^{(\lambda')}(\underset{\sim}{k}') e_j^{(\lambda)}(\underset{\sim}{k}) G_{ji}^{mo}(\omega',\omega) \\
& + ick_k e_i^{(\lambda')}(\underset{\sim}{k}') e_j^{(\lambda)}(\underset{\sim}{k}) A_{ijk}^{mo}(\omega,\omega') + ick'_k e_i^{(\lambda')}(\underset{\sim}{k}') e_j^{(\lambda)}(\underset{\sim}{k}) A_{jik}^{mo}(\omega',\omega) \Big\}.
\end{aligned}
\tag{3.3.10}
$$

The corresponding rate for this process is obtained directly using the Fermi Rule.

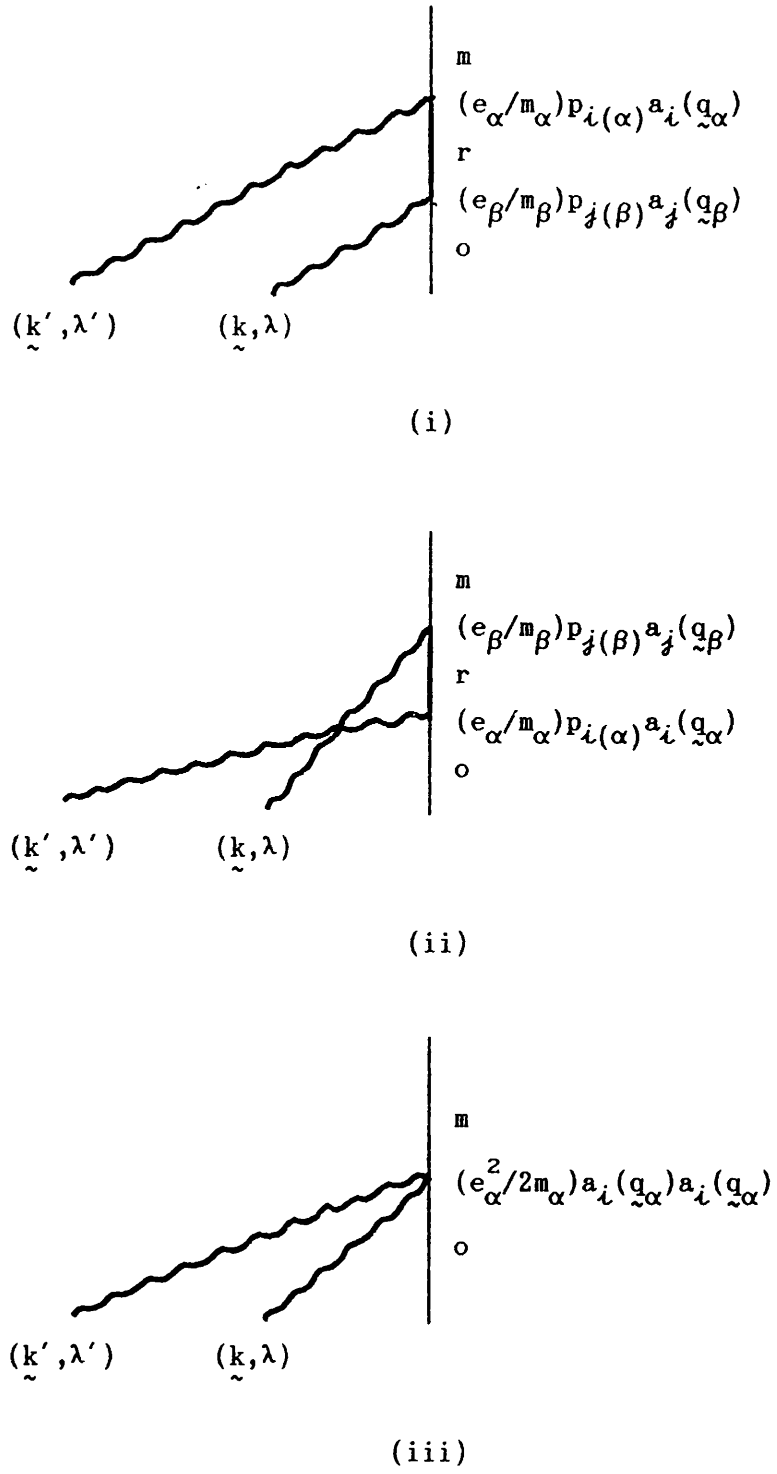
If we choose the minimal-coupling Hamiltonian (3.3.2), on the other hand, then we need to consider the interactions represented by the graphs shown in Fig 3.4, where the sums are assumed. The major difference between this and the multipolar form is apparent; Fig 3.4 contains terms of all orders, since the mode expansion for the vector potential, (1.1.39), contains the factor $\exp[i\underset{\sim}{k}.\underset{\sim}{q}]$. Truncation of the terms generated, at an appropriate point, will therefore be necessary in order to compare the result with (3.3.10).

In previous studies where the electric dipole approximation has been invoked the contribution from Fig 3.4 (iii) is identically zero since the initial and final molecular states are different and the interaction is then simply a field term. Despite this fact it was helpful to the working to retain this term as an artefact. Here this

TABLE 3.3.1 DYNAMIC MOLECULAR POLARIZABILITY TENSORS: ELECTRIC DIPOLE-DIPOLE, DIPOLE-QUADRUPOLE AND ELECTRIC DIPOLE - MAGNETIC DIPOLE FORMS.

$\alpha_{ij}^{mo}(\omega,-\omega')$	$=$	$\sum_r \left\{ \frac{\mu_i^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} + \frac{\mu_j^{mr}\mu_i^{ro}}{E_{ro}+\hbar ck'} \right\}$
$G_{ij}^{mo}(\omega,-\omega')$	$=$	$\sum_r \left\{ \frac{\mu_i^{mr}m_j^{ro}}{E_{ro}-\hbar ck} + \frac{m_j^{mr}\mu_i^{ro}}{E_{ro}+\hbar ck'} \right\}$
$G_{ji}^{mo}(-\omega',\omega)$	$=$	$\sum_r \left\{ \frac{\mu_j^{mr}m_i^{ro}}{E_{ro}+\hbar ck'} + \frac{m_i^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} \right\}$
$A_{ijk}^{mo}(\omega,-\omega')$	$=$	$\sum_r \left\{ \frac{\mu_i^{mr}Q_{jk}^{ro}}{E_{ro}-\hbar ck} + \frac{Q_{jk}^{mr}\mu_i^{ro}}{E_{ro}+\hbar ck'} \right\}$
$A_{jik}^{mo}(-\omega',\omega)$	$=$	$\sum_r \left\{ \frac{\mu_j^{mr}Q_{ik}^{ro}}{E_{ro}+\hbar ck'} + \frac{Q_{ik}^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} \right\}$

FIG 3.4 : TIME-ORDERED GRAPHS FOR TWO-PHOTON ABSORPTION IN THE MINIMAL-COUPLING FORMALISM



term is non-zero and may be written, with the use of the new sum rules, in a useful form for combination with those terms which arise from the other two graphs.

Considering graphs (i) and (ii) firstly, the matrix element may be written down to the correct order by keeping only the first two terms of the expansion of $\exp[i\underset{\sim}{k}.\underset{\sim}{q}]$. Assuming as implicit the particle labels α for p_i and β for p_j we then obtain

$$M_{fi}(i+ii) = -\sum_{\alpha}\sum_{\beta}\left(e_{\alpha}e_{\beta}/m_{\alpha}m_{\beta}\right)\left(\frac{nn'}{kk'}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 cV}\right)e'_i e_j e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}$$

$$\times\left\{\sum_r \langle m|p_i(1+i\underset{\sim}{k}'.(\underset{\sim}{q}_{\alpha}-\underset{\sim}{R})+..)|r\rangle\langle r|p_j(1+i\underset{\sim}{k}.(\underset{\sim}{q}_{\beta}-\underset{\sim}{R})+..)|o\rangle/(E_{ro}-\hbar ck)\right.$$

$$\left.+\sum_r \langle m|p_j(1+i\underset{\sim}{k}.(\underset{\sim}{q}_{\beta}-\underset{\sim}{R})+..)|r\rangle\langle r|p_i(1+i\underset{\sim}{k}'.(\underset{\sim}{q}_{\alpha}-\underset{\sim}{R})+..)|o\rangle/(E_{ro}-\hbar ck')\right\}.$$

(3.3.11)

This expression may be broken down into parts which are easier to consider separately. The pure dipole part is simply given by the first term of each expansion (ie which corresponds to $\exp[i\underset{\sim}{k}.(\underset{\sim}{q}-\underset{\sim}{R})] \simeq 1$ in the electric dipole approximation) so that

$$M^{(dip)}_{fi} = -\sum_{\alpha}\sum_{\beta}\left(\frac{e}{m}\right)^2\left(\frac{nn'}{kk'}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 cV}\right)e'_i e_j \sum_r\left\{\frac{p_i^{mr}p_j^{ro}}{E_{ro}-\hbar ck}+\frac{p_j^{mr}p_i^{ro}}{E_{ro}-\hbar ck'}\right\}e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}$$

(3.3.12)

Now we may convert the momentum matrix elements of (3.3.12) into dipole transition moments using

$$p_i^{st} = (im/\hbar)E_{st}q_i^{st}, \qquad (3.3.13)$$

noting that (3.3.13) is not applicable to diagonal terms. This does not present a problem, though, since an inspection of the appropriate terms of (3.3.12), following the use of (3.3.13), shows that they are zero in any case and the resulting term may be written with the sum over all r. This is a common feature of such demonstrations. The sums over α and β are incorporated into the definitions of the molecular transition dipole moments to simplify the matrix element, which may be written as

$$M_{fi}^{(dip)} = \left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left(\frac{n'\hbar ck'}{2\varepsilon_0 V}\right)^{1/2} e'_i e_j$$
$$\times\left\{\alpha_{ij}^{mo}(\omega,\omega') + \sum_r \left\{-1 + \frac{E_{mr}E_{ro}}{\hbar ck\hbar ck'}\right\}\left\{\frac{\mu_i^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} + \frac{\mu_j^{mr}\mu_i^{ro}}{E_{ro}-\hbar ck'}\right\}\right\}e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}. \tag{3.3.14}$$

Note that overall energy conservation, namely

$$E_{mr} + E_{ro} = \hbar ck + \hbar ck' \tag{3.3.15}$$

in this case, does not influence the energies of the virtual states and we cannot cancel the energy parts of (3.3.14).

The conservation law (3.3.15) may be used to show that the second term of this expression vanishes. Following the addition of the terms in each set of curly brackets a subsequent simplification gives

$$M_{fi}^{(dip)} = \left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left(\frac{n'\hbar ck'}{2\varepsilon_0 V}\right)^{1/2} e'_i e_j$$
$$\times\left\{\alpha_{ij}^{mo}(\omega,\omega') + \sum_r \frac{E_{mr}\mu_i^{mr}\mu_j^{ro} - E_{ro}\mu_j^{mr}\mu_i^{ro}}{\hbar ck\hbar ck'}\right\}e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}, \tag{3.3.16}$$

the second term of which vanishes with the use of the sum rule (3.2.1) giving the multipolar result (3.3.7) up to electric dipole.

This equivalence to electric dipole merely agrees with those previous studies cited. However, such studies are extended here by examining the terms of the next order, that is by including electric quadrupole and magnetic dipole coupling. These terms are easily treated by applying the sum rules derived in section 3.2. Returning to (3.3.11), we pick up the remaining terms. Converting one of the moments gives, suppressing the α label from p_i and p_j,

$$M'_{fi}(i+ii) = \sum_{\alpha} \left(e_\alpha/m_\alpha\right)\left(\frac{nn'}{kk'}\right)^{1/2}\left(\frac{1}{2\varepsilon_0 cV}\right)e'_i e_j e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}$$

$$\times\left\{ k_k \sum_r \left(\frac{E_{mr}}{E_{ro}-\hbar ck}\right)\mu_i^{mr}\langle r|p_j(\underset{\sim}{q}_\alpha-\underset{\sim}{R})_k|o\rangle + \left(\frac{E_{ro}}{E_{ro}-\hbar ck'}\right)\langle m|p_j(\underset{\sim}{q}_\alpha-\underset{\sim}{R})_k|r\rangle\mu_i^{ro}\right.$$

$$\left. + k'_k \sum_r \left(\frac{E_{ro}}{E_{ro}-\hbar ck}\right)\langle m|p_i(\underset{\sim}{q}_\alpha-\underset{\sim}{R})_k|r\rangle\mu_j^{ro} + \left(\frac{E_{mr}}{E_{ro}-\hbar ck'}\right)\mu_j^{mr}\langle r|p_i(\underset{\sim}{q}_\alpha-\underset{\sim}{R})_k|o\rangle\right\} . \tag{3.3.17}$$

Using the sum rule (3.2.11) we obtain

$$M'_{fi}(i+ii) = \left(\frac{nn'}{kk'}\right)^{1/2}\left(\frac{1}{2\varepsilon_0 cV}\right)e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}$$

$$\times\left\{(i/\hbar)k_k e'_i e_j \sum_r \left\{\left(\frac{E_{mr}E_{ro}}{E_{ro}-\hbar ck}\right)\mu_i^{mr}Q_{jk}^{ro} + \left(\frac{E_{mr}E_{ro}}{E_{ro}-\hbar ck'}\right)Q_{jk}^{mr}\mu_i^{ro}\right\}\right.$$

$$+(i/\hbar)k'_k e'_i e_j \sum_r \left\{\left(\frac{E_{mr}E_{ro}}{E_{ro}-\hbar ck}\right)Q_{ik}^{mr}\mu_j^{ro} + \left(\frac{E_{mr}E_{ro}}{E_{ro}-\hbar ck'}\right)\mu_j^{mr}Q_{ik}^{ro}\right\}$$

$$+ke'_i b_j \sum_r \left\{\left(\frac{E_{mr}}{E_{ro}-\hbar ck}\right)\mu_i^{mr}m_j^{ro} + \left(\frac{E_{ro}}{E_{ro}-\hbar ck'}\right)m_j^{mr}\mu_i^{ro}\right\}$$

$$\left.+k' b'_i e_j \sum_r \left\{\left(\frac{E_{ro}}{E_{ro}-\hbar ck}\right)m_i^{mr}\mu_j^{ro} + \left(\frac{E_{mr}}{E_{ro}-\hbar ck'}\right)\mu_j^{mr}m_i^{ro}\right\}\right\} \tag{3.3.18}$$

Finally we have the matrix element corresponding to Fig 3.4(iii). Having expanded the exponential part of the mode expansion for $\underset{\sim}{a}(\underset{\sim}{r})$ the first non-zero term is given[1] by

$$M_{fi}(iii) = 2i\sum_{\alpha}(e_{\alpha}^{2}/2m_{\alpha})\left(\frac{n\hbar}{2\varepsilon_{0}ckV}\right)^{1/2}\left(\frac{n'\hbar}{2\varepsilon_{0}ck'V}\right)^{1/2}$$

$$\times e_{i}'e_{i}\langle m|(\underset{\sim}{k}+\underset{\sim}{k}').(\underset{\sim}{q}_{\alpha}-\underset{\sim}{R})|o\rangle e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}. \tag{3.3.19}$$

It is sufficient to take only this term from the expansion, as the next term is of too high an order. The products $e_{i}'e_{i}k_{j}q_{j}^{mo}$ and $e_{i}'e_{i}k_{j}'q_{j}^{mo}$ in this expression can be expanded into summations of the form of the terms in (3.3.18), using the sum rules (3.2.30) and (3.2.31). This leads to

$$M_{fi}(iii) = \left(\frac{nn'}{kk'}\right)^{1/2}\left(\frac{1}{2\varepsilon_{0}cV}\right)e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}}$$

$$\times\left\{(i/\hbar)k_{k}e_{i}'e_{j}\sum_{r}\left(E_{ro}\mu_{i}^{mr}Q_{jk}^{ro}-E_{mr}Q_{jk}^{mr}\mu_{i}^{ro}\right)+ke_{i}'b_{j}\sum_{r}\left(\mu_{i}^{mr}m_{j}^{ro}-m_{j}^{mr}\mu_{i}^{ro}\right)\right.$$

$$\left.+(i/\hbar)k_{k}'e_{i}'e_{j}\sum_{r}\left(E_{ro}\mu_{j}^{mr}Q_{ik}^{ro}-E_{mr}Q_{ik}^{mr}\mu_{j}^{ro}\right)+k'b_{i}'e_{j}\sum_{r}\left(\mu_{j}^{mr}m_{i}^{ro}-m_{i}^{mr}\mu_{j}^{ro}\right)\right\}. \tag{3.3.20}$$

Adding (3.3.18) to (3.3.20) gives (3.3.21).

---

[1] The expression contains a numerical factor of two since the interaction is quadratic in the field.

$$
\begin{aligned}
M'_{fi}(\text{i-iii}) = {} & \left(\frac{nn'}{kk'}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 V}\right)e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{R}} \\
& \times\Bigg\{(i/\hbar)k'k_k e'_i e_j \sum_r \left\{\left(\frac{E_{ro}}{E_{ro}-\hbar ck}\right)\mu_i^{mr}Q_{jk}^{ro} + \left(\frac{E_{mr}}{E_{ro}-\hbar ck'}\right)Q_{jk}^{mr}\mu_i^{ro}\right\} \\
& +(i/\hbar)kk'_k e'_i e_j \sum_r \left\{\left(\frac{E_{mr}}{E_{ro}-\hbar ck}\right)Q_{ik}^{mr}\mu_j^{ro} + \left(\frac{E_{ro}}{E_{ro}-\hbar ck'}\right)\mu_j^{mr}Q_{ik}^{ro}\right\} \\
& +kk'e'_i b_j \sum_r \left\{\frac{\mu_i^{mr}m_j^{ro}}{E_{ro}-\hbar ck} + \frac{m_j^{mr}\mu_i^{ro}}{E_{ro}-\hbar ck'}\right\} +kk'b'_i e_j \sum_r \left\{\frac{m_i^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} + \frac{\mu_j^{mr}m_i^{ro}}{E_{ro}-\hbar ck'}\right\}\Bigg\}
\end{aligned}
\tag{3.3.21}
$$

The magnetic dipole terms are in their final form but the quadrupole terms still contain unwanted energy factors. These terms may be easily rewritten using an identity, similar to (3.2.6) but derived for absorption cases, to give the final expression. So, after recovering the dipole polarizabilty term, the final matrix element is identical to the multipolar result (3.3.10).

It has been shown that the equivalent interaction Hamiltonians which occur in the multipolar and minimal-coupling formalisms predict identical rates for two-photon absorption. The predictions go further than a discussion in the electric dipole approximation and the sum rules used will be useful for comparative studies of other energy-conserving phenomena to such orders. From a chemical point of view, however, it is preferable to write the interactions in terms of the electromagnetic fields rather than the potentials and the matrix elements in terms of molecular properties such as polarizabilities. Thus the transformation to the multipolar form of the interaction must be seen to be fitting for such studies.

In the following sections the two forms of interaction are used to examine, in lesser detail, the process of scattering.

3.4 Differential Raman scattering

Raman scattering is an incoherent, two-photon optical process. A molecule will absorb a single photon from an incident beam and emit a photon of a different frequency such that the frequency difference is equal to the frequency of a rotational or vibrational molecular state. The molecule will usually return to its original electronic state after the virtual excitation. The Raman phenomenon [46] therefore gives rise to a valuable vibrational spectrum of transitions which are infra-red forbidden because of the difference in selection rules between the one- and two-photon processes.

If the molecule is chiral, however, the Raman scattering rate may be different for the cases where the incident beam is left- or right-circularly polarized [11]. The difference is small compared with the total scattering rate and the effect is predicted only when the vector potential is not approximated to a constant value over the extent of the molecule. This dictates the inclusion of magnetic dipole and electric quadrupole interactions (it is noted that the quadrupole contribution to the differential effect does not vanish for freely rotating molecules as it does for optical rotation and circular dichroism [11]). It is therefore useful to consider these higher-order interactions using the two forms of interaction Hamiltonian.

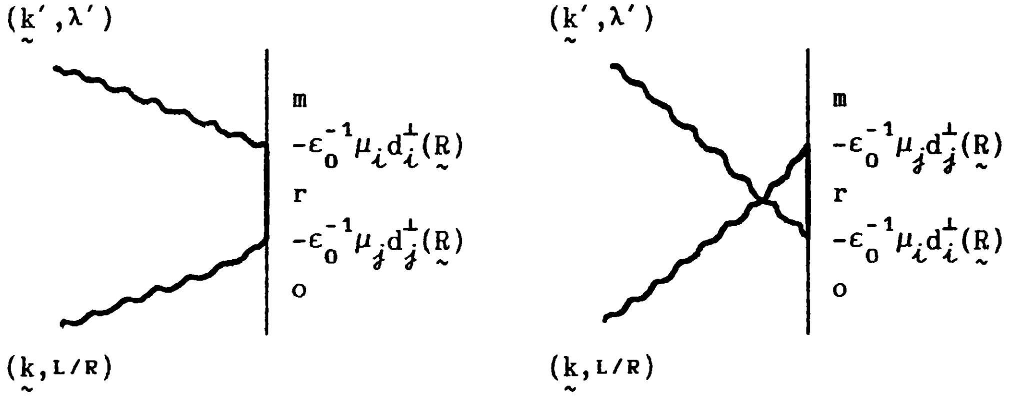
The multipolar treatment follows as before; the graphs of Figs 3.1-3 for two-photon absorption have their counterparts for Raman scattering. Fig 3.5, for example, shows the dipole interaction. The polarization label L/R indicates the choice of left- and right-circularly polarized beams and the scattered photon occupies the mode $(\underset{\sim}{k}',\lambda')$. The multipolar matrix element is again calculated directly using the second-order perturbation interaction. The matrix element for Raman scattering in the electric dipole approximation is then given, from Fig 3.5, by (3.4.1).

$$M_{fi}^{(dip)} = -\left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left(\frac{\hbar ck'}{2\varepsilon_0 V}\right)^{1/2}\bar{e}'_i e_j \sum_r \left\{\frac{\mu_i^{mr}\mu_j^{ro}}{E_{ro}-\hbar ck} + \frac{\mu_j^{mr}\mu_i^{ro}}{E_{ro}+\hbar ck'}\right\} e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}}. \tag{3.4.1}$$

This term is the leading contribution to the scattering amplitude; likewise the higher-order terms may be written down. The scattering rate may be expressed in terms of a radiant intensity [11] or more usually as a scattering cross section using the modulus square of this matrix element, in which case (3.4.1) leads to the multipolar form of the Kramers-Heisenberg dispersion formula [3-4,47-48].

In terms of the molecular polarizability tensors defined in Table 3.3.1, (3.4.1) and the magnetic dipole and electric quadrupole

FIG 3.5 : TIME-ORDERED GRAPHS FOR RAMAN SCATTERING:
ELECTRIC DIPOLE INTERACTION



contributions may be combined to give the total multipolar matrix element

$$M_{fi}(L/R\rightarrow\lambda) = -(nkk')^{1/2}\left(\frac{\hbar}{2\varepsilon_0 V}\right)e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}}\Big\{c\bar{e}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})\alpha_{ij}^{mo}(\omega,-\omega')$$

$$+\ \bar{e}_i^{(\lambda')}(\underset{\sim}{k}')b_j^{(L/R)}(\underset{\sim}{k})G_{ij}^{mo}(\omega,-\omega') + \bar{b}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})G_{ji}^{mo}(-\omega',\omega)$$

$$+ick_k\bar{e}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})A_{ijk}^{mo}(\omega,-\omega')\ -ick'_k\bar{e}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})A_{jik}^{mo}(-\omega',\omega)\Big\}$$

(3.4.2)

To compare this result with the minimal-coupling form we first extract the electric dipole interaction from graphs (i) and (ii) of Fig 3.6. This is the result which would be obtained if the vector potential was considered constant in the region of the molecule. Hence

$$M_{fi}^{(dip)} = -\sum_{\alpha}\sum_{\beta}\left(\frac{e}{m}\right)^2\left(\frac{n}{kk'}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 cV}\right)\bar{e}'_i e_j\sum_r\left\{\frac{p_i^{mr}p_j^{ro}}{E_{ro}-\hbar ck}+\frac{p_j^{mr}p_i^{ro}}{E_{ro}+\hbar ck'}\right\}e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}}$$

(3.4.3)

Converting the momentum transition moments into their dipole forms and noting the conservation result

$$E_{mr} + E_{ro} = \hbar ck - \hbar ck' \qquad (3.4.4)$$

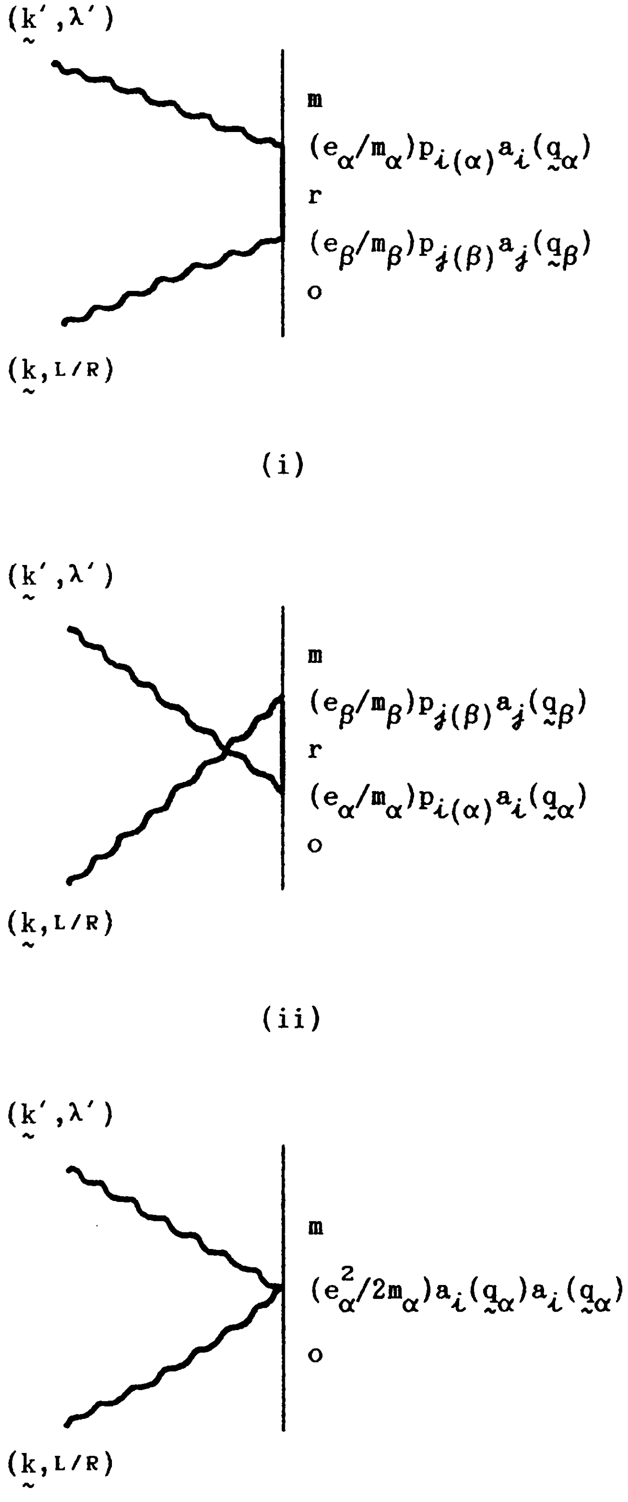
allows us to write this as

$$M_{fi}^{(dip)} = -\left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left(\frac{\hbar ck'}{2\varepsilon_0 V}\right)^{1/2}\bar{e}'_i e_j\alpha_{ij}^{mo}(\omega,-\omega')e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}},$$

(3.4.5)

where (3.2.1) has been employed to sum a term similar to the second term of (3.3.16).

FIG 3.6 : TIME-ORDERED GRAPHS FOR RAMAN SCATTERING:
MINIMAL COUPLING INTERACTIONS



(i)

(ii)

(iii)

(3.4.5) agrees with the corresponding multipolar term (3.4.1), which confirms the earlier equivalence demonstrations in the electric dipole approximation. We may proceed to the higher-order terms.

Adding the contribution from Fig 3.6 (iii) to the remaining terms from graphs (i) and (ii) leads us to consider the quantity

$$\begin{aligned} M'_{fi} \;=\; & -i \sum_{\alpha} \sum_{\beta} \left(e_{\alpha} e_{\beta}/m_{\alpha} m_{\beta}\right) \left(\frac{n}{kk'}\right)^{1/2} \left(\frac{\hbar}{2\varepsilon_0 c V}\right) \bar{e}'_i e_j e^{i(\underset{\sim}{k}-\underset{\sim}{k}').} \\ & \times \Bigg\{ k_k \sum_r \left\{ p_i^{mr} \langle r | p_j (\underset{\sim}{q}-\underset{\sim}{R})_k | o\rangle / (E_{ro}-\hbar ck) + \langle m | p_j (\underset{\sim}{q}-\underset{\sim}{R})_k | r \rangle p_i^{ro} / (E_{ro}+\hbar ck') \right\} \\ & - k'_k \sum_r \left\{ \langle m | p_i (\underset{\sim}{q}-\underset{\sim}{R})_k | r\rangle p_j^{ro} / (E_{ro}-\hbar ck) + p_j^{mr} \langle r | p_i (\underset{\sim}{q}-\underset{\sim}{R})_k | o \rangle / (E_{ro}+\hbar ck') \right\} \Bigg\} \\ & + 2i \sum_{\alpha} (e_{\alpha}^2/2m_{\alpha}) \left(\frac{n}{kk'}\right)^{1/2} \left(\frac{\hbar}{2\varepsilon_0 c V}\right) \bar{e}'_i e_i \langle m | (\underset{\sim}{k}-\underset{\sim}{k}').(\underset{\sim}{q}_{\alpha}-\underset{\sim}{R}) | o \rangle e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}} \end{aligned} \tag{3.4.6}$$

It has already been shown in Section 3.2 how best to deal with such terms. The multipolar equivalent of the total expression above is obtained following the use of the sum rules (3.2.11) and (3.2.30/31). After combining the resulting terms we obtain

$$\begin{aligned} M'_{fi} = & -\left(\frac{n}{kk'}\right)^{1/2} \left(\frac{\hbar}{2\varepsilon_0 V}\right) e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}} \Bigg\{ kk' \bar{e}'_i b_j G_{ij}^{mo}(\omega,-\omega') + kk' \bar{b}'_i e_j G_{ji}^{mo}(-\omega',\omega) \\ & + (i/\hbar) k' k_k \bar{e}'_i e_j \sum_r \left\{ \left(\frac{E_{ro}}{E_{ro}-\hbar ck}\right) \mu_i^{mr} Q_{jk}^{ro} - \left(\frac{E_{mr}}{E_{mr}-\hbar ck}\right) Q_{jk}^{mr} \mu_i^{ro} \right\} \\ & + (i/\hbar) k k'_k \bar{e}'_i e_j \sum_r \left\{ \left(\frac{-E_{mr}}{E_{mr}+\hbar ck'}\right) Q_{ik}^{mr} \mu_j^{ro} + \left(\frac{E_{ro}}{E_{ro}+\hbar ck'}\right) \mu_j^{mr} Q_{ik}^{ro} \right\} \Bigg\} \end{aligned} \tag{3.4.7}$$

The G tensor terms appear in their final form but the dipole-quadrupole terms must be adapted. The use of (3.2.6) enables us to adopt the tensor form of the result by eliminating the energy factors in the numerator. The subsequent expression is then identical to that of (3.4.2).

The terms of (3.4.2) which include the higher-order coupling have a magnitude which is of the order of 10^{-3} times that of the dipole polarizability term but they are nevertheless required to explain the differential effects. These effects arise from the modulus square which is required for the scattering cross section; the cross terms include the products $\alpha_{ij}^{mo}(\omega,-\omega')\bar{G}_{k\ell}^{mo}(\omega,-\omega')$, $\alpha_{ij}^{mo}(\omega,-\omega')\bar{A}_{k\ell m}^{mo}(\omega,-\omega')$ etc, multiplied by the corresponding polarization vectors. Now since

$$\underset{\sim}{b}^{(L/R)}(\underset{\sim}{k}) = \mp i\underset{\sim}{e}^{(L/R)}(\underset{\sim}{k}) \tag{3.4.8}$$

the form of these vectors is such that the difference in the absorption rates $(\Gamma_L - \Gamma_R)$ is non-zero; the quadrupole term also remains even after rotational averaging. Thus chiral molecules, for which the selection rules allow each type of interaction, scatter the two forms of polarized light at different rates, giving rise to a potential spectroscopic technique.

The next section discusses the more specific case of Rayleigh scattering, which shows some subtle differences.

3.5 Differential Rayleigh scattering

Rayleigh (elastic) scattering is a specific form of the more general case detailed in the previous section; the final state of the molecule following the scattering of a photon is the same as its initial state. In order that energy conservation is obeyed the emitted photon must enter a mode in which it has the same energy as the absorbed photon. Thus we may write $|\underset{\sim}{k}| = |\underset{\sim}{k}'|$ and denote the final molecular state as $|o\rangle$; the polarizabilities must now only be functions of $\omega = ck$. The direction of the emitted photon may vary. For example, photons of optical frequencies are scattered in the forward direction by crystal lattices, in which case $\underset{\sim}{k} = \underset{\sim}{k}'$ and the process is coherent.

The equivalence of matrix elements generated by the two forms of Hamiltonian has not been explicitly shown for this special case. Although the description follows closely from that of the Raman case, there are worthy differences; for example the term quadratic in the vector potential is non-zero, even in the electric dipole approximation, because the initial and final molecular states are identical. These new features are accounted here.

The calculation of the multipolar matrix element shows nothing new. The result is similar to that obtained for Raman scattering; the corresponding terms must take the same signs, differing only in the forms of the polarizabilities. The minimal-coupling derivation, however, does differ slightly from the Raman case. The pure dipole contribution may be shown to give

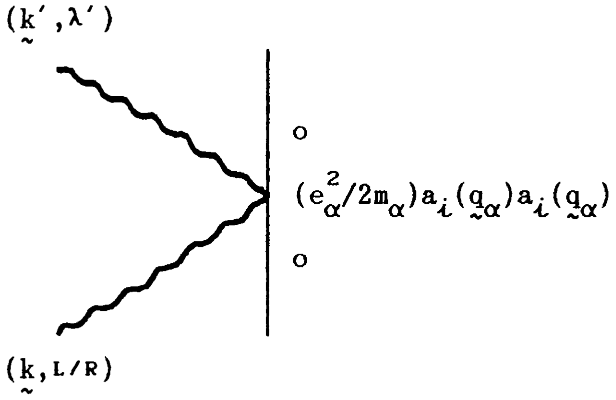
$$M_{fi}^{(dip)} = -\left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\bar{e}_i' e_j \alpha_{ij}^{oo}(\omega,-\omega)\, e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}}$$

$$-\sum_\alpha (e_\alpha^2/m_\alpha)\left(\frac{n\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\bar{e}_i' e_j \delta_{ij}\, e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}} , \tag{3.5.1}$$

which differs from the corresponding Raman result (3.4.5) by the appearance of the second term, which now does not sum to zero using (3.2.1) because of the choice of molecular states.

The remaining terms from the $\underset{\sim}{p}.\underset{\sim}{a}(\underset{\sim}{q})$ graphs are standard and are converted into their multipolar form using (3.2.11). The first term of the series of contributions from Fig 3.7(i), however, is now non-zero. That is,

FIG 3.7: SEAGULL GRAPH FOR RAYLEIGH SCATTERING IN THE MINIMAL COUPLING METHOD



(i)

$$M_{fi}(i) =$$

$$2\sum_\alpha n^{1/2}(e_\alpha^2/2m_\alpha)\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)\bar{e}'_i e_i\langle o|1 + i(\underset{\sim}{k}-\underset{\sim}{k}').(\underset{\sim}{q}_\alpha-\underset{\sim}{R})|o\rangle e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}}. \tag{3.5.2}$$

It is this term which is identical to the second term of (3.5.1) but of opposite sign. Using the sum rules (3.2.30/31) the second term of (3.5.2) may be added to those from the other graphs, giving the total matrix element

$$\begin{aligned} M_{fi}(L/R\to\lambda) = -n^{1/2}\left(\frac{\hbar k}{2\varepsilon_0 V}\right)e^{i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{R}}\Big\{ & c\bar{e}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})\alpha_{ij}^{oo}(\omega,-\omega) \\ & +\bar{e}_i^{(\lambda')}(\underset{\sim}{k}')b_j^{(L/R)}(\underset{\sim}{k})G_{ij}^{oo}(\omega,-\omega) +\bar{b}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})G_{ji}^{oo}(-\omega,\omega) \\ & +ick_k\bar{e}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})A_{ijk}^{oo}(\omega,-\omega) -ick'_k\bar{e}_i^{(\lambda')}(\underset{\sim}{k}')e_j^{(L/R)}(\underset{\sim}{k})A_{jik}^{oo}(-\omega,\omega)\Big\} \end{aligned} \tag{3.5.3}$$

which agrees with the multipolar result.

It has been shown how the theory of QED is applied and demonstrated how the multipolar and minimal-coupling Hamiltonians, equivalent by canonical transformation, may give identical results for interactions on the energy shell. Previous works on this subject have been extended by the inclusion of electric quadrupole and magnetic dipole interactions. The conditions of this equivalence [39], namely that i) those matrix elements calculated must describe physical processes in which energy is conserved and ii) that every possible graph to the required order in the field must be included, deny any claim to the contrary. A consideration of the terms arising from the minimal-coupling seagull graph, for example, dismisses Fiutak's claim [20] that equivalence only applies to first order processes. The electric dipole approximation, which is often adopted for calculations irrespective of the form of Hamiltonian, is in most cases a valid choice [49]; the optical wavelengths of photons associated with electronic transitions may be typically 10^3 times the extent of the molecule. However, the higher-order interactions discussed here may not be negligible. We have already seen the necessity to include such interactions when examining the responses of optically active molecules, whose low molecular symmetry leads to the interference of the relative contributions and so to such phemomena. Also, transitions which are electric-quadrupole or magnetic-dipole allowed often have a low probability of proceeding through electric dipole coupling and so their matrix elements may be significant.

From the calculations of the previous sections we have seen that the multipolar formalism lends itself better to the problems of considering higher-order interactions. The $-\varepsilon_0^{-1}\underset{\sim}{\mu}.\underset{\sim}{d}^{\perp}(\underset{\sim}{R})$ interaction is simply replaced by the integral $-\varepsilon_0^{-1}\int\underset{\sim}{p}(\underset{\sim}{r}).\underset{\sim}{d}^{\perp}(\underset{\sim}{r})d^3\underset{\sim}{r}$, which contains the complete electric multipole expansion, and a corresponding magnetic term, from which the multipolar interaction terms are obtained. The required matrix elements then directly follow. In the minimal-coupling formalism all coupling is described by the two interaction terms. An expansion of these terms shows that for higher-order processes the number of terms generated quickly rises, with a loss of obvious physical significance. This compares with the more favourable multipolar results in terms of molecular polarizabilities and interactions in terms of the fields rather than the potentials. The multipolar interaction thus describes the dynamical, internal electromagnetic field $\underset{\sim}{e}(\underset{\sim}{r})$ with an interaction similar to the external field interaction $-\underset{\sim}{\mu}.\underset{\sim}{E}(\underset{\sim}{r})$ used in semi-classical theories and allows straightforward calculation of radiative interactions in a useful form.

CHAPTER 4

HIGHER-ORDER CONTRIBUTIONS TO THE DISPERSION INTERACTION

4.1 Introduction

The physical properties of solids and fluids are determined by the interactions between the constituent atoms and molecules. It is now well-known that molecular interaction energies depend upon the extent of molecular separation and that at large separations retardation effects become dominant over electrostatic coupling.

In the initial studies of interactions between neutral molecules the quantum-mechanical Hamiltonian was written simply as a sum of molecular terms and an intermolecular potential; the dipole-dipole term. The second-order perturbation result in this term is the familiar London R^{-6} dispersion interaction [45,50-51]. Retardation effects are unimportant and the result is valid at separations $R \ll \lambda$ $(2\pi k^{-1})$, where λ is of the order of the wavelength of the lowest-lying molecular transitions. However, when $R \geq \lambda$ the Coulomb potential energy is not sufficient to describe the interaction and we must consider the interactions of the molecules with the field, ie retardation; the Hamiltonian should be the coupled system. The result when molecular separation is much greater than these characteristic wavelengths is the Casimir-Polder R^{-7} dependence (see for example [52-57]), which was calculated following the experimental observations of Overbeek et al [58]. It is appropriate in these cases to express the result in terms of physical properties of the isolated molecules eg polarizabilities. The dependence on separation and the replacement of the London R^{-6} result by an R^{-7} term has been observed for example by Tabor et al [59], although these are of course the asymptotic values of a more complicated expression.

Quantum electrodynamics is ideal for studying such interactions since it allows for the finite propagation of light. Intermolecular forces are treated as radiation-molecule couplings, with the field mediating exchange of energy in the form of virtual photons between the molecules. The energy shifts are calculated by the use of perturbation theory, the results realised through the use of time-ordered diagrams; for two-photon exchange the fourth-order term of the perturbation expansion is required.

As noted in Chapter 1, for neutral molecules the electrostatic interactions are completely cancelled in the multipolar Hamiltonian, giving a purely retarded result. The dispersion interaction has been investigated using the multipolar Hamiltonian by Power [45] and Craig and Thirunamachandran [11] for the whole range of molecular separation outside overlap. However, their results only contain terms up to a product of the polarizabilities of the two molecules. Magnetic dipole interactions have been considered [11,60] with application to effects arising from the chirality of the molecules but these results too are only valid for freely rotating molecules.

This chapter extends the discussion of the interaction between neutral molecules. Electric-quadrupole and magnetic-dipole interactions are considered, the results given firstly for oriented molecules. The diamagnetic interaction must also be determined, since it gives a result of similar order to the terms involving two magnetic-dipole interactions. Rotationally-averaged expressions are presented as well, as are results for the near- and far-zones. Results are expressed where appropriate in terms of molecular polarizability and susceptibility tensors; the rotatory strength R^{ro} is used elsewhere.

We start with an account of the electric-dipole interaction for an oriented pair. This is an important result as the method used in this section is largely followed in subsequent sections. Magnetic dipole and electric quadrupole terms are then discussed; these terms may be confined to one centre or split between the two molecules. These higher-order interactions are important for molecules which have small electric-dipole coupling with the field or low-lying states accessible from the ground state by non-zero electric quadrupole and magnetic dipole matrix elements. They are also important when considering molecules with large magnetic susceptibilities and when considering the interaction between optically active molecules. In such cases the dispersion force differs according to the relative chirality of the pair, an effect called chiral discrimination, and the magnetic-dipole interactions are required to account for this. The same graphs are used for the calculations except that at some of the interaction vertices we use these higher-order interaction terms. The corresponding contributions to the energy shift are determined; the diamagnetic interaction at one centre is obtained using third-order perturbation theory since it is second-order in the field.

These results are summarised in a later section and some useful identities are given in an appendix.

4.2 The electric-dipole contribution

We wish to calculate the pure electric-dipole contribution to the dispersion energy. The interaction Hamiltonian is given by

$$H_{int} = -\varepsilon_0^{-1}\underset{\sim}{\mu}(A).\underset{\sim}{d}^{\perp}(\underset{\sim}{R}_A) -\varepsilon_0^{-1}\underset{\sim}{\mu}(\underset{\sim}{B}).\underset{\sim}{d}^{\perp}(\underset{\sim}{R}_B). \tag{4.2.1}$$

The energy shift is calculated using the fourth-order perturbation result;

$$\Delta E = -\sum_{III}\sum_{II}\sum_{I}\frac{\langle 0|H_{int}|III\rangle\langle III|H_{int}|II\rangle\langle II|H_{int}|I\rangle\langle I|H_{int}|0\rangle}{(E_{III}-E_0)(E_{II}-E_0)(E_I-E_0)} \; . \tag{4.2.2}$$

There are twelve contributions to the fourth-order result, shown by the time-ordered graphs on Page 97. The virtual photons are indicated by internal wavy lines and are denoted by a wavevector $\underset{\sim}{p}$ and a polarization λ; the molecules occupy intermediate electronic states, labelled r for molecule A and s for molecule B. These labels will be assumed as implicit in the working. Energy conservation applies only between the initial and final total states of the system. The intermediate states may lend energy to or borrow energy from the vacuum, subject to uncertainty restrictions. To evaluate the total contribution from a graph it is necessary to sum over the wavevectors and polarizations of the virtual photons as well as over the virtual molecular states.

The energy denominators for graphs (i-xii) are given in Table 4.3.1. Summing the contribution from each of these graphs gives a total energy shift [11] of

$$\Delta E\ (\text{Total}) = \Delta E\ (\text{i-xii})$$

$$= -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar c p}{2\varepsilon_0 V}\right)\left(\frac{\hbar c p'}{2\varepsilon_0 V}\right)\mu_i^{or}\mu_j^{ro}\mu_k^{os}\mu_l^{so}$$

$$\times\ (\delta_{ik}-\hat{p}_i\hat{p}_k)(\delta_{jl}-\hat{p}'_j\hat{p}'_l)e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}\sum_a^{xii} c_a^1 D_a^{-1} \quad . \tag{4.2.3}$$

The sum over a is a sum of the reciprocal of the energy denominator arising from each graph as given by (4.2.2). The value of this sum has been determined [11] and appears in Table 4.3.2 as S_1.

The expression (4.2.3) may be written in the symmetric form

$$\Delta E = \frac{-1}{128\pi^6\varepsilon_0^2\hbar c}\sum_{r,s}\mu_i^{or}\mu_j^{ro}\mu_k^{os}\mu_\ell^{so}\iint pp'(\tilde{\alpha}_{ik}\tilde{\alpha}'_{j\ell}+\tilde{\alpha}'_{ik}\tilde{\alpha}_{j\ell})e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}$$

$$\times\frac{(k_r+k_s+p)}{(k_r+k_s)(k_r+p)(k_s+p)}\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)d^3\underset{\sim}{p}\,d^3\underset{\sim}{p}' \qquad (4.2.4)$$

where

$$\tilde{\alpha}_{ij} = (\delta_{ij}-\hat{p}_i\hat{p}_j)\ ;\ \tilde{\alpha}'_{ij} = (\delta_{ij}-\hat{p}'_i\hat{p}'_j) \qquad (4.2.5)$$

It is convenient at this point to define also the quantities α_{ij} and β_{ij}; these are useful shorthand expressions for terms which appear frequently in the study of intermolecular interactions. We define

$$\alpha_{ij} = (\delta_{ij}-\hat{R}_i\hat{R}_j)\ ;\ \beta_{ij} = (\delta_{ij}-3\hat{R}_i\hat{R}_j). \qquad (4.2.6)$$

Performing the angular integration in (4.2.4) gives the expression (4.2.8), which for clarity has been written using the quantity $\tau_{ij}(pR)$, which is defined below. Again this is a widely used shorthand form, found regularly in the literature. See for example [45]. We have

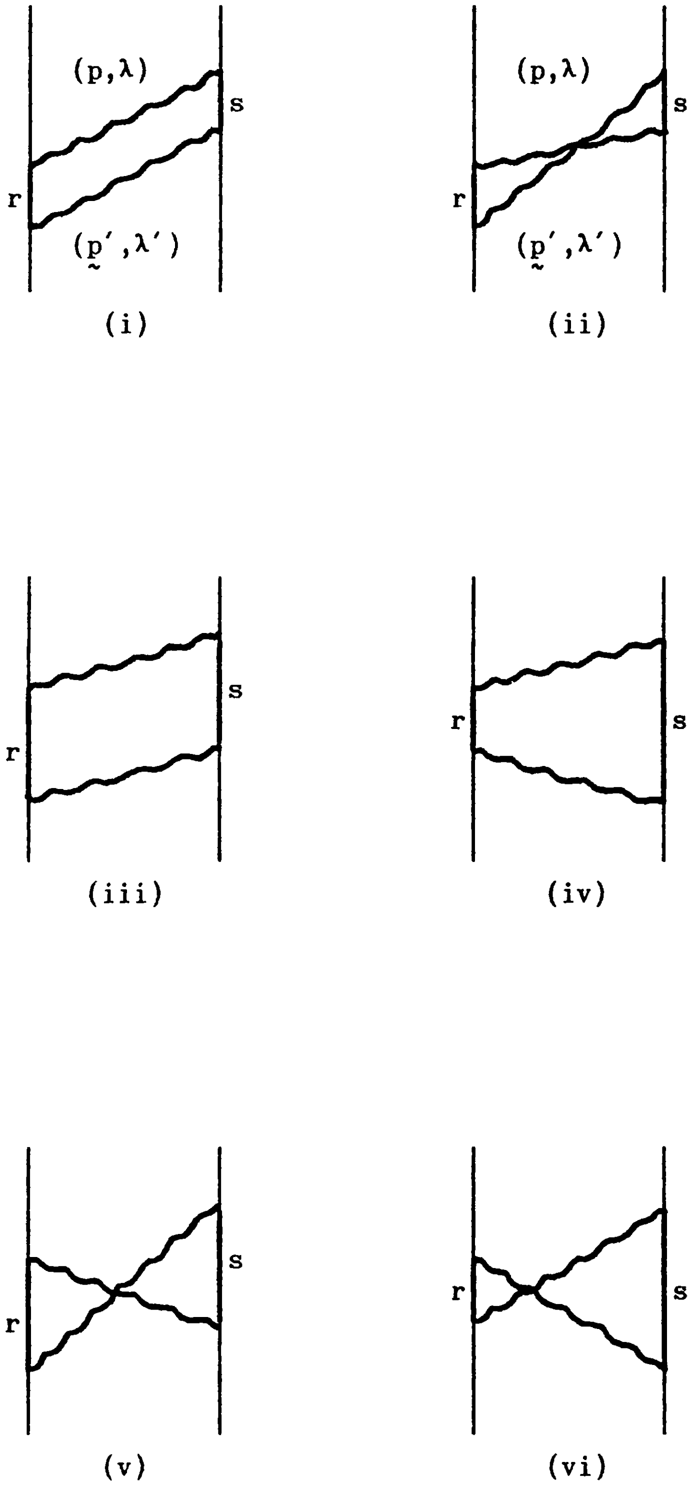
$$\tau_{ij}(pR) = \alpha_{ij}\frac{\sin pR}{pR} + \beta_{ij}\left(\frac{\cos pR}{p^2R^2}-\frac{\sin pR}{p^3R^3}\right) \qquad (4.2.7)$$

The total energy shift is now given by

$$\Delta E = \frac{-1}{8\pi^4\varepsilon_0^2\hbar c}\sum_{r,s}\mu_i^{or}\mu_j^{ro}\mu_k^{os}\mu_\ell^{so}\int_0^\infty\int_0^\infty\Big[\tau_{ik}(pR)\tau_{j\ell}(p'R)+\tau_{ik}(p'R)\tau_{j\ell}(pR)\Big]$$

$$\times\frac{p^3p'^3(k_r+k_s+p)}{(k_r+k_s)(k_r+p)(k_s+p)}\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)dp\,dp' \qquad (4.2.8)$$

FIG 4.1 : TIME-ORDERED GRAPHS FOR THE DISPERSION INTERACTION
IN THE ELECTRIC-DIPOLE APPROXIMATION



(i) (ii) (iii) (iv) (v) (vi)

+ reflections

Integrating over p′ gives (4.2.10), with $\omega_{ij}(pR)$ defined by

$$\omega_{ij}(pR) = \alpha_{ij}\frac{\cos pR}{pR} - \beta_{ij}\left(\frac{\sin pR}{p^2R^2} + \frac{\cos pR}{p^3R^3}\right) \tag{4.2.9}$$

Hence

$$\Delta E = \frac{-1}{8\pi^3\varepsilon_0^2\hbar c}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}\mu_k^{os}\mu_\ell^{so}}{(k_r+k_s)}$$

$$\times\int_0^\infty \frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}\Big[\tau_{ik}(pR)\omega_{j\ell}(pR)+\tau_{j\ell}(pR)\omega_{ik}(pR)\Big]p^6dp \tag{4.2.10}$$

Expanding (4.2.10) and collecting the terms gives a result which may be simplified using standard trigonometric identities to give

$$\Delta E = \frac{-1}{8\pi^3\varepsilon_0^2\hbar cR^2}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}\mu_k^{os}\mu_\ell^{so}}{(k_r+k_s)}\int_0^\infty\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}$$

$$\times\left[\sin 2pR\left(A_{ijk\ell} - \frac{C_{ijk\ell}}{p^2R^2} + \frac{E_{ijk\ell}}{p^4R^4}\right) + \cos 2pR\left(\frac{B_{ijk\ell}}{pR} - \frac{D_{ijk\ell}}{p^3R^3}\right)\right]p^4dp$$

(4.2.11)

with $A_{ijk\ell}$ - $E_{ijk\ell}$ given by (4.2.12)

$$\begin{aligned}
A_{ijk\ell} &= \alpha_{ik}\alpha_{j\ell}\\
B_{ijk\ell} &= \alpha_{ik}\beta_{j\ell} + \beta_{ik}\alpha_{j\ell}\\
C_{ijk\ell} &= \alpha_{ik}\beta_{j\ell} + \beta_{ik}\alpha_{j\ell} + \beta_{ik}\beta_{j\ell} \quad .\\
D_{ijk\ell} &= 2\beta_{ik}\beta_{j\ell}\\
E_{ijk\ell} &= \beta_{ik}\beta_{j\ell}
\end{aligned} \tag{4.2.12}$$

Writing (4.2.11) in terms of exponentials leads to the result

$$\Delta E = \frac{-1}{8\pi^3\varepsilon_0^2\hbar c R^2}\sum_{r,s}\mu_i^{or}\mu_j^{ro}\mu_k^{os}\mu_\ell^{so}$$
$$\times\int_0^\infty \frac{k_r k_s p^4 e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(A_{ijk\ell} + \frac{B_{ijk\ell}}{pR} + \frac{C_{ijk\ell}}{p^2R^2} + \frac{D_{ijk\ell}}{p^3R^3} + \frac{E_{ijk\ell}}{p^4R^4}\right)dp \tag{4.2.13}$$

Defining the dynamic polarizability of a molecule by the expression

$$\alpha_{ij}(icu) \quad = \quad 2\sum_r \frac{E_{ro}}{E_{ro}^{\ 2}+(\hbar cu)^2}\,\mu_i^{or}\mu_j^{ro} \tag{4.2.14}$$

with a frequency (icu) the above form may be written as

$$\Delta E = \frac{-\hbar c}{32\pi^3\varepsilon_0^2R^2}\int_0^\infty \alpha_{ij}^{A}(icp)\alpha_{k\ell}^{B}(icp)p^4e^{-2pR}\left(A_{ijk\ell}+\frac{B_{ijk\ell}}{pR}+\frac{C_{ijk\ell}}{p^2R^2}+\frac{D_{ijk\ell}}{p^3R^3}+\frac{E_{ijk\ell}}{p^4R^4}\right)dp \tag{4.2.15}$$

This result may be compared with that obtained by Craig and Thirunamachandran [11] by taking the rotational average; we regain their result, which is shown below.

$$\Delta E = \frac{-1}{36\pi^3\varepsilon_0^2\hbar c R^2}\sum_{r,s}|\underset{\sim}{\mu}^{ro}|^2|\underset{\sim}{\mu}^{so}|^2$$
$$\times\int_0^\infty \frac{k_r k_s p^4 e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(1 + \frac{2}{pR} + \frac{5}{p^2R^2} + \frac{6}{p^3R^3} + \frac{3}{p^4R^4}\right)dp \tag{4.2.16}$$

The form of (4.2.16) in the limiting cases of large and small molecular separation is given below. In the wave-zone limit the separation is much greater than the wavelength of the lowest lying molecular transitions λ_r and λ_s; we may write $k_rR,\ k_sR \gg 1$. The near-zone, with separations much smaller than the molecular transition wavelengths λ_r and λ_s, is defined by $k_rR, k_sR \ll 1$. The limiting results are obtained from (4.2.16) by making the approximations;

Wave-zone: $k_r^2, k_s^2 \gg p^2$, and

Near-zone: $e^{-2pR} \simeq 1$; it is sufficient to retain only the term in $(pR)^{-4}$ as the major contribution. This gives the results below.

NEAR-ZONE LIMIT

$$\Delta E = \frac{-1}{24\pi^2\varepsilon_0^2R^6}\sum_{r,s}\frac{|\underset{\sim}{\mu}^{ro}|^2|\underset{\sim}{\mu}^{so}|^2}{(E_{ro}+E_{so})}\,, \qquad (4.2.17)$$

which may be written in terms of dynamic polarizabilities as

$$\Delta E = \frac{-3}{32\pi^3\varepsilon_0^2R^6}\int_{-\infty}^{\infty}\alpha^A(icu)\alpha^B(icu)du\ . \qquad (4.2.18)$$

FAR-ZONE LIMIT

$$\Delta E = \frac{-23\hbar c}{64\pi^3\varepsilon_0^2}\,\frac{\alpha(A)\alpha(B)}{R^7} \qquad (4.2.19)$$

In (4.2.19) $\alpha(A)$ is the static polarizability for molecule A defined as

$$\alpha(A) = (2/3)\sum_r |\underset{\sim}{\mu}^{ro}|^2/E_{ro} \qquad (4.2.20)$$

The electric-dipole result is important because the method is largely followed in subsequent sections. In the sum over the energy denominators, each term, denoted D_a^{-1}, appears with the same sign and the terms are combined in a specific but convenient order such that the variables p and p′ are separate and the respective integrals may be done. In following sections similar sums will need to be evaluated and so we shall briefly look at this method and give some useful definitions of quantities which will be required.

4.3 Methods and definitions

The interaction Hamiltonian is given by

$$H_{int} = -\varepsilon_0^{-1}\underset{\sim}{\mu}(A).\underset{\sim}{d}^{\perp}(\underset{\sim}{R}_A) -\varepsilon_0^{-1}\underset{\sim}{\mu}(B).\underset{\sim}{d}^{\perp}(\underset{\sim}{R}_B) -\underset{\sim}{m}(A).\underset{\sim}{b}(\underset{\sim}{R}_A) -\underset{\sim}{m}(B).\underset{\sim}{b}(\underset{\sim}{R}_B)$$

$$-\varepsilon_0^{-1}Q_{ij}(A)\nabla_j d_i^{\perp}(\underset{\sim}{R}_A) -\varepsilon_0^{-1}Q_{k\ell}(B)\nabla_\ell d_k^{\perp}(\underset{\sim}{R}_B) +\frac{e^2}{8m}\sum_\alpha\left\{(\underset{\sim}{q}_\alpha(B)-\underset{\sim}{R}_B)\times\underset{\sim}{b}(\underset{\sim}{R}_B)\right\}^2. \tag{4.3.1}$$

The graphs on page 97 are modified by including the appropriate number of new interactions at the vertices. This increases the number of graphs which make contributions; there may be twelve, twenty-four or forty-eight contributions to the fourth-order interaction. In each case we must sum over all the possible intermediate states for each graph. However, as we shall see, it is always possible for each set of results to write the total in a form similar to (4.2.3), where there is a factor common to each expression which contains all the vector and angular dependence. We are then left to evaluate a sum, similar to S_1, which is over the product of the energy differences in the denominators of the perturbation result. In the sum S_1, however, all of the terms appear with the coefficient of unity. In the cases which we shall consider the coefficients may be plus or minus unity, following the factorization: we must evaluate new sums.

Table 4.3.1 shows all the relevant information pertaining to each graph. The quantity $\underset{\sim}{x}_a$ refers to the signs, in the exponential part of the field expansions, of the wavevectors $\underset{\sim}{p}$ and $\underset{\sim}{p}'$ of the virtual photons which are created or annihilated at each vertex. By considering the symmetry of each expression with respect to the interchanges $\underset{\sim}{p} \Rightarrow -\underset{\sim}{p}$ and/or $\underset{\sim}{p}' \Rightarrow -\underset{\sim}{p}'$ we may write a total result, as in (4.2.3), with $\exp[i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}]$ as a common factor. Where the expressions are antisymmetric to the required changes a coefficient of minus one results to that contribution. It is these coefficients which are given in Table (4.3.1) for the appropriate cases. Note that in the case of the electric-dipole interaction, each term is symmetric to these changes.

The sums of terms with the coefficients in Table 4.3.1 have been evaluated and appear in Table 4.3.2. These results will be referred to in the text. It was largely possible to deduce these results from the value of S_1; the terms were combined in an identical manner, in order to write down the quantities

$$\hbar^3 c^3 \left(\frac{C^n_{i}}{D_{i}} + \frac{C^n_{iii}}{D_{iii}} + \frac{C^n_{iv}}{D_{iv}} + \frac{C^n_{vii}}{D_{vii}} + \frac{C^n_{ix}}{D_{ix}} + \frac{C^n_{x}}{D_{x}} \right) \tag{4.3.2}$$

and

$$\hbar^3 c^3 \left(\frac{C^n_{ii}}{D_{ii}} + \frac{C^n_{v}}{D_{v}} + \frac{C^n_{vi}}{D_{vi}} + \frac{C^n_{viii}}{D_{viii}} + \frac{C^n_{xi}}{D_{xi}} + \frac{C^n_{xii}}{D_{xii}} \right) \tag{4.3.3}$$

and hence obtain the total sum for n = 2-5.

In the previous section the trigonometric quantity $\tau_{ij}(pR)$ was defined in order to simplify the expression (4.2.8). The explicit working will be elaborated upon in the appendix, (Section 4.8), but if we look at (4.3.6), in Table 4.3.4, we see the form of the angular integral. In an integral such as (4.3.6) the quantity $\tilde{\alpha}_{ik}$ on the left hand side may arise from the sum over the polarizations of one of the virtual photons exchanged between the molecules (see the appendix to this chapter). However, if we are considering magnetic-dipole interactions the sum over photon polarization vectors is modified by the presence of the magnetic field vector and we will require an integral of the form (4.3.5). When considering electric-quadrupole

TABLE 4.3.1 SUMMARY OF THE CONTRIBUTIONS FROM THE DISPERSION GRAPHS

Graph	$\underset{\sim}{x}_a/i$	C_a^1	C_a^2	C_a^3	C_a^4	C_a^5	$(hc)^{-3}D_a^{-1}$
i	$(\underset{\sim}{p}+\underset{\sim}{p}')$	+	+	+	+	+	$(p+p')(k_s+p)(k_r+p')$
ii	$(\underset{\sim}{p}+\underset{\sim}{p}')$	+	-	-	+	-	$(p+p')(k_s+p')(k_r+p')$
iii	$(\underset{\sim}{p}+\underset{\sim}{p}')$	+	+	+	+	+	$(k_r+k_s)(k_s+p)(k_r+p')$
iv	$(\underset{\sim}{p}-\underset{\sim}{p}')$	+	+	-	-	-	$(k_r+k_s)(k_s+p)(k_s+p')$
v	$-(\underset{\sim}{p}-\underset{\sim}{p}')$	+	-	+	-	-	$(k_r+k_s+p+p')(k_s+p')(k_r+p')$
vi	$-(\underset{\sim}{p}-\underset{\sim}{p}')$	+	-	+	-	-	$(k_r+k_s+p+p')(k_s+p')(k_s+p)$
vii	$-(\underset{\sim}{p}+\underset{\sim}{p}')$	+	+	+	+	-	$(p+p')(k_s+p')(k_r+p)$
viii	$-(\underset{\sim}{p}+\underset{\sim}{p}')$	+	-	-	+	+	$(p+p')(k_s+p)(k_r+p)$
ix	$-(\underset{\sim}{p}+\underset{\sim}{p}')$	+	+	+	+	-	$(k_r+k_s)(k_r+p)(k_s+p')$
x	$-(\underset{\sim}{p}-\underset{\sim}{p}')$	+	+	-	-	+	$(k_r+k_s)(k_r+p)(k_r+p')$
xi	$-(\underset{\sim}{p}-\underset{\sim}{p}')$	+	-	+	-	-	$(k_r+k_s+p+p')(k_r+p)(k_s+p)$
xii	$-(\underset{\sim}{p}-\underset{\sim}{p}')$	+	-	+	-	-	$(k_r+k_s+p+p')(k_r+p)(k_r+p')$

TABLE 4.3.2 RESULTS OF SUMS REQUIRED TO DETERMINE THE DISPERSION INTERACTIONS

S_n	SUM	VALUE × $(\hbar c)^3$
S_1	$\sum_{a=i}^{xii} C_a^1 D_a^{-1}$	$\frac{4(k_r+k_s+p)}{(k_r+k_s)(k_r+p)(k_s+p)}\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)$
S_2	$\sum_{a=i}^{xii} C_a^2 D_a^{-1}$	$\frac{4p}{(k_r+k_s)(k_r+p)(k_s+p)}\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)$
S_3	$\sum_{a=i}^{xii} C_a^3 D_a^{-1}$	$\frac{4p'}{(k_r+k_s)(k_r+p')(k_s+p')}\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)$
S_4	$\sum_{a=i}^{xii} C_a^4 D_a^{-1}$	$\frac{4(k_r+k_s+p')}{(k_r+k_s)(k_r+p')(k_s+p')}\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)$
S_5	$\sum_{a=i}^{xii} C_a^5 D_a^{-1}$	$\frac{2k_r}{(k_r+k_s)}\left(\frac{1}{(k_r+p)(k_s+p)} \frac{1}{(k_r+p')(k_s+p')}\right)\left(\frac{1}{p+p'} + \frac{1}{p-p'}\right)$

TABLE 4.3.3 A SUM REQUIRED TO DETERMINE THE DIAMAGNETIC CONTRIBUTION TO THE DISPERSION INTERACTION

SUM	VALUE × $(\hbar c)^2$
$D_i^{-1} - D_{ii}^{-1} + D_{iii}^{-1}$	$\frac{2}{(k_r+p')}\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)$

interactions the sum over polarization is the same as the electric-dipole case but the gradient operation (from the interaction Hamiltonian) on the exponential part of the mode expansion for the electric displacement field (1.1.40) brings down an additional component of the photon unit wavevector. This requires the results of the integrals on the left hand sides of (4.3.7/8), which may be defined analogously using the quantities $\sigma_{ijk}(pR)$ and $\xi_{ijkl}(pR)$.

TABLE 4.3.4: RESULTS OF SOLID-ANGLE INTEGRALS FOR VIRTUAL PHOTONS OF WAVEVECTOR $\underset{\sim}{p}$

$$\frac{1}{4\pi}\int e^{i\underset{\sim}{p}.\underset{\sim}{R}}\,d\Omega = \frac{\sin pR}{pR} \tag{4.3.4}$$

$$\frac{1}{4\pi}\int \hat{p}_i e^{i\underset{\sim}{p}.\underset{\sim}{R}}\,d\Omega = -i\eta_i(pR) \tag{4.3.5}$$

$$\frac{1}{4\pi}\int \tilde{\alpha}_{ik} e^{i\underset{\sim}{p}.\underset{\sim}{R}}\,d\Omega = \tau_{ik}(pR) \tag{4.3.6}$$

$$\frac{1}{4\pi}\int \tilde{\alpha}_{ij}\hat{p}_k e^{i\underset{\sim}{p}.\underset{\sim}{R}}\,d\Omega = i\sigma_{ijk}(pR) \tag{4.3.7}$$

$$\frac{1}{4\pi}\int \tilde{\alpha}_{ij}\hat{p}_k\hat{p}_l e^{i\underset{\sim}{p}.\underset{\sim}{R}}\,d\Omega = \xi_{ijkl}(pR) \tag{4.3.8}$$

However, these integrals had not previously been evaluated and so these new results have been determined and are presented for the first time in Table 4.3.4 with $\sigma_{ijk}(pR)$ and $\xi_{ijk\ell}(pR)$ given by (4.3.9) and (4.3.10) respectively. These results will be referred to in the working and are grouped together below for convenience.

In Table 4.3.4 $\tau_{ik}(pR)$ is defined by (4.2.7),

$$\begin{aligned}\sigma_{ijk}(pR) = \Bigg\{ & \hat{R}_i\hat{R}_j\hat{R}_k\left(\frac{\cos pR}{pR} - 6\frac{\sin pR}{p^2R^2} - 15\frac{\cos pR}{p^3R^3} + 15\frac{\sin pR}{p^4R^4}\right)\\ & +(\delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i)\left(\frac{\sin pR}{p^2R^2} + 3\frac{\cos pR}{p^3R^3} - 3\frac{\sin pR}{p^4R^4}\right)\\ & -\delta_{ij}\hat{R}_k\left(\frac{\cos pR}{pR} - 2\frac{\sin pR}{p^2R^2} - 3\frac{\cos pR}{p^3R^3} + 3\frac{\sin pR}{p^4R^4}\right)\Bigg\}\end{aligned} \tag{4.3.9}$$

and $\xi_{ijk\ell}(pR)$ is defined as

$$\begin{aligned}\xi_{ijk\ell}(pR) = \Bigg\{ & -\hat{R}_i\hat{R}_j\hat{R}_k\hat{R}_\ell\left(\frac{\sin pR}{pR} + 10\frac{\cos pR}{p^2R^2} - 45\frac{\sin pR}{p^3R^3} - 105\frac{\cos pR}{p^4R^4} + 105\frac{\sin pR}{p^5R^5}\right)\\ & +(\delta_{ik}\delta_{j\ell} + \delta_{jk}\delta_{i\ell})\left(\frac{\sin pR}{p^3R^3} + 3\frac{\cos pR}{p^4R^4} - 3\frac{\sin pR}{p^5R^5}\right)\\ & -\delta_{ij}\delta_{k\ell}\left(\frac{\cos pR}{p^2R^2} - 2\frac{\sin pR}{p^3R^3} - 3\frac{\cos pR}{p^4R^4} + 3\frac{\sin pR}{p^5R^5}\right)\\ & +(\delta_{ik}\hat{R}_j\hat{R}_\ell + \delta_{i\ell}\hat{R}_j\hat{R}_k + \delta_{jk}\hat{R}_i\hat{R}_\ell + \delta_{j\ell}\hat{R}_i\hat{R}_k + \delta_{k\ell}\hat{R}_i\hat{R}_j)\\ & \times\left(\frac{\cos pR}{p^2R^2} - 6\frac{\sin pR}{p^3R^3} - 15\frac{\cos pR}{p^4R^4} + 15\frac{\sin pR}{p^5R^5}\right)\\ & +\delta_{ij}\hat{R}_k\hat{R}_\ell\left(\frac{\sin pR}{pR} + 4\frac{\cos pR}{p^2R^2} - 9\frac{\sin pR}{p^3R^3} - 15\frac{\cos pR}{p^4R^4} + 15\frac{\sin pR}{p^5R^5}\right)\Bigg\}\end{aligned} \tag{4.3.10}$$

In (4.3.5) we also require the quantity $\eta_i(pR)$ given below.

$$\eta_i(pR) = \hat{R}_i\left(\frac{\cos pR}{pR} - \frac{\sin pR}{p^2R^2}\right) . \tag{4.3.11}$$

One last consideration using this method is the p′-integration. On page 98 the quantity $\omega_{ij}(pR)$, which is very similar in form to $\tau_{ij}(pR)$, was introduced. The pair $\{\tau_{ij}(p'R),\omega_{ij}(pR)\}$ are related by the integral

$$\int_{-\infty}^{\infty} \frac{\tau_{ij}(p'R)p'^3}{(p+p')}\, dp' = p^3\pi\omega_{ij}(pR) \tag{4.3.12}$$

Similar expressions, outlined more fully in the appendix to this chapter, relate the pairs $\{\eta_i(p'R),\rho_i(pR)\}$, $\{\sigma_{ijk}(p'R),\nu_{ijk}(pR)\}$, and $\{\xi_{ijk\ell}(p'R),\phi_{ijk\ell}(pR)\}$. For example $\rho_i(pR)$ is given by

$$\rho_i(pR) = -\hat{R}_i\left(\frac{\sin pR}{pR} + \frac{\cos pR}{p^2R^2}\right) \tag{4.3.13}$$

All of these quantities will be used in the following sections, with the explicit forms of $\nu_{ijk}(pR)$ and $\phi_{ijk\ell}(pR)$ given in the appendix to the chapter.

4.4 Magnetic-dipole contributions

In general the selection rules which apply to optical transitions in molecules will exclude magnetic-dipole interactions if electric-dipole coupling is allowed. This is a consequence of the symmetry of the two operators; the former is symmetric to inversion whilst the latter is antisymmetric and so coupling is not allowed by both to states of the same symmetry. However in optically active (chiral) molecules, which possess no improper axis of rotation, these selection rules are broken and both electric-dipole and magnetic-dipole interactions are allowed. Certain optical properties unique to chiral molecules are observed as a consequence; optical rotation, circular dichroism and differential Rayleigh and Raman scattering are examples [61-63] (such optical behaviour may also be induced in achiral molecules from interaction with adjacent chiral molecules eg benzophenone shows circular dichroism as a solute in the chiral solvent 2-octanol).

The dispersion interaction between two molecules is also dependent on the chirality of the pair. If a molecule has enantiomers R and S then the interaction of molecule A(R) with B(R) differs from the interaction of A(R) with B(S). Similarly there is discrimination between the interactions A(R)-A(R) and A(R)-A(S). Although smaller by 2-3 orders of magnitude than the electric-dipole coupling, the magnetic-dipole interaction must be taken into account to explain such phenomena: it is the interference of the electric-magnetic terms in the transition matrix elements which produces these effects.

To extend the near- and far-zone discriminatory results of Craig et al [11], we have chosen to investigate the magnetic-dipole contributions to the dispersion interaction at all intermolecular separations outside overlap. This will be followed by an account of the interaction between two achiral molecules, one of which having a large magnetic susceptibility, which although does not show discrimination, is of the same order. Firstly though, there follows an account of the interaction between an achiral molecule and the enantiomeric pair of a different species.

Each of the derivations follows the method outlined in the previous Section. A comparison with the dipole-dipole case shows differences stemming from the nature of the mode expansions for the magnetic and electric displacement fields, such as the summations over polarization vectors, and of course the inclusion of the magnetic-dipole transition moments.

a) *Interaction between an electric dipole polarizable molecule and a chiral molecule.*

As given by (4.3.1) the interaction Hamiltonian now includes the term $-\underset{\sim}{m}(\underset{\sim}{B}).\underset{\sim}{b}(\underset{\sim}{R}_B)$ for molecule B. Hence the required time-ordered graphs may be deduced from Fig 4.1 (page 97); this interaction may replace the electric-dipole interaction $-\varepsilon_0^{-1}\underset{\sim}{\mu}(\underset{\sim}{B}).\underset{\sim}{d}(\underset{\sim}{R}_B)$ at either vertex for B, giving a total of twenty-four graphs to consider. The resulting two sets of (twelve) graphs are dealt with separately at first until it is possible to combine them, giving a non-zero result for oriented molecules. Rotational averaging leads to a vanishing result.

It is instructive to initially consider the contribution from one of the pairs of twelve graphs. For the arbitrarily chosen pair (vi)a and (vi)b the interactions are shown in Fig 4.2, overleaf, and for clarity the electric-dipole interactions have been omitted.

Using Fig 4.2 for the graphs (vi,a-b) we obtain the combined fourth-order contribution

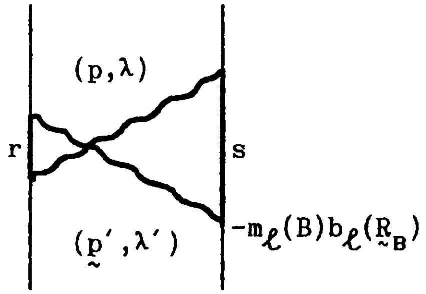
$$\Delta E\ (vi,a\text{-}b)$$

$$= -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar^2 c p p'}{4\varepsilon_0^2 V^2}\right)\mu_i^{or}\mu_j^{ro}$$

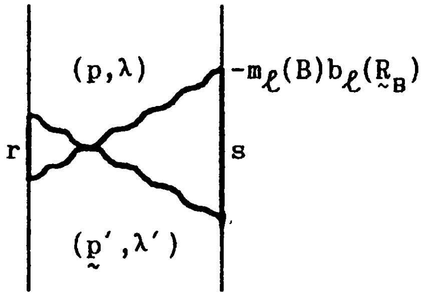
$$\times\left\{\varepsilon_{i\ell m}\mu_k^{os}m_\ell^{so}\hat{p}_m\tilde{\alpha}'_{jk} + \varepsilon_{j\ell m}m_\ell^{os}\mu_k^{so}\hat{p}'_m\tilde{\alpha}_{ik}\right\}e^{-i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}}D_{vi}^{-1}\ , \qquad (4.4.1)$$

using the definition (4.2.5) for $\tilde{\alpha}'_{jk}$ and $\tilde{\alpha}_{ik}$. Similar results are

FIG 4.2 : TIME-ORDERED GRAPHS FOR THE DISPERSION INTERACTION:
HIGHER ORDER INTERACTION WITH ONE MAGNETIC-DIPOLE VERTEX



(via)



(vib)

obtained from the remaining graphs by choosing the index ℓ for the magnetic-dipole interaction. The first term of (4.4.1) arises from (vi)a. For example, since the $(\underset{\sim}{p},\lambda)$ photon is created at the $-m_{\ell}(\underset{\sim}{B})b_{\ell}(\underset{\sim}{R}_B)$ vertex, the sum resulting over the polarizations $\lambda = 1,2$ gives $\varepsilon_{i\ell m}\hat{p}_m$ as a factor. The next aim is to combine all twelve sets of terms.

The two terms of (4.4.1) may be combined by observing that

$$\varepsilon_{i\ell m}\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_{\ell}^{so}\hat{p}_m\tilde{\alpha}'_{jk} = \varepsilon_{j\ell m}\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_{\ell}^{so}\hat{p}'_m\tilde{\alpha}_{ik} \qquad (4.4.2)$$

upon interchange of both the dummies i and j and the labels $\underset{\sim}{p}$ and $\underset{\sim}{p}'$. Of course $\underset{\sim}{p}$ and $\underset{\sim}{p}'$ must be interchanged everywhere, including in the exponent, as must the moduli p and p′ in the denominator, which is unchanged. Now since the electric-dipole transition moments are real and the magnetic-dipole transition moments are imaginary, (4.4.1) becomes

$$\Delta E\ (vi,a\text{-}b)$$

$$= -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar^2 cpp'}{4\varepsilon_0^2 V^2}\right)\varepsilon_{j\ell m}\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_{\ell}^{so}\hat{p}'_m\tilde{\alpha}_{ik}\left\{e^{i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}} - e^{-i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}}\right\}D_{vi}^{-1}. \qquad (4.4.3)$$

The two terms of (4.4.3) reinforce following the changes $\underset{\sim}{p}' \Rightarrow -\underset{\sim}{p}'$ in the first term and $p \Rightarrow -p$ in the second noting that $\tilde{\alpha}_{ik}$ is invariant to this latter change. The numerical coefficient is then +1/2. Adding the remaining terms gives a total

ΔE (Total) =

$$= -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar^2 cpp'}{2\varepsilon_0^2 V^2}\right)\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_\ell^{so}\varepsilon_{j\ell m}\hat{p}'_m\tilde{\alpha}_{ik}e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}S_5 \ , \qquad (4.4.4)$$

with the corresponding coefficients given in Table 4.3.1 in the column headed C_a^5 and the resulting sum given by S_5 in Table 4.3.2. For instance, with the (-) outside in (4.4.4) the entry for (vi), above, is a (-) in the column C_a^5.

Before proceeding let us compare (4.4.4) with (4.2.3), the dipole-dipole interaction. The three major differences are the new sum (S_5 replaces S_1); the interchange of moments for B ($\mu_\ell^{so} \Rightarrow m_\ell^{so}$); and the new form of the angular part resulting from the sum over the product of the electric and magnetic polarization vectors ie $\varepsilon_{j\ell m}\hat{p}'_m\tilde{\alpha}_{ik}$ replaces $\tilde{\alpha}_{ik}\tilde{\alpha}'_{j\ell}$. This final point illustrates the simplification which the magnetic-dipole term brings to the working; the solid angle integrals are simpler functions of the wavevectors. In this case we will require the integral (4.3.5) instead of (4.3.6) for the integral over $d\Omega'$.

To continue, (4.4.4) is simplified by substituting for S_5 and summing over the wavevectors; following this the next step is to perform the angular integration. The result is simplified by substituting for the quantities $\tau_{ik}(pR)$ and $\eta_m(p'R)$ from (4.2.7) and (4.3.11). This gives

$$\Delta E = \frac{i}{4\pi^4\varepsilon_0^2\hbar c^2}\varepsilon_{j\ell m}\sum_{r,s}k_r\frac{\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_\ell^{so}}{(k_r+k_s)}\int_0^\infty\int_0^\infty\tau_{ik}(pR)\eta_m(p'R)p^3p'^3$$

$$\times\left(\frac{1}{(k_r+p)(k_s+p)}-\frac{1}{(k_r+p')(k_s+p')}\right)\left(\frac{1}{p+p'}+\frac{1}{p-p'}\right)dp'dp \ . \qquad (4.4.5)$$

The standard integrals (4.3.12) and (4.8.10) are used to simplify (4.4.5). The even integrands in both are firstly obtained by the combination of the two terms in the final bracket of the above expression, a process which yields the infinite limits. The quantities $\omega_{ik}(pR)$ and $\rho_m(pR)$ in the resulting expression then take their definitions (4.2.9) and (4.3.13) from previous sections. Hence

$$\Delta E = \frac{-i}{4\pi^3\varepsilon_0^2\hbar c^2}\varepsilon_{j\ell m}\sum_{r,s} k_r \frac{\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_\ell^{so}}{(k_r+k_s)}$$

$$\times\int_0^\infty \frac{1}{(k_r+p)(k_s+p)}\Big[\tau_{ik}(pR)\rho_m(pR) + \eta_m(pR)\omega_{ik}(pR)\Big]p^6\,dp \quad . \qquad (4.4.6)$$

Expanding (4.4.6) and collecting the terms gives

$$\Delta E = \frac{i}{4\pi^3\varepsilon_0^2\hbar c^2R^2}\varepsilon_{j\ell m}\hat{R}_m\sum_{r,s} k_r \frac{\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_\ell^{so}}{(k_r+k_s)}\int_0^\infty \frac{1}{(k_r+p)(k_s+p)}$$

$$\times\left[\sin 2pR\left(\frac{\alpha_{ik}+\beta_{ik}}{pR} - \frac{\beta_{ik}}{p^3R^3}\right) + \cos 2pR\left(-\alpha_{ik} + \frac{2\beta_{ik}}{p^2R^2}\right)\right]p^4\,dp \quad , \qquad (4.4.7)$$

which is the analogous form to (4.2.11), with α_{ik} and β_{ik} given by (4.2.6). In subsequent derivations the equivalent expression will be omitted but this double angle form will be assumed. From here it follows easily that the final energy shift is given by

$$\Delta E = \frac{-i}{4\pi^3\varepsilon_0^2\hbar c^2R^2}\varepsilon_{j\ell m}\hat{R}_m\sum_{r,s}\mu_i^{or}\mu_j^{ro}\mu_k^{os}m_\ell^{so}$$

$$\times\int_0^\infty \frac{k_r p^5 e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(\alpha_{ik} + \frac{\alpha_{ik}+\beta_{ik}}{pR} + \frac{2\beta_{ik}}{p^2R^2} + \frac{\beta_{ik}}{p^3R^3}\right)dp \quad , \qquad (4.4.8)$$

which, in terms of the polarizability of molecule A and the mixed electric-magnetic analogue $G_{kl}(B)$ for B, is given by

$$\Delta E = \frac{-\hbar}{16\pi^3\varepsilon_0^2R^2}\varepsilon_{jlm}\hat{R}_m\int_0^\infty \alpha_{ij}^{A}(icp)G_{kl}^{B}(icp)p^4e^{-2pR}\left(\alpha_{ik}+\frac{\alpha_{ik}+\beta_{ik}}{pR}+\frac{2\beta_{ik}}{p^2R^2}+\frac{\beta_{ik}}{p^3R^3}\right)dp. \tag{4.4.9}$$

In (4.4.9) $G_{kl}(B)$ is given by

$$G_{kl}^{oo}(icu) = 2i\sum_r \frac{\hbar cu}{E_{so}^2+(\hbar cu)^2}\mu_k^{os}m_l^{so} . \tag{4.4.10}$$

It is difficult to compare the energy shift (4.4.9) with the dipole-dipole result (4.2.13). The magnitude of the shift depends on the geometrical coefficients, which are complicated. Note though that the polarizability $G_{kl}(B)$ is small compared with $\alpha_{kl}(B)$.

The description of results is limited here to the fluid phase, in which the molecules are allowed to rotate freely. We may see that the energy shift (4.4.9) vanishes under rotational averaging by examining the first term. The rotational average will introduce a factor

$$\delta_{ij}\delta_{kl}\varepsilon_{jlm}\alpha_{ik} = \varepsilon_{ikm}\alpha_{ik} = 0 \tag{4.4.11}$$

to the expression. Now because ε_{ikm} is antisymmetric to interchange of $i \leftrightarrow k$ whereas α_{ik} is symmetric, the term vanishes. Therefore unless the molecules have fixed orientation there is no discriminatory dispersion interaction between a chiral and an achiral molecule. The discriminatory contribution for oriented molecules may be obtained from (4.4.9) by rewriting the expression in terms of the rotatory strength for molecule B (see the following subsection (b) for its definition) a quantity which changes sign with enantiomer.

b) *Interaction between two chiral molecules.*

Progressing from this result we next determine the interaction between two chiral molecules. The intermediate states of both molecules may now couple to the molecular ground state through electric- or magnetic-dipole, due to the low molecular symmetry. The Hamiltonian now contains the additional term $-\underset{\sim}{m}(\underset{\sim}{A}).\underset{\sim}{b}(\underset{\sim}{R}_A)$; we allow a magnetic-dipole interaction at each centre. Because there are two vertices at each centre there are four times as many graphs to consider as in the pure electric-dipole case; there are forty-eight in total. The graphs (vi,a-d) are shown in Fig 4.3 and their contribution is given below.

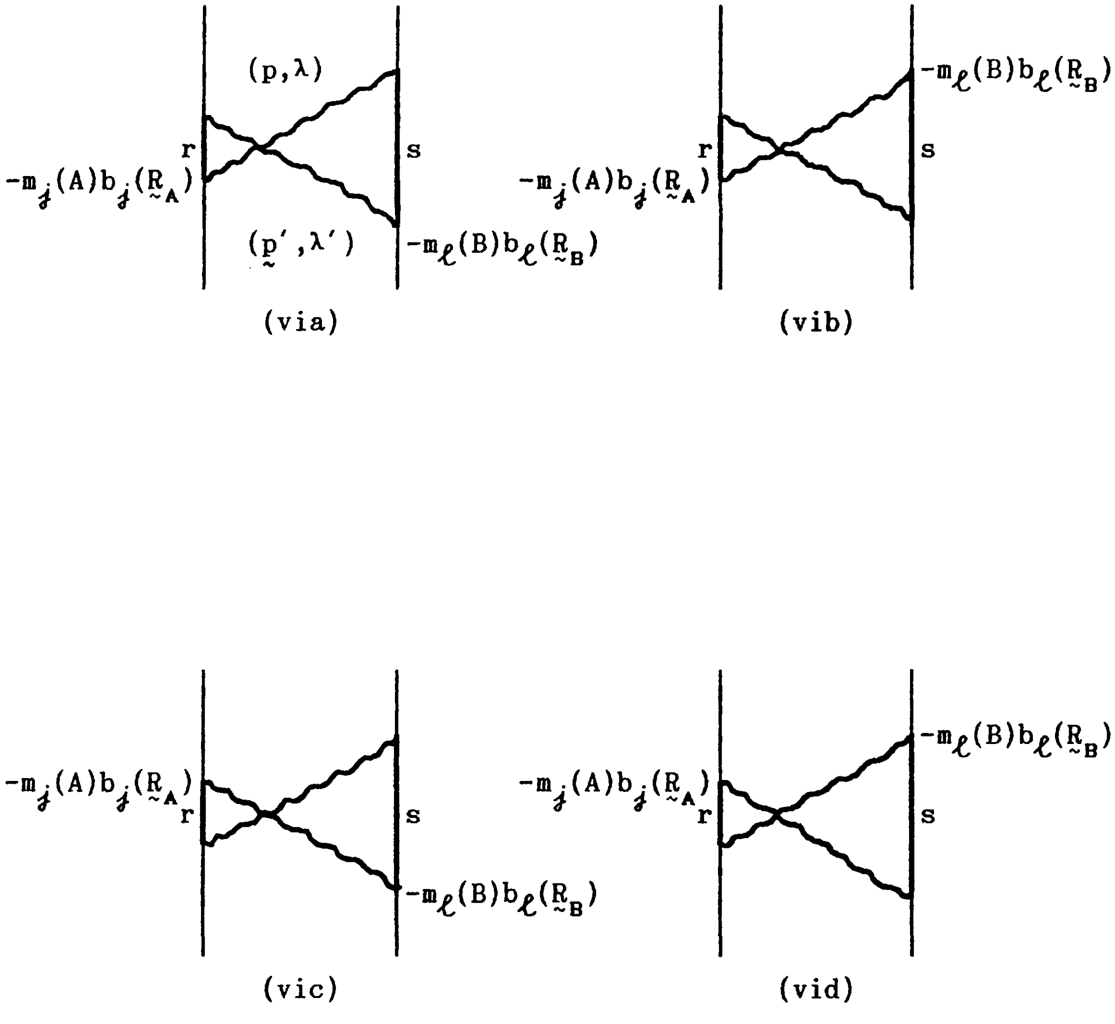
The resulting energy shift consists of two parts, one symmetric and one antisymmetric to interchange of p and p′. The two parts are treated separately at first, following the same procedure as above and are then combined to give the final result. The rotationally-averaged result is quoted and the near- and far-zone results are then determined.

Using Fig 4.3 for the graphs (vi,a-d) the fourth-order energy shift is given by

$$\begin{aligned}\Delta E\ (vi,a\text{-}d) &\\ = +\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}&\left(\frac{\hbar^2pp'}{4\varepsilon_0^2V^2}\right)\mu_i^{or}m_j^{ro}\mu_k^{os}m_\ell^{so}\\ &\times\left\{\tilde{\alpha}_{ik}\tilde{\alpha}'_{j\ell}-\varepsilon_{i\ell m}\varepsilon_{kjn}\hat{p}_m\hat{p}'_n-\varepsilon_{i\ell m}\varepsilon_{kjn}\hat{p}'_m\hat{p}_n+\tilde{\alpha}'_{ik}\tilde{\alpha}_{j\ell}\right\}e^{-i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}}D_{vi}^{-1}.\end{aligned}\tag{4.4.12}$$

Examining this expression we see that it contains two types of terms; the second and third, corresponding to the graphs (vi)a and (vi)d respectively, are of the mixed electric-magnetic type,

FIG 4.3 : TIME-ORDERED GRAPHS FOR THE DISPERSION INTERACTION:
GRAPHS LEADING TO DISCRIMINATORY EFFECTS



resembling in part the form of the terms in case (a); graphs (vi)b and (vi)c lead to the first and fourth terms of (4.4.12) and take the form of dipole-dipole interactions. In the latter type one photon is created and annihilated by magnetic-dipole coupling with the field and the other by electric-dipole coupling. Now the sums over electric and magnetic dipole polarization vectors are identical; hence the form of (4.4.12).

The terms inside the curly brackets in (4.4.12) are common to each set of combined results for the graphs a-d, provided we choose the indices j and ℓ for the magnetic-dipole interactions, and so the total energy shift may be written as one expression. The sum is then broken into two parts, one symmetric- and one anti-symmetric to the interchanges $\underset{\sim}{p} \Rightarrow -\underset{\sim}{p}$ and/or $\underset{\sim}{p}' \Rightarrow -\underset{\sim}{p}'$. Making the appropriate changes to each of the component terms such that the exponential part is common leads to a total energy shift which is given by

$$\Delta E \text{ (Total)} = \Delta E_s + \Delta E_a \ , \tag{4.4.13}$$

with

$$\Delta E_s = -\sum_{r,s} \sum_{\underset{\sim}{p}\underset{\sim}{p}'} \left(\frac{\hbar^2 pp'}{4\varepsilon_0^2 V^2} \right) \mu_i^{or} m_j^{ro} \mu_k^{os} m_\ell^{so} \left\{ \tilde{\alpha}_{ik} \tilde{\alpha}'_{j\ell} + \tilde{\alpha}'_{ik} \tilde{\alpha}_{j\ell} \right\} e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}} S_2 , \tag{4.4.14}$$

$$\Delta E_a = +\sum_{r,s} \sum_{\underset{\sim}{p}\underset{\sim}{p}'} \left(\frac{\hbar^2 pp'}{4\varepsilon_0^2 V^2} \right) \mu_i^{or} m_j^{ro} \mu_k^{os} m_\ell^{so} \varepsilon_{i\ell m} \varepsilon_{kjn} \left\{ \hat{p}_m \hat{p}'_n + \hat{p}'_m \hat{p}_n \right\} e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}} S_3 , \tag{4.4.15}$$

where S_2 and S_3 are the sums corresponding to the coefficients C_a^2 and C_a^3 of the appropriate terms and are given in Table 4.3.2 .

We follow the method used above; after substituting for the sums the angular integration is followed by performing the p- or p′-integral. Straightforward manipulation gives the final result.

Considering the symmetric term firstly, it may be written as

$$\Delta E_s = \frac{-1}{4\pi^4\varepsilon_0^2\hbar c^3}\sum_{r,s}\frac{\mu_i^{or}m_j^{ro}\mu_k^{os}m_\ell^{so}}{(k_r+k_s)}\int_0^\infty\int_0^\infty\left\{\tau_{ik}(pR)\tau_{j\ell}(p'R)+\tau_{ik}(p'R)\tau_{j\ell}(pR)\right\}$$

$$\times\left(\frac{p}{(k_r+p)(k_s+p)}\right)\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)p^3p'^3\,dp'\,dp \qquad (4.4.16)$$

which we see is very similar to the dipole-dipole equivalent form (4.2.8), as noted above. The factor p replaces (k_r+k_s+p) as a result of the new sum, and of course the transition moments are different. Hence we may write down the energy shift directly as

$$\Delta E_s = \frac{-1}{4\pi^3\varepsilon_0^2\hbar c^3}\sum_{r,s}\frac{\mu_i^{or}m_j^{ro}\mu_k^{os}m_\ell^{so}}{(k_r+k_s)}$$

$$\times\int_0^\infty\frac{1}{(k_r+p)(k_s+p)}\left[\tau_{ik}(pR)\omega_{j\ell}(pR)+\omega_{ik}(pR)\tau_{j\ell}(pR)\right]p^7\,dp\,. \qquad (4.4.17)$$

by inference. Expansion of (4.4.17) and collection of the terms leads to the final result below.

$$\Delta E_s = \frac{-1}{4\pi^3\varepsilon_0^2\hbar c^3R^2}\sum_{r,s}\mu_i^{or}m_j^{ro}\mu_k^{os}m_\ell^{so}\int_0^\infty\frac{p^6e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}$$

$$\times\left(A_{ikj\ell}+\frac{B_{ikj\ell}}{pR}+\frac{B_{ikj\ell}+C_{ikj\ell}}{p^2R^2}+\frac{2C_{ikj\ell}}{p^3R^3}+\frac{C_{ikj\ell}}{p^4R^4}\right)dp\;, \qquad (4.4.18)$$

with

$$\begin{aligned} A_{ikjl} &= \alpha_{ik}\alpha_{jl} \\ B_{ikjl} &= \alpha_{ik}\beta_{jl}+\beta_{ik}\alpha_{jl} \quad . \\ C_{ikjl} &= \beta_{ik}\beta_{jl} \end{aligned} \tag{4.4.19}$$

The result is similar to (4.2.13); p^6 replaces $k_r k_s p^4$ in the integrand but the two are dimensionally equivalent. Of course this is not the full result. We must add the remaining terms before making any comparisons.

Returning to the antisymmetric part we regain the cross terms

$$\Delta E_a = +\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar^2 pp'}{4\varepsilon_0^2 V^2}\right)\mu_i^{or} m_j^{ro} \mu_k^{os} m_l^{so} \varepsilon_{ilm}\varepsilon_{kjn}\left\{\hat{p}_m\hat{p}'_n + \hat{p}'_m\hat{p}_n\right\} e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}} S_3 \tag{4.4.20}$$

which should prove no difficulty since it was noted in (a) that such terms provide simpler working.

Substituting for S_3 and integrating using (4.3.5) for both photons gives

$$\Delta E_a = \frac{-1}{4\pi^4\varepsilon_0^2\hbar c^3}\left\{\varepsilon_{ilm}\varepsilon_{kjn}+\varepsilon_{iln}\varepsilon_{kjm}\right\}\sum_{r,s}\frac{\mu_i^{or} m_j^{ro} \mu_k^{os} m_l^{so}}{(k_r+k_s)}\int_0^\infty\int_0^\infty \eta_m(pR)\eta_n(p'R)p^3 p'^3$$
$$\times\left(\frac{p'}{(k_r+p')(k_s+p')}\right)\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)dp\,dp' \tag{4.4.21}$$

after interchanging $m \leftrightarrow n$ in the second term of (4.4.20) for simplicity. The two terms of (4.4.21) may be combined since the integrand is even in p and the use of (4.8.10) to evaluate the p-integral gives

$$\Delta E_a = \frac{1}{4\pi^3\varepsilon_0^2\hbar c^3}\left\{\varepsilon_{i\ell m}\varepsilon_{kjn}+\varepsilon_{i\ell n}\varepsilon_{kjm}\right\}\sum_{r,s}\frac{\mu_i^{or}m_j^{ro}\mu_k^{os}m_\ell^{so}}{(k_r+k_s)}$$

$$\times\int_0^\infty\frac{1}{(k_r+p')(k_s+p')}\Big[\rho_m(p'R)\eta_n(p'R)\Big]p'^7dp' \ . \qquad (4.4.22)$$

Dropping the primes and simply substituting for $\rho_m(pR)$ and $\eta_n(pR)$ gives the final result

$$\Delta E_a = \frac{-1}{4\pi^3\varepsilon_0^2\hbar c^3R^2}\,\varepsilon_{i\ell m}\varepsilon_{kjn}\hat{R}_m\hat{R}_n\sum_{r,s}\mu_i^{or}m_j^{ro}\mu_k^{os}m_\ell^{so}$$

$$\times\int_0^\infty\frac{p^6e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(1+\frac{2}{pR}+\frac{1}{p^2R^2}\right)dp \ . \qquad (4.4.23)$$

Now defining

$$D_{ikj\ell} = \varepsilon_{i\ell m}\varepsilon_{kjn}\hat{R}_m\hat{R}_n \qquad (4.4.24)$$

and combining this result with (4.4.18) gives the total result

$$\Delta E = \frac{-1}{4\pi^3\varepsilon_0^2\hbar c^3R^2}\sum_{r,s}\mu_i^{or}m_j^{ro}\mu_k^{os}m_\ell^{so}\int_0^\infty\frac{p^6e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}$$

$$\times\left(A_{ikj\ell}+D_{ikj\ell}+\frac{B_{ikj\ell}+2D_{ikj\ell}}{pR}+\frac{B_{ikj\ell}+C_{ikj\ell}+D_{ikj\ell}}{p^2R^2}+\frac{2C_{ikj\ell}}{p^3R^3}+\frac{C_{ikj\ell}}{p^4R^4}\right)dp.$$

$$(4.4.25)$$

The result may be given in a number of forms, for example in terms of moments, polarizabilities or rotatory strengths. Its form above is similar to (4.2.13), although the coefficients of the terms are different; we can see that the near-zone result (obtained from the final term) will similarly have an R^{-6} dependence on intermolecular separation, although it will be orders of magnitude smaller due to the magnetic-dipole interactions. The near- and far-zone results will be given shortly.

In terms of the mixed electric-magnetic polarizability for each molecule given by (4.4.10) the oriented result is given by

$$\Delta E = \frac{\hbar}{16\pi^3\varepsilon_0^2cR^2}\int_0^\infty G_{ij}^{A}(icp)G_{k\ell}^{B}(icp)p^4e^{-2pR}$$
$$\times\left(A_{ikj\ell}+D_{ikj\ell}+\frac{B_{ikj\ell}+2D_{ikj\ell}}{pR}+\frac{B_{ikj\ell}+C_{ikj\ell}+D_{ikj\ell}}{p^2R^2}+\frac{2C_{ikj\ell}}{p^3R^3}+\frac{C_{ikj\ell}}{p^4R^4}\right)dp. \tag{4.4.26}$$

It is this term which accounts for the discriminatory dispersion interaction [11], since the polarizability $G_{ij}^{oo}(icp)$ changes sign with enantiomer. A fuller description accompanies the summary in Section 4.7, which compares all of the results.

Let us apply this result to the fluid phase. Rotationally averaging (4.4.25) gives such an interaction of freely rotating molecules in terms of the transition moments. We obtain

$$\Delta E = \frac{-1}{18\pi^3\varepsilon_0^2\hbar c^3R^4}\sum_{r,s}(\underset{\sim}{\mu}^{or}\cdot\underset{\sim}{m}^{ro})(\underset{\sim}{\mu}^{os}\cdot\underset{\sim}{m}^{so})\int_0^\infty\frac{p^4e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(4+\frac{6}{pR}+\frac{3}{p^2R^2}\right)dp. \tag{4.4.27}$$

In the limits of small and large intermolecular separation (4.4.27) takes the forms shown overleaf.

NEAR-ZONE LIMIT

$$\Delta E_{N-Z} = \frac{1}{12\pi^2\varepsilon_0^2 c^2 R^6} \sum_{r,s} \frac{R^{ro}R^{so}}{(E_{ro} + E_{so})} . \qquad (4.4.28)$$

FAR-ZONE LIMIT

$$\Delta E_{F-Z} = \frac{\hbar^3 c}{3\pi^3\varepsilon_0^2 R^9} \sum_{r,s} \frac{R^{ro}R^{so}}{(E_{ro}^2 \; E_{so}^2)} . \qquad (4.4.29)$$

R^{ro} and R^{so} are the rotatory strengths for the two molecules defined by

$$R^{to} = \mathrm{Im}(\underset{\sim}{\mu}^{ot}.\underset{\sim}{m}^{to}) \; ; \qquad (4.4.30)$$

the rotatory strengths are thus real quantities, since the magnetic dipole transition moments are complex, and change sign with enantiomer since $\underset{\sim}{\mu}$ is antisymmetric to inversion whereas $\underset{\sim}{m}$ is symmetric. The sign of the dispersion interaction in (4.4.28/29) thus changes with enantiomer, although relative sign cannot be determined if the two molecules are chemically different. For like molecules we see that the R-R and S-S interactions are repulsive, whilst the different enantiomers attract. Note that the far-zone interaction now has R^{-9} dependence on intermolecular separation.

c) *Interaction between an electric dipole polarizable molecule and a magnetic dipole polarizable molecule.*

The discriminatory result obtained above relied on the constraint that the two magnetic-dipole vertices were on different centres. Here we consider the remaining case where such interactions are confined to one centre; molecule B. This interaction is of the same order as that in (b) and is important for molecules with large magnetic susceptibilities. The twelve required time-ordered graphs are deduced directly from Fig 4.1; graph (vi) for this case is given in Fig 4.4.

The contributions to the energy shift are determined and added in the usual way, with the result expressed in terms of the polarizability α of molecule A and the magnetic susceptibility χ of molecule B, which will be defined when required. Again near- and far-zone results are given.

Using Fig 4.4 for graph (vi) we obtain

$$\Delta E\ (\mathrm{vi}) = -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar^2 pp'}{4\varepsilon_0^2 V^2}\right)\mu_i^{or}\mu_j^{ro}m_k^{os}m_l^{so}\varepsilon_{ilm}\varepsilon_{jkn}\hat{p}_m\hat{p}'_n e^{-i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}}D_{vi}^{-1}, \tag{4.4.31}$$

which, as we expect, is very similar to the cross terms of case (b) above, and so the derivation will largely follow that of ΔE_a in that case. Similar terms arise from the eleven other graphs, all with a negative coefficient. Note that (4.4.31) changes sign when we substitute $\underset{\sim}{p} \Rightarrow -\underset{\sim}{p}$. Combining the terms in the usual way gives

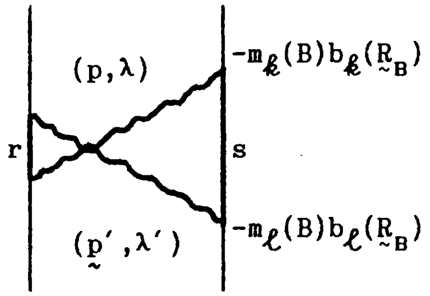
$$\Delta E\ (\mathrm{Total}) = -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar^2 pp'}{4\varepsilon_0^2 V^2}\right)\mu_i^{or}\mu_j^{ro}m_k^{os}m_l^{so}\varepsilon_{ikm}\varepsilon_{jln}\hat{p}_m\hat{p}'_n e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}S_4\ , \tag{4.4.32}$$

if we note also that

$$\varepsilon_{ilm}\varepsilon_{jkn}m_k^{os}m_l^{so} = \varepsilon_{ikm}\varepsilon_{jln}m_k^{os}m_l^{so}\ , \tag{4.4.33}$$

since this term contains a product of magnetic-dipole transition moments. Again, S_4 is given in Table 4.3.2 . Substituting for S_4 and proceeding;

FIG 4.4 : TIME-ORDERED GRAPH FOR THE DISPERSION INTERACTION:
MOLECULE WITH LARGE MAGNETIC SUSCEPTIBILITY



(vi)

$$\Delta E = \frac{1}{4\pi^4\varepsilon_0^2\hbar c^3}\varepsilon_{ikm}\varepsilon_{jln}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}m_k^{os}m_l^{so}}{(k_r+k_s)}\int_0^\infty\int_0^\infty \eta_n(p'R)\eta_m(pR)p^3p'^3$$

$$\times\left(\frac{(k_r+k_s+p')}{(k_r+p')(k_s+p')}\right)\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)dp\,dp' \ , \qquad (4.4.34)$$

which is directly comparable with (4.4.21). Hence, deducing the integrated form of (4.4.34) and dropping the primes, we get

$$\Delta E = \frac{-1}{4\pi^3\varepsilon_0^2\hbar c^3}\varepsilon_{ikm}\varepsilon_{jln}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}m_k^{os}m_l^{so}}{(k_r+k_s)}\int_0^\infty\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}\eta_n(pR)\rho_m(pR)p^6dp$$

$$(4.4.35)$$

The R-dependence of (4.4.35) is identical to that in (4.4.22); the final form of the integral is then

$$\Delta E = \frac{1}{8\pi^3\varepsilon_0^2\hbar c^3R^2}\varepsilon_{ikm}\varepsilon_{jln}\hat{R}_m\hat{R}_n\sum_{r,s}\mu_i^{or}\mu_j^{ro}m_k^{os}m_l^{so}$$

$$\times\int_0^\infty\frac{k_rk_sp^4e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(1+\frac{2}{pR}+\frac{1}{p^2R^2}\right)dp \ . \qquad (4.4.36)$$

which is the oriented result for the interaction between an electric-dipole polarizable molecule and a magnetic-dipole polarizable molecule. Observe that in the near-zone the interaction takes the inverse fourth power in the intermolecular separation, as will be shown below. Rotationally averaging this result gives

$$\Delta E = \frac{1}{36\pi^3\varepsilon_0^2\hbar c^3 R^2}\sum_{r,s}|\underset{\sim}{\mu}^{ro}|^2|\underset{\sim}{m}^{so}|^2\int_0^\infty \frac{k_r k_s p^4 e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(1+\frac{2}{pR}+\frac{1}{p^2R^2}\right)dp. \tag{4.4.37}$$

The oriented result in terms of the polarizability for A and the magnetic susceptibility $\chi_{k\ell}(B)$ for B is given by

$$\Delta E = \frac{\hbar}{32\pi^3\varepsilon_0^2 cR^2}\varepsilon_{ikm}\varepsilon_{j\ell n}\hat{R}_m\hat{R}_n\int_0^\infty \alpha_{ij}^{A}(icp)\chi_{k\ell}^{B}(icp)p^4e^{-2pR}\left(1+\frac{2}{pR}+\frac{1}{p^2R^2}\right)dp \tag{4.4.38}$$

with

$$\chi_{k\ell}^{B}(icp) = 2\sum_r \frac{E_{so}}{E_{so}^2+(\hbar cu)^2}\, m_k^{os}m_\ell^{so} \tag{4.4.39}$$

Consider the values of (4.4.37) in the limits of small and large intermolecular separation; these are the fluid phase interactions. It is easily shown that (4.4.37) reduces to give the expressions below.

<u>NEAR-ZONE LIMIT</u>

$$\Delta E_{N-Z} = \frac{1}{72\pi^2\varepsilon_0^2\hbar c^3R^4}\sum_{r,s}\frac{E_{ro}E_{so}}{(E_{ro}+E_{so})}|\underset{\sim}{\mu}^{ro}|^2|\underset{\sim}{m}^{so}|^2 . \tag{4.4.40}$$

<u>FAR-ZONE LIMIT</u>

$$\Delta E_{F-Z} = \frac{9\hbar}{64\pi^3 c\varepsilon_0^2}\,\frac{\alpha^A(0)\chi^B(0)}{R^7} , \tag{4.4.41}$$

where the isotropic, static polarizability $\alpha(0)$ and susceptibility

$\chi(0)$ are defined by (4.2.20) and (4.4.42), below, respectively.

$$\chi^{B}(0) = \frac{2}{3}\sum_{s}\frac{|m^{so}|^{2}}{E_{so}} . \tag{4.4.42}$$

The far-zone result (4.4.41) shows an R^{-7} dependence on intermolecular separation. It will be convenient to combine this result later with the diamagnetic contribution to the dispersion interaction, since the two results are of similar form and taken together describe the pure magnetic-dipole interactions of a molecule.

4.5 Electric-quadrupole contributions

A consistent study of the dispersion interaction up to the order of the magnetic-dipole interaction must also include electric-quadrupole contributions, since the two forms of coupling are of the same order, approximately a factor of α, the fine structure constant, times the magnitude of the electric-dipole interaction.

Analogously to the previous section the electric-quadrupole results have three contributions; there may be one or two quadrupole vertices, and these may be confined to one centre or shared by the two molecules. The derivations have similarities with both the pure dipole-dipole case and with the magnetic-dipole interactions discussed in Section 4.4; minor variations arise simply from the nature of the interaction terms.

a) *Interaction between an electric dipole polarizable molecule and a dipole-quadrupole polarizable molecule.*

We start with the case of one electric-quadrupole vertex, at molecule B. As in Section 4.4 (a) we are required to evaluate the contribution from the twenty-four time-ordered graphs which account for this interaction. Since the electric quadrupole interacts with the electric displacement field much of the working follows the form of Section 4.2, with the electric-quadrupole moment replacing the electric-dipole moment in each expression. However, here the relative sign of the contribution from each graph depends on whether the quadrupole interaction creates or annihilates a photon; a creation gives a -i, whereas annihilation gives +i. Further, since the quadrupole interaction contains the gradient operator, the resulting expressions contain an additional wavevector component, brought down from the exponential part of the field expansion, which dimensionally counteracts the additional length which the quadrupole moment has compared with the dipole moment. Once evaluated, these terms must be written in a suitable form so that they may be combined; the working then follows as before.

A consequence of the higher power of $\underset{\sim}{p}$ or $\underset{\sim}{p}'$ is that additional integrals are required. These new standard integrals were presented in Section 4.3 .

From Fig 4.5 (vi) we get

ΔE (vi,a-b)

$$= -i\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar c p}{2\varepsilon_0 V}\right)\left(\frac{\hbar c p'}{2\varepsilon_0 V}\right)\mu_i^{or}\mu_j^{ro}\mu_k^{os}Q_{\ell m}^{so}\left\{B_{ijk\ell m} - A_{ijk\ell m}\right\}e^{-i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}}D_{vi}^{-1} \tag{4.5.1}$$

where

$$B_{ijk\ell m} = p'\tilde{\alpha}_{ik}\tilde{\alpha}'_{jm}\hat{p}'_{\ell} \quad ; \quad A_{ijk\ell m} = p\tilde{\alpha}_{im}\tilde{\alpha}'_{jk}\hat{p}_{\ell} \ , \tag{4.5.2}$$

and $\tilde{\alpha}_{ik}$ and $\tilde{\alpha}'_{jm}$ take the same definition as in Section 4.4. Let us examine (4.5.1) briefly. The (-) comes from the fourth-order perturbation result, whose sign is unaffected by exchange of two photons. That is, the four interactions with the electric displacement field give a numerical factor of +1. In (vi)b the quadrupole vertex annihilates the $(\underset{\sim}{p}',\lambda')$ photon with $\nabla_{\ell}\exp[i\underset{\sim}{p}'.\underset{\sim}{R}]$ giving the ip'_{ℓ} in $B_{ijk\ell m}$. $A_{ijk\ell m}$ appears with a $(-i)$ since in (vi)a the quadrupole vertex creates the $(\underset{\sim}{p},\lambda)$ photon. Each of the remaining pairs of terms include the quantities $A_{ijk\ell m}$ and $B_{ijk\ell m}$, although the signs and the exponential factors vary. Each pair must be manipulated such that the total sum may be written as one expression. Now since

i) $B_{ijk\ell m}$ is antisymmetric to the change $\underset{\sim}{p}' \Rightarrow -\underset{\sim}{p}'$, and
ii) $A_{ijk\ell m}$ is antisymmetric to the change $\underset{\sim}{p} \Rightarrow -\underset{\sim}{p}$,

we may combine all of the terms and write

$$\Delta E\ (\text{Total}) = \Delta E\ (\text{i-xii,a-b})$$

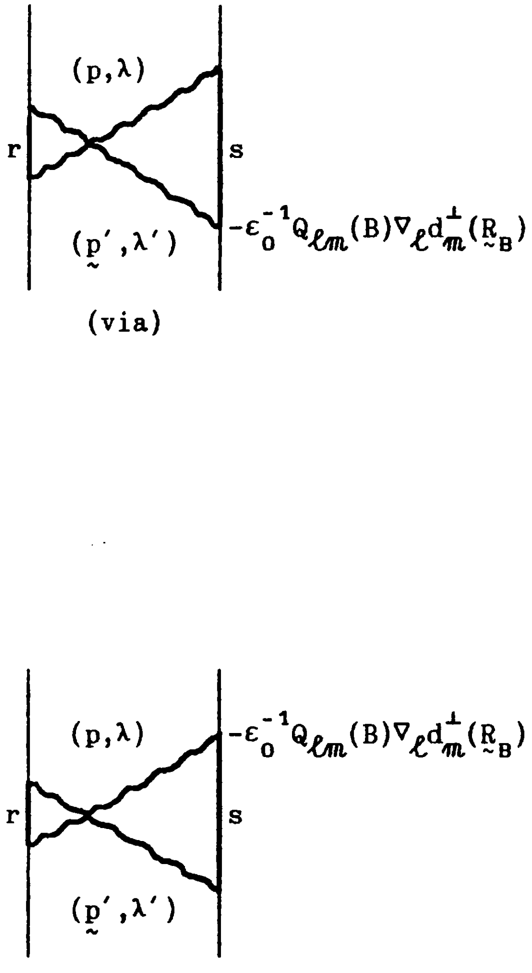
$$= -i\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar cp}{2\varepsilon_0 V}\right)\left(\frac{\hbar cp'}{2\varepsilon_0 V}\right)\mu_i^{or}\mu_j^{ro}\mu_k^{os}Q_{\ell m}^{so}\left\{A_{ijk\ell m} + B_{ijk\ell m}\right\}e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}S_1. \tag{4.5.3}$$

Note that each term now has the same sign; the sum is identical to that in the pure electric-dipole case. Substituting for S_1 in (4.5.3) and performing the angular integration gives

$$\Delta E = \frac{1}{4\pi^4\varepsilon_0^2\hbar c}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}\mu_k^{os}Q_{\ell m}^{so}}{(k_r+k_s)}\int_0^\infty\int_0^\infty p^3p'^3dp'dp\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)$$
$$\times\left[p'\tau_{ik}(pR)\sigma_{jm\ell}(p'R) + p\sigma_{im\ell}(pR)\tau_{jk}(p'R)\right] , \tag{4.5.4}$$

using the definitions (4.2.7) for $\tau_{ij}(pR)$ and (4.3.9) for $\sigma_{ijk}(pR)$. Integration over p' gives

FIG 4.5 : TIME-ORDERED GRAPHS FOR THE DISPERSION INTERACTION.
HIGHER ORDER CONTRIBUTION: ONE ELECTRIC-QUADRUPOLE VERTEX



(via)

(vib)

$$\Delta E = \frac{1}{4\pi^3\varepsilon_0^2\hbar c}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}\mu_k^{os}Q_{\ell m}^{so}}{(k_r+k_s)}$$

$$\times\int_0^\infty\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}\Big[\tau_{ik}(pR)\nu_{jm\ell}(pR) + \sigma_{im\ell}(pR)\omega_{jk}(pR)\Big]p^7dp\ , \qquad (4.5.5)$$

where $\nu_{jm\ell}$ is a quantity which was used in Section 4.4 and is given in full in the appendix. Comparing (4.5.5) with the pure dipole equivalent form, (4.2.10), we see that the quadrupole interaction complicates the expression slightly; p^7 replaces p^6, and we require the quantities $\nu(pR)$ and $\sigma(pR)$ in favour of $\omega(pR)$ and $\tau(pR)$. Before we proceed from here we use the fact that the moments are real to interchange the indices $i \leftrightarrow j$ in (4.5.5) and write the second term as $\sigma_{jm\ell}(pR)\omega_{ik}(pR)$. This eases their combination later.

Written out in full (4.5.5) contains a large number of terms, each with a complicated geometrical coefficient. However it is possible to write (4.5.5) in the usual double angle form, and hence proceed as before, by introducing a matrix form to deal with these terms. A considerable simplication is then achieved by combining these terms to give the result

$$\Delta E = \frac{-1}{4\pi^3\varepsilon_0^2\hbar cR^2}\sum_{r,s}\mu_i^{or}\mu_j^{ro}\mu_k^{os}Q_{\ell m}^{so}$$

$$\times\int_0^\infty\frac{k_rk_sp^5e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(A_{i-m} + \frac{B_{i-m}}{pR} + \frac{C_{i-m}}{p^2R^2} + \frac{D_{i-m}}{p^3R^3} + \frac{E_{i-m}}{p^4R^4} + \frac{F_{i-m}}{p^5R^5}\right)dp\ . \qquad (4.5.6)$$

The general form of (4.5.6) is important. The coefficients A_{i-m} - F_{i-m} are required in order to extract the useful interaction energies in the appropriate cases from this result but take up too much space to be given here; they are derived and given on page 144 at the end of this section. The above form may be written as

$$\Delta E =$$

$$\frac{-\hbar c}{16\pi^3\varepsilon_0^2R^2}\int_0^\infty \alpha_{ij}^{A}(icp)A_{k\ell m}^{B}(icp)p^5e^{-2pR}\left(A_{i-m}+\frac{B_{i-m}}{pR}+\frac{C_{i-m}}{p^2R^2}+\frac{D_{i-m}}{p^3R^3}+\frac{E_{i-m}}{p^4R^4}+\frac{F_{i-m}}{p^5R^5}\right)dp, \tag{4.5.7}$$

where $A_{k\ell m}$ is the mixed dipole-quadrupole dynamic polarizability defined by

$$A_{k\ell m}^{B}(icu) \quad = \quad 2\sum_r \frac{E_{so}}{E_{so}^2+(\hbar cu)^2}\,\mu_k^{os}Q_{\ell m}^{so} \tag{4.5.8}$$

The discussion of results is limited here to the fluid phases. It would be of interest, although tedious, to determine the limiting values of (4.5.6) in the near- and far-zones and compare them with those of (4.2.13). Comparing (4.5.6) with (4.2.13), the dipole-dipole result, it is evident that the term in $(pR)^{-5}$ will cause this interaction to fall off more quickly with intermolecular separation.

If we allow independent molecular rotation, to give the fluid phase interaction, then we must take the rotational average of (4.5.7). This result vanishes. This may be seen by examining the result more closely: the tensors $\alpha_{ij}^{A}(icp)$ and $A_{k\ell m}^{B}(icp)$ are second and third rank respectively. Considering the first term of (4.5.7) as an example, rotational averaging will therefore give a factor of $\delta_{ij}\varepsilon_{k\ell m}A_{i-m}$, the first term of which is, upon expansion of A_{i-m} using (4.5.36) and (4.5.39), $\delta_{ij}\varepsilon_{k\ell m}\alpha_{ik}\hat{R}_j\hat{R}_\ell\hat{R}_m$. Since $\varepsilon_{k\ell m}$ is antisymmetric to interchange of ℓ and m and $\hat{R}_\ell\hat{R}_m$ is symmetric, the term goes out. The remaining terms follow similarly.

b) *Interaction between two dipole-quadrupole polarizable molecules.*

We next consider the case where two molecules interact through electric-dipole *and* electric-quadrupole coupling. Since the electric-quadrupole vertices occur at different molecular centres each equivalent graph from Fig 4.1 (page 97) must have four counterparts here, corresponding to the permutations of assigning the interactions. Hence there are forty-eight contributions to be evaluated, analogously to Section 4.4(b). The relative sign of each now depends on the exact nature of the quadrupole coupling: if the two interactions create and annihilate, respectively, either virtual photon then the term will have a numerical coefficient of (i)(-i) = 1; otherwise we get -1 ie two creations/two annihilations leads to an overall minus.

The interaction terms may be chosen with the indices

$$\begin{aligned} H_{int} = & -\varepsilon_0^{-1}\mu_i(A)d_i^{\perp}(\underset{\sim}{R}_A) \quad -\varepsilon_0^{-1}Q_{jk}(A)\nabla_j d_k^{\perp}(\underset{\sim}{R}_A) \\ & -\varepsilon_0^{-1}\mu_l(B)d_l^{\perp}(\underset{\sim}{R}_B) \quad -\varepsilon_0^{-1}Q_{mn}(B)\nabla_m d_n^{\perp}(\underset{\sim}{R}_B). \end{aligned} \tag{4.5.9}$$

The second and fourth terms of (4.5.9) are represented on the graphs overleaf as 'Quad'. The contribution from these graphs is found to be

$$\Delta E\ (vi,a\text{-}d)$$

$$= -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar cp}{2\varepsilon_0 V}\right)\left(\frac{\hbar cp'}{2\varepsilon_0 V}\right)\mu_i^{or}Q_{jk}^{ro}\mu_l^{os}Q_{mn}^{so}K^-_{ijklmn}e^{-i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}}D_{vi}^{-1} \tag{4.5.10}$$

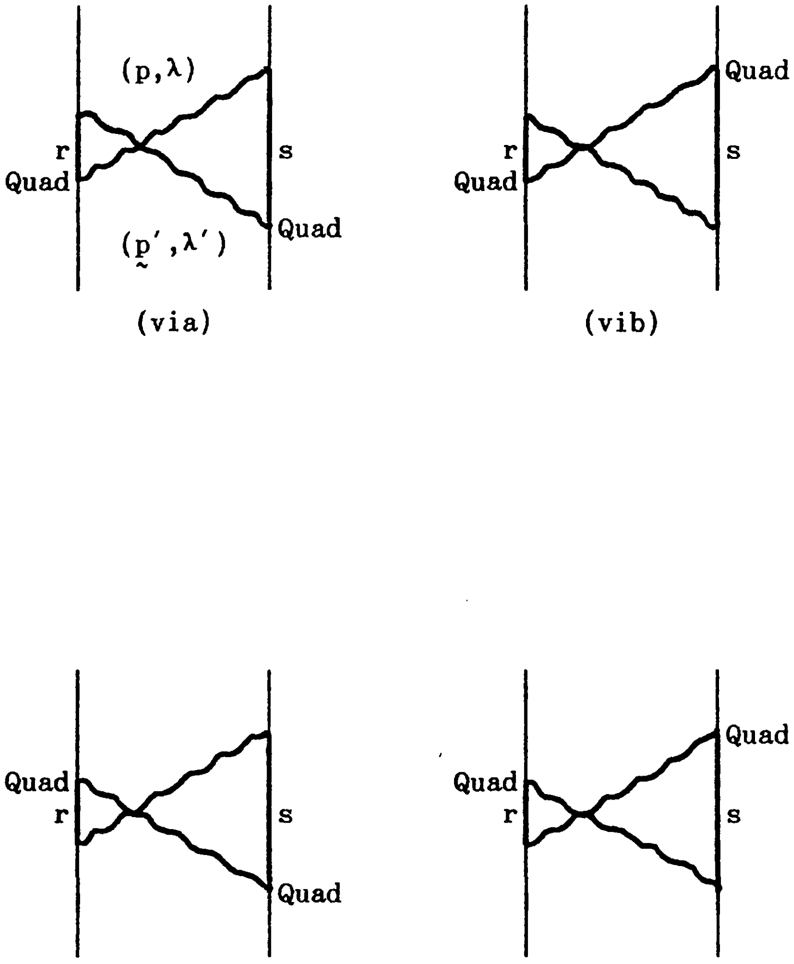
$$\text{with}\quad K^-_{ijklmn} = \left\{-A_{ijklmn} + B_{ijklmn} + C_{ijklmn} - D_{ijklmn}\right\}, \tag{4.5.11}$$

and

$$A_{ijklmn} = p'p\hat{p}'_j\hat{p}_m\tilde{\alpha}_{in}\tilde{\alpha}'_{kl} \quad ; \quad B_{ijklmn} = p'p'\hat{p}'_j\hat{p}'_m\tilde{\alpha}_{il}\tilde{\alpha}'_{kn}; \tag{4.5.12}$$

$$C_{ijklmn} = pp\hat{p}_j\hat{p}_m\tilde{\alpha}_{kn}\tilde{\alpha}'_{il} \quad ; \quad D_{ijklmn} = pp'\hat{p}_j\hat{p}'_m\tilde{\alpha}_{kl}\tilde{\alpha}'_{in} . \tag{4.5.13}$$

FIG 4.6: TIME-ORDERED GRAPHS FOR THE DISPERSION INTERACTION: ELECTRIC DIPOLE-QUADRUPOLE CONTRIBUTION



(via) (vib)

(vic) (vid)

In (4.5.10) the (-) in K^- refers to the sign of the terms A and D. The term $A_{ijk\ell mn}$ arises from the graph (vi)a etc; hence the (-) since the $(\tilde{p}',\lambda')$ photon is created at A and the $(\tilde{p},\lambda)$ photon at B. Similar expressions occur from the other graphs; the pairs (A,D) and (B,C) also occur with the same sign in the remaining eleven sets. We wish to manipulate (4.5.10) in order to write it with K^+ as a factor ie so that all four terms have the same sign. By the normal method we then obtain a total

$$\Delta E\ (\text{i-xii,a-d}) = -\sum_{r,s}\sum_{\tilde{p}\tilde{p}'}\left(\frac{\hbar cp}{2\varepsilon_0 V}\right)\left(\frac{\hbar cp'}{2\varepsilon_0 V}\right)\mu_i^{or}Q_{jk}^{ro}\mu_\ell^{os}Q_{mn}^{so}K^+_{ijk\ell mn}e^{i(\tilde{p}+\tilde{p}').\tilde{R}}S_1, \tag{4.5.14}$$

where we again see that the sum S_1 is identical to the pure dipole case; this is a characteristic of electric multipole interactions. Substituting for S_1 and integrating over the solid angle using the definition (4.3.10) for $\xi_{ijk\ell}$ (page 106) gives

$$\Delta E = \frac{-1}{4\pi^4\varepsilon_0^2\hbar c}\sum_{r,s}\frac{\mu_i^{or}Q_{jk}^{ro}\mu_\ell^{os}Q_{mn}^{so}}{(k_r+k_s)}\int_0^\infty\int_0^\infty p^3p'^3dp'dp\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)$$
$$\times\Big[p'p'\tau_{i\ell}(pR)\xi_{knjm}(p'R)-pp'\sigma_{inm}(pR)\sigma_{k\ell j}(p'R)$$
$$-pp'\sigma_{k\ell j}(pR)\sigma_{inm}(p'R)+pp\xi_{knjm}(pR)\tau_{i\ell}(p'R)\Big] \tag{4.5.15}$$

The p'-integral in the first term of (4.5.15) introduces the new quantity $\phi_{knjm}(pR)$ mentioned briefly in Section 4.3. $\phi_{knjm}(pR)$ takes its definition from (4.8.14). This yields

$$\Delta E = \frac{-1}{4\pi^3\varepsilon_0^2\hbar c}\sum_{r,s}\frac{\mu_i^{or}Q_{jk}^{ro}\mu_\ell^{os}Q_{mn}^{so}}{(k_r+k_s)}\int_0^\infty\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}p^8dp$$

$$\times\Big[\tau_{i\ell}(pR)\phi_{knjm}(pR)-\sigma_{inm}(pR)\nu_{k\ell j}(pR)-\sigma_{k\ell j}(pR)\nu_{inm}(pR)+\xi_{knjm}(pR)\omega_{i\ell}(pR)\Big] \tag{4.5.16}$$

The integrand, as expected, contains the factor p^8 since there is an additional quadrupole interaction compared with the result in (b). The expansion of (4.5.16) is effected in a similar manner to that of (4.5.5), by writing the terms in matrix form. There it was possible to combine both terms. However, here the final form is written as the sum of two terms formed by combination of the first and last and second and third terms respectively of (4.5.16). This leads to the expected form

$$\Delta E = \frac{-1}{8\pi^3\varepsilon_0^2\hbar cR^2}\sum_{r,s}\mu_i^{or}Q_{jk}^{ro}\mu_\ell^{os}Q_{mn}^{so}$$

$$\times\int_0^\infty\frac{k_rk_sp^6e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(A_{i-n}+2\frac{B_{i-n}}{pR}+\frac{C_{i-n}}{p^2R^2}+2\frac{D_{i-n}}{p^3R^3}+\frac{E_{i-n}}{p^4R^4}+2\frac{F_{i-n}}{p^5R^5}+\frac{G_{i-n}}{p^6R^6}\right)dp \tag{4.5.17}$$

where again A_{i-n} - G_{i-n} are given at the end of this section. We then obtain

$$\Delta E = \frac{-\hbar c}{32\pi^3\varepsilon_0^2R^2}\int_0^\infty A_{ijk}^{A}(icp)A_{\ell mn}^{B}(icp)p^6e^{-2pR}$$

$$\left(A_{i-n}+2\frac{B_{i-n}}{pR}+\frac{C_{i-n}}{p^2R^2}+2\frac{D_{i-n}}{p^3R^3}+\frac{E_{i-n}}{p^4R^4}+2\frac{F_{i-n}}{p^5R^5}+\frac{G_{i-n}}{p^6R^6}\right)dp \tag{4.5.18}$$

Again the general form of (4.5.18) is important. The term in $(pR)^{-6}$, which results from this higher-order interaction, will result in a steeper fall-off of the intermolecular interaction than in (b) or compared with the dipole-dipole case.

Let us consider this result for freely-rotating molecules. As an example the first term of (4.5.18), after averaging, contains the factor $2\varepsilon_{ijk}\varepsilon_{\ell mn}\alpha_{i\ell}\hat{R}_k\hat{R}_n\hat{R}_j\hat{R}_m$ which is identically zero. Hence we find that this result vanishes under rotational averaging, as we expect for a dipole-quadrupole coupling at one centre.

c) *Interaction between an electric dipole polarizable molecule and an electric quadrupole polarizable molecule.*

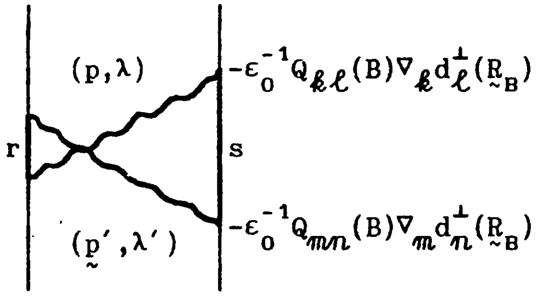
The final case of interest is one where both quadrupole interactions are confined to one centre. This is an important term for a quadrupole polarizable molecule since the interaction is not affected by molecular rotation ie the energy shift is non-zero even after rotational averaging and so may be detected in fluid mixtures. There are twelve graphs which contribute to this interaction, one of which is shown in Fig 4.7 cf Fig 4.4. Again the relative signs of the contributions from these graphs depends on whether the photons are created or annihilated at B.

For graph (vi) we obtain

$$\Delta E\ (vi) = -\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar cp^2}{2\varepsilon_0 V}\right)\left(\frac{\hbar cp'^2}{2\varepsilon_0 V}\right)\mu_i^{or}\mu_j^{ro}Q_{k\ell}^{os}Q_{mn}^{so}\hat{p}_m\hat{p}'_k\tilde{\alpha}_{in}\tilde{\alpha}'_{j\ell}e^{-i(\underset{\sim}{p}-\underset{\sim}{p}').\underset{\sim}{R}}\tilde{D}_{vi}^{-1}, \tag{4.5.19}$$

following the sum over polarizations. Since the two quadrupole interactions are at B then (4.5.19) (and each of the other eleven terms) contains one unit vector $\hat{p}$ with a prime and one without, corresponding to exchange of the two virtual photons. Let us rationalise the sign of (4.5.19). The (-) follows from the sign of the

FIG 4.7 : TIME-ORDERED GRAPH FOR A HIGHER ORDER DISPERSION TERM: ONE-CENTRE ELECTRIC-QUADRUPOLE CONTRIBUTION.



(vi)

perturbation result only. In (vi) we see one photon absorbed and one emitted at B; as discussed this gives a (+) factor.

We wish to write (4.5.19) with the prime on the m-wavevector and with $\exp[i(\underset{\sim}{p}+\underset{\sim}{p}')]$ as a factor in order to combine it with the other terms. By interchanging the indices $k \Leftrightarrow m$ *and* $\ell \Leftrightarrow n$ and changing $\underset{\sim}{p} \Rightarrow -\underset{\sim}{p}$ in (4.5.19) it is possible to write the total as

$$\Delta E\ (i\text{-}xii) = +\sum_{r,s}\sum_{\underset{\sim}{p}\underset{\sim}{p}'}\left(\frac{\hbar c p}{2\varepsilon_0 V}\right)^{2}\left(\frac{\hbar c p'}{2\varepsilon_0 V}\right)^{2}\mu_i^{or}\mu_j^{ro}Q_{k\ell}^{os}Q_{mn}^{so}\hat{p}_k\hat{p}'_m\tilde{\alpha}_{i\ell}\tilde{\alpha}'_{jn}e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}S_1 \tag{4.5.20}$$

since the quadrupole transition moments are real. Substituting for S_1 leads to (4.5.21)

$$\Delta E = \frac{-1}{4\pi^4\varepsilon_0^2\hbar c}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}Q_{k\ell}^{os}Q_{mn}^{so}}{(k_r+k_s)}$$
$$\times\int_0^\infty\int_0^\infty p^4p'^4\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)\sigma_{i\ell k}(pR)\sigma_{jnm}(p'R)\,dp'\,dp\ , \tag{4.5.21}$$

which on p′-integration gives

$$\Delta E = \frac{-1}{4\pi^3\varepsilon_0^2\hbar c}\sum_{r,s}\frac{\mu_i^{or}\mu_j^{ro}Q_{k\ell}^{os}Q_{mn}^{so}}{(k_r+k_s)}\int_0^\infty\frac{(k_r+k_s+p)}{(k_r+p)(k_s+p)}\sigma_{i\ell k}(pR)\nu_{jnm}(pR)p^8\,dp. \tag{4.5.22}$$

The integral in (4.5.22) is identical in form to one of the terms of (4.5.16); the derivation from here onwards is identical, leading to (4.5.23), below, which only differs from (4.5.17) in the pre-integral factor ie the moments are different. The constants $A'_{i-n} - G'_{i-n}$ have already been determined in the calculation of $A_{i-n} - G_{i-n}$ and are given later (page 144). Thus we obtain

$$\Delta E = \frac{-1}{8\pi^3\varepsilon_0^2\hbar c R^2}\sum_{r,s}\mu_i^{or}\mu_j^{ro}Q_{k\ell}^{os}Q_{mn}^{so}$$
$$\times\int_0^\infty \frac{k_r k_s p^6 e^{-2pR}}{(k_r^2+p^2)(k_s^2+p^2)}\left(A'_{i-n}+2\frac{B'_{i-n}}{pR}+\frac{C'_{i-n}}{p^2R^2}+2\frac{D'_{i-n}}{p^3R^3}+\frac{E'_{i-n}}{p^4R^4}+2\frac{F'_{i-n}}{p^5R^5}+\frac{G'_{i-n}}{p^6R^6}\right)dp. \tag{4.5.23}$$

In terms of polarizabilities, this result may be expressed as

$$\Delta E\ (\text{Total})$$
$$= \frac{-\hbar c}{32\pi^3\varepsilon_0^2R^2}\int_0^\infty \alpha_{ij}^{A}(icp)\theta_{k\ell mn}^{B}(icp)p^6e^{-2pR}$$
$$\times\left(A'_{i-n}+2\frac{B'_{i-n}}{pR}+\frac{C'_{i-n}}{p^2R^2}+2\frac{D'_{i-n}}{p^3R^3}+\frac{E'_{i-n}}{p^4R^4}+2\frac{F'_{i-n}}{p^5R^5}+\frac{G'_{i-n}}{p^6R^6}\right)dp \tag{4.5.24}$$

where $\theta_{k\ell mn}$ is the quadrupole-quadrupole polarizability defined by

$$\theta_{ijk\ell}^{oo}(icu) = 2\sum_r \frac{E_{ro}}{E_{ro}^2+(\hbar cu)^2}Q_{ij}^{or}Q_{k\ell}^{ro}\ . \tag{4.5.25}$$

This is the general result for the interaction of a dipole polarizable molecule and a quadrupole polarizable molecule at any separation. Below we shall consider such an interaction for molecules in the fluid phase.

Let us consider the limiting values of (4.5.24). Firstly we take the rotational average. Assuming the notation of Andrews and Thirunamachandran [64] we write

$$\langle\mu_i^{or}\mu_j^{ro}Q_{k\ell}^{os}Q_{mn}^{so}\rangle = \langle l_{i\phi}l_{j\gamma}\rangle\langle l_{k\lambda}l_{\ell\mu}l_{m\nu}l_{n\omega}\rangle\mu_\phi^{or}\mu_\gamma^{ro}Q_{\lambda\mu}^{os}Q_{\nu\omega}^{so} \tag{4.5.26}$$

Now since the quadrupole moment tensor is traceless, it can be shown that (4.5.26) reduces to

$$90^{-1}\delta_{ij}(-2\delta_{k\ell}\delta_{mn} + 3\delta_{km}\delta_{\ell n} + 3\delta_{kn}\delta_{\ell m})|\underset{\sim}{\mu}^{ro}|^{2}Q_{\lambda\mu}^{os}Q_{\lambda\mu}^{so}$$

(4.5.27)

It is then necessary to evaluate $\delta_{ij}(-2\delta_{k\ell}\delta_{mn} +3\delta_{km}\delta_{\ell n} +3\delta_{kn}\delta_{\ell m})A'_{i-n}$ etc in order to determine the far-zone result (which retains all of the terms). The near-zone result requires only the evaluation of the G'_{i-n} term. The resulting expressions are given below.

NEAR-ZONE LIMIT

$$\Delta E = \frac{-3}{8\pi^{2}\varepsilon_{0}^{2}R^{8}}\sum_{r,s}\frac{|\underset{\sim}{\mu}^{ro}|^{2}Q_{\lambda\mu}^{os}Q_{\lambda\mu}^{so}}{(E_{ro}+E_{so})}$$

(4.5.28)

This is the short-range interaction which shows an R^{-8} dependence on intermolecular separation. The far-zone limit (4.5.29) is appropriate for dilute gas mixtures.

FAR-ZONE LIMIT

$$\Delta E = \frac{-1593}{1280}\frac{\hbar c}{\pi^{3}\varepsilon_{0}^{2}R^{9}}\alpha^{A}(0)\theta_{\lambda\mu\lambda\mu}^{B}(0)$$

(4.5.29)

with $\theta_{\lambda\mu\lambda\mu}^{B}(0)$ defined by

$$\theta_{\lambda\mu\lambda\mu}^{B}(0) = \frac{1}{15}\sum_{r,s}\frac{Q_{\lambda\mu}^{os}Q_{\lambda\mu}^{so}}{E_{so}}$$

(4.5.30)

The numerical factor in (4.5.29) differs from that obtained by Thirunamachandran [65] by a factor of sixteen. This factor arises from the change of unit (SI vs Gaussian).

CONSTANTS OBTAINED FOR THE ORIENTED QUADRUPOLE RESULTS

The results (4.5.7), (4.5.18) and (4.5.24) are incomplete in that the coefficients for each term have not been given. The general form of each result may be seen clearly: each is a function of the products of the electric-dipole, electric-quadrupole or mixed dipole-quadrupole polarizabilities for the molecules and a sum of terms with increasing negative power in (pR), which have coefficients N_{i-m} (N = A - F), N_{i-n} and N'_{i-n} (N, N′ = A - G) which have a numerical factor and a factor which depends on the orientation of the intermolecular axis. It is of interest to give these coefficients and to outline how they were obtained since the complete expressions then contain all the information required to determine the quadrupolar, intermolecular interactions of molecules at any separation, whether oriented or allowed to freely rotate.

The determination of these coefficients relies on the evaluation of the expanded forms of the products $\tau_{ik}(pR)\nu_{jm\ell}(pR)$ and $\sigma_{im\ell}(pR)\omega_{jk}(pR)$ in (4.5.5), $\tau_{i\ell}(pR)\phi_{knjm}(pR)$, $\sigma_{inm}(pR)\nu_{k\ell j}(pR)$, $\sigma_{k\ell j}(pR)\nu_{inm}(pR)$ and $\xi_{knjm}(pR)\omega_{i\ell}(pR)$ in (4.5.16) and $\sigma_{i\ell k}(pR)\nu_{jnm}$ in (4.5.22), where each of the Greek quantities takes its previous definition with the appropriate choices of index.

Such products may be determined by rewriting the latter quantities in a matrix form with the help of some new definitions. Let us define the column vectors U_{ij}, V_{ijk} and $W_{ijk\ell}$ by

$$U_{ij} = \begin{pmatrix} \alpha_{ij} \\ \beta_{ij} \end{pmatrix} , \qquad V_{ijk} = \begin{pmatrix} a_{ijk} \\ b_{ijk} \\ c_{ijk} \end{pmatrix} , \qquad W_{ijkl} = \begin{pmatrix} a_{ijkl} \\ b_{ijkl} \\ c_{ijkl} \\ d_{ijkl} \\ e_{ijkl} \end{pmatrix} \tag{4.5.31}$$

with

$$\alpha_{ij} = (\delta_{ij} - \hat{R}_i \hat{R}_j) \quad ; \qquad \beta_{ij} = (\delta_{ij} - 3\hat{R}_i \hat{R}_j) \ , \tag{4.5.32}$$

$$\begin{aligned} a_{ijk} &= \hat{R}_i \hat{R}_j \hat{R}_k \\ b_{ijk} &= (\delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i) \qquad , \text{ and} \\ c_{ijk} &= -\delta_{ij}\hat{R}_k \end{aligned} \tag{4.5.33}$$

$$\begin{aligned} a_{ijkl} &= -\hat{R}_i \hat{R}_j \hat{R}_k \hat{R}_l \\ b_{ijkl} &= (\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}) \\ c_{ijkl} &= -\delta_{ij}\delta_{kl} \\ d_{ijkl} &= (\delta_{ik}\hat{R}_j\hat{R}_l + \delta_{il}\hat{R}_j\hat{R}_k + \delta_{jk}\hat{R}_i\hat{R}_l + \delta_{jl}\hat{R}_i\hat{R}_k + \delta_{kl}\hat{R}_i\hat{R}_j) \\ e_{ijkl} &= \delta_{ij}\hat{R}_k\hat{R}_l \end{aligned} \quad . \tag{4.5.34}$$

We then have, for instance,

$$\tau_{ik}(pR) = \begin{pmatrix} \dfrac{\sin pR}{pR} & \dfrac{\cos pR}{p^2R^2} & \dfrac{\sin pR}{p^3R^3} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & -1 \end{pmatrix} U_{ik} \tag{4.5.35}$$

Similar expressions follow for $\sigma_{iml}(pR)$, $\xi_{knjm}(pR)$ etc, using the vectors U_{ij}, V_{ijk} and W_{ijkl}. The required coefficients N_{i-m} etc are then obtained directly by collecting the coefficients of the trigonometric products resulting from $\tau_{ik}(pR)\nu_{jml}(pR)$ etc; the latter are then written in double angle form (see for example (4.2.11)) and the final result follows from the exponential form of the expressions. In this way the coefficients may be written in a matrix form, with a numerical factor. Thus we obtain

$$N_{i-m} = U^{T}_{ik} M^{2-3}_{N} V_{jml} , \qquad N = A,B,..F \qquad (4.5.36)$$

$$N_{i-n} = U^{T}_{il} M^{2-5}_{N} W_{knjm} + V^{T}_{inm} M^{3-3}_{N} V_{klj} , \qquad N = A,B,..G \qquad (4.5.37)$$

$$N'_{i-n} = V^{T}_{ilk} M^{3-3}_{N'} V_{jnm} , \qquad N' = A',B',..G', \qquad (4.5.38)$$

where T denotes the transpose of the vector and M^{r-s} is an r×s matrix. These matrices are given overleaf.

Table 4.5.1: MATRICES OF CONSTANTS OBTAINED FOR THE ORIENTED QUADRUPOLE RESULTS

$$M_A^{2-3} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} ; \; M_B^{2-3} = \begin{pmatrix} 6 & -1 & 2 \\ 1 & 0 & 1 \end{pmatrix} ; \; M_C^{2-3} = \begin{pmatrix} -15 & 3 & -3 \\ -7 & 1 & -3 \end{pmatrix}$$

$$M_D^{2-3} = \begin{pmatrix} 15 & -3 & 3 \\ 21 & -4 & 5 \end{pmatrix} ; \; M_E^{2-3} = \begin{pmatrix} 0 & 0 & 0 \\ 30 & -6 & 6 \end{pmatrix} ; \; M_F^{2-3} = \begin{pmatrix} 0 & 0 & 0 \\ 15 & -3 & 3 \end{pmatrix} \tag{4.5.39}$$

$$M_A^{2-5} = \begin{pmatrix} -2 & 0 & 0 & 0 & -2 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} ; \quad M_A^{3-3} = \begin{pmatrix} 2 & 0 & 2 \\ 0 & 0 & 0 \\ 2 & 0 & 2 \end{pmatrix}$$

$$M_B^{2-5} = \begin{pmatrix} -10 & 0 & -1 & -1 & -4 \\ -1 & 0 & 0 & 0 & -1 \end{pmatrix} ; \quad M_B^{3-3} = \begin{pmatrix} 12 & -1 & 8 \\ -1 & 0 & -1 \\ 8 & -1 & 4 \end{pmatrix}$$

$$M_C^{2-5} = \begin{pmatrix} -90 & 2 & -4 & -12 & -18 \\ -22 & 0 & -2 & -2 & -10 \end{pmatrix} ; \quad M_C^{3-3} = \begin{pmatrix} -132 & 18 & -60 \\ 18 & -2 & 10 \\ -60 & 10 & -20 \end{pmatrix}$$

$$M_D^{2-5} = \begin{pmatrix} -105 & 3 & -3 & -15 & -15 \\ -55 & 1 & -3 & -7 & -13 \end{pmatrix} ; \quad M_D^{3-3} = \begin{pmatrix} -210 & 36 & -66 \\ 36 & -6 & 12 \\ -66 & 12 & -18 \end{pmatrix}$$

$$M_E^{2-5} = \begin{pmatrix} -210 & 6 & -6 & -30 & -30 \\ -300 & 8 & -10 & -42 & -48 \end{pmatrix} ; \quad M_E^{3-3} = \begin{pmatrix} 810 & -156 & 186 \\ -156 & 30 & -36 \\ 186 & -36 & 42 \end{pmatrix}$$

$$M_F^{2-5} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ -210 & 6 & -6 & -30 & -30 \end{pmatrix} ; \quad M_F^{3-3} = \begin{pmatrix} 450 & -90 & 90 \\ -90 & 18 & -18 \\ 90 & -18 & 18 \end{pmatrix}$$

$$M_G^{2-5} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ -210 & 6 & -6 & -30 & -30 \end{pmatrix} ; \quad M_G^{3-3} = \begin{pmatrix} -450 & 90 & -90 \\ 90 & -18 & 18 \\ -90 & 18 & -18 \end{pmatrix} \tag{4.5.40}$$

$$M_{A'}^{3-3} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} ; \quad M_{B'}^{3-3} = \begin{pmatrix} 6 & -1 & 2 \\ 0 & 0 & 0 \\ 6 & -1 & 2 \end{pmatrix}$$

$$M_{C'}^{3-3} = \begin{pmatrix} 66 & -9 & 30 \\ -9 & 1 & -5 \\ 30 & -5 & 10 \end{pmatrix} ; \quad M_{D'}^{3-3} = \begin{pmatrix} 105 & -18 & 33 \\ -18 & 3 & -6 \\ 33 & -6 & 9 \end{pmatrix}$$

$$M_{E'}^{3-3} = \begin{pmatrix} 405 & -78 & 93 \\ -78 & 15 & -18 \\ 93 & -18 & 21 \end{pmatrix} ; \quad M_{F'}^{3-3} = \begin{pmatrix} 225 & -45 & 45 \\ -45 & 9 & -9 \\ 45 & -9 & 9 \end{pmatrix}$$

$$M_{G'}^{3-3} = \begin{pmatrix} 225 & -45 & 45 \\ -45 & 9 & -9 \\ 45 & -9 & 9 \end{pmatrix} \tag{4.5.41}$$

4.6 The diamagnetic contribution

The interaction Hamiltonian (4.3.1) includes all terms of the required order for intermolecular coupling involving the exchange of two photons. Section 4.4 discussed interactions involving the magnetic-dipole moment; to complete a study of the magnetic field interactions we must consider the final term of (4.3.1), the diamagnetic term. This term is second order in the magnetic field and so the energy shift corresponding to two-photon exchange is obtained using overall third-order perturbation theory, a first order interaction in this term. Straightforward manipulation leads to a result which is similar in form to the final case of Section 4.4 (where the magnetic-dipole interactions were confined to B); the two results are therefore combined.

The relevant time-ordered graphs are shown in Fig 4.8. Note that there are only three in this case, corresponding to the intermediate states where there may be one or two virtual photons present and molecule A may be excited or in its ground state; the two-photon interaction at B does not cause an excitation. Hence the molecule B in its ground state must have a non-zero expectation value for the second rank coordinate tensor.

The total energy shift is given by

$$\Delta E = \sum_{II} \sum_{I} \frac{\langle o|H_{int}|II\rangle\langle II|H_{int}|I\rangle\langle I|H_{int}|o\rangle}{(E_{II}-E_o)(E_I-E_o)} , \qquad (4.6.1)$$

with H_{int} given by (4.3.1). It was stated in Chapter 3 that each two-photon interaction carries an additional factor of two because of the possible permutations arising from the sums over wavevector in the definitions of the fields. Including this factor we obtain for the first graph

ΔE (i)

$$= \frac{e^2\hbar^2}{16m\varepsilon_0^2V^2}\varepsilon_{klm}\varepsilon_{kun}\sum_{\alpha}\sum_{r}\mu_i^{or}\mu_j^{ro}\langle q_{\alpha l}q_{\alpha u}\rangle^B\sum_{\underset{\sim}{p},\underset{\sim}{p}'}\sum_{\lambda,\lambda'}pp'\bar{e}_i\bar{e}'_j b_m b'_n e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}D_i^{-1}, \tag{4.6.2}$$

where $\sum_{\alpha}\langle q_{\alpha l}q_{\alpha u}\rangle^B$ denotes the expectation value of

$$\sum_{\alpha}(\underset{\sim}{q}_{\alpha}(B)-\underset{\sim}{R}_B)_l(\underset{\sim}{q}_{\alpha}(B)-\underset{\sim}{R}_B)_u \tag{4.6.3}$$

for the ground state of molecule B. The other pair of terms are similar and combining the three in the usual fashion gives a total, after summing over the polarizations, of

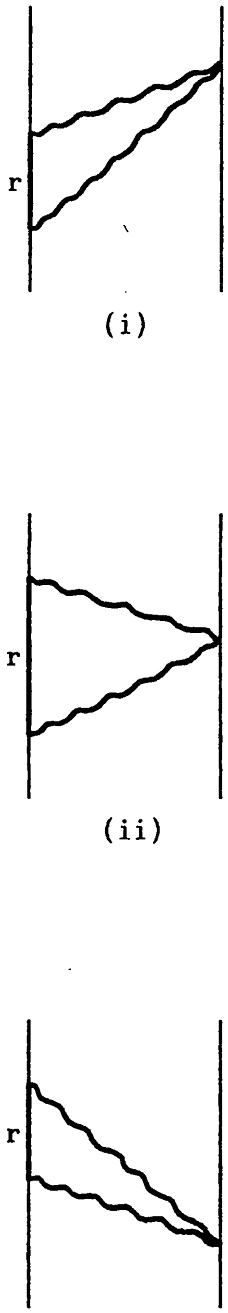
ΔE (Total) = ΔE (i-iii)

$$= \frac{e^2\hbar^2}{16m\varepsilon_0^2V^2}\varepsilon_{klm}\varepsilon_{kun}\varepsilon_{iml}\varepsilon_{jng}\sum_{\alpha}\sum_{r}\mu_i^{or}\mu_j^{ro}\langle q_{\alpha l}q_{\alpha u}\rangle^B\sum_{\underset{\sim}{p}\underset{\sim}{p}'}pp'\hat{p}_l\hat{p}'_g e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}$$
$$\times\left\{D_i^{-1} - D_{ii}^{-1} + D_{iii}^{-1}\right\} \tag{4.6.4}$$

(4.6.4) includes a complicated product of four Levi-Civita tensors. This arises partly from the component form of the interaction term at B; two are generated by the sum over polarizations. This product of tensors may be written in a simpler form as a sum of terms involving Kronecker delta tensors by applying the usual contraction identities.

Taking the value of the sum over the energy denominators from Table 4.3.3, summing over the wavevectors and proceeding as before we obtain from (4.6.4)

FIG 4.8 : TIME-ORDERED GRAPHS FOR THE DIAMAGNETIC CONTRIBUTION TO THE DISPERSION INTERACTION



$$\frac{e^2}{8m}\sum_{\alpha}\left\{(\underset{\sim}{q}_{\alpha}(B)-\underset{\sim}{R}_{B})\times\underset{\sim}{b}(\underset{\sim}{R}_{B})\right\}^2$$

(i)

$$\frac{e^2}{8m}\sum_{\alpha}\left\{(\underset{\sim}{q}_{\alpha}(B)-\underset{\sim}{R}_{B})\times\underset{\sim}{b}(\underset{\sim}{R}_{B})\right\}^2$$

(ii)

$$\frac{e^2}{8m}\sum_{\alpha}\left\{(\underset{\sim}{q}_{\alpha}(B)-\underset{\sim}{R}_{B})\times\underset{\sim}{b}(\underset{\sim}{R}_{B})\right\}^2$$

(iii)

$$\Delta E = \frac{-e^2}{32\pi^4 m\varepsilon_0^2 c^2} C_{ij\ell ufg} \sum_\alpha \sum_r \mu_i^{or} \mu_j^{ro} \langle q_{\alpha\ell} q_{\alpha u} \rangle^B$$

$$\times \int_0^\infty \int_0^\infty \eta_g(p'R)\eta_f(pR)p^3 p'^3 \frac{1}{(k_r+p')} \left(\frac{1}{p+p'} - \frac{1}{p-p'} \right) dp dp' \; , \tag{4.6.5}$$

where

$$C_{ij\ell ufg} = \delta_{i\ell}\delta_{ju}\delta_{fg} - \delta_{i\ell}\delta_{jf}\delta_{ug} - \delta_{ig}\delta_{ju}\delta_{\ell f} + \delta_{ij}\delta_{\ell f}\delta_{ug} \tag{4.6.6}$$

as outlined above. Upon integration this gives

$$\Delta E = \frac{e^2}{32\pi^3 m\varepsilon_0^2 c^2} C_{ij\ell ufg} \sum_\alpha \sum_r \mu_i^{or} \mu_j^{ro} \langle q_{\alpha\ell} q_{\alpha u} \rangle^B \int_0^\infty \frac{1}{(k_r+p')} \eta_g(p'R)\rho_f(p'R)p'^6 dp' , \tag{4.6.7}$$

which may be simplified to

$$\Delta E = \frac{-e^2}{64\pi^3 m\varepsilon_0^2 c^2 R^2} C_{ij\ell ufg} \hat{R}_f \hat{R}_g \sum_\alpha \sum_r \mu_i^{or} \mu_j^{ro} \langle q_{\alpha\ell} q_{\alpha u} \rangle^B$$

$$\times \int_0^\infty \frac{k_r p^4 e^{-2pR}}{(k_r^2+p^2)} \left(1 + \frac{2}{pR} + \frac{1}{p^2R^2} \right) dp. \tag{4.6.8}$$

This is now a familiar form. However, if we compare (4.6.8) with (4.4.37) we see that the major difference between the two expressions is the absence here of those parts which depend on the excited states s of B, a consequence of the nature of the interaction term. Rotationally averaging this result gives

$$\Delta E = \frac{-e^2}{144\pi^3 m\varepsilon_0^2 c^2 R^2} \sum_\alpha \sum_r |\underset{\sim}{\mu}^{ro}|^2 \langle \underset{\sim}{q}_\alpha^2 \rangle^B \int_0^\infty \frac{k_r p^4 e^{-2pR}}{(k_r^2+p^2)} \left(1 + \frac{2}{pR} + \frac{1}{p^2R^2} \right) dp, \tag{4.6.9}$$

which agrees with that obtained by Thirunamachandran [65]. The oriented result in terms of the polarizability for molecule A is given by

$$\Delta E = \frac{-e^2\hbar}{128\pi^3 m\varepsilon_0^2 cR^2} C_{ij\ell u\ell g}\hat{R}_\ell\hat{R}_g \sum_\alpha \int_0^\infty \alpha_{ij}^A(icp)\langle q_{\alpha\ell}q_{\alpha u}\rangle^B p^4 e^{-2pR}\left(1 + \frac{2}{pR} + \frac{1}{p^2R^2}\right)dp \tag{4.6.10}$$

We find that in the near-zone (4.6.10) vanishes; this may be physically rationalised since the intermolecular coupling of a two-photon interaction at one centre with a polarizability at the other cannot be described in terms of non-retarded coupling, appropriate for the near-zone.

In the far-zone we obtain the result

$$\Delta E_{F-Z} = \frac{-3\hbar e^2}{128\pi^3\varepsilon_0^2 mcR^7}\sum_\alpha \alpha^A(0)\langle \underset{\sim}{q}_\alpha^2\rangle^B \; . \tag{4.6.11}$$

The diamagnetic contribution to the dispersion interaction in the far-zone therefore takes an inverse seventh power in the intermolecular separation. This result, in terms of the static polarizability of molecule A, is similar in form to the contribution from the magnetic susceptibility of molecule B (4.4.41). It is convenient to combine the two results to write

$$\Delta E_{F-Z}^{mag} = \frac{9\hbar}{64\pi^3\varepsilon_0^2 cR^7}\alpha^A(0)\chi_B'(0) \tag{4.6.12}$$

where $\chi_B'(0)$ is the diamagnetic susceptibility of B in its ground state, given by

$$\chi'_B(0) = \left\{\chi^B(0) - \frac{e^2}{6m}\sum_\alpha \langle \underset{\sim}{q}_\alpha^2\rangle^B\right\} . \qquad (4.6.13)$$

The magnetic susceptibility $\chi(0)$ and the static polarizability $\alpha(0)$ of a molecule are both positive in magnitude but the sign of the diamagnetic susceptibility depends on the competition between the two terms on the right hand side of (4.6.13). If $\chi'_B(0)$ is negative the molecule is said to be diamagnetic.

The following Section summarises and discusses the results from this and the previous Sections to present an overall view of the dispersion interaction to this order.

4.7 Summary

In this Chapter quantum electrodynamics has been applied to the calculation of dispersion energies between molecules with different polarizability characteristics. In order to do so the electric-dipole approximation was lifted and electric-quadrupole, magnetic-dipole and diamagnetic interactions were considered. It was assumed that no incident fields were present on the molecules, as such fields can modify the intermolecular energies [65,66]. In each of the results the properties of the molecules are described entirely by one of the forms of polarizability defined in the text.

There follows a summary of these results, which apply to interactions between chiral as well as achiral molecules, beginning with the electric dipole-dipole interaction. Subsequent results, which similarly are valid for all intermolecular separations, will generally be smaller in magnitude than this interaction, and hence not the dominant terms usually, although when considering the interaction between chiral molecules the higher-order mixed electric-magnetic terms are the lowest order terms which account for the discriminatory effect. Allowing for this, in the description of the results attention is then focused primarily on the dependence of the interaction on intermolecular separation.

The derivations and the main results given at the end of each Section apply to the interaction of oriented molecules at any separation. From these general results we may obtain more specific expressions by making certain assumptions, appropriate to the physical case in question. For instance, should we wish to know from these results the interaction between oriented molecules in the near-zone then we simply retain the final term of each expression following the assumption that the photon wavevectors are much greater than the wavevectors of the molecular transitions.

In this account the results discussion is confined to interactions between molecules in the gas and liquid phases. Our assumption is then to allow free rotation and the expressions are modified by taking the rotational average to account for this. In particular the far-zone results apply to mixtures of dilute gases. Table 4.7.1 shows the R-dependence of the various interactions in the two limiting cases, given in the two right-hand columns. The column headings Molecule A and Molecule B indicate, through the appropriate polarizability, which interactions couple the two molecules. For example, $\alpha^{A}(0)$ for A and $G^{B}(0)$ for molecule B refers to a μ-μ type interaction for one molecule and μ-m coupling at the other, as described using the time-ordered graphs. The horizontal lines partition terms of different order.

To put this discussion into some physical perspective, an approximate value should be attached to R in the two cases. Experiments conducted by Tabor and Winterton [59] investigating how molecular interaction varies with intermolecular separation have quoted results for separations of mica surfaces of between 5nm and 30nm. They assume that the molecular case does not differ markedly from the condensed phase interaction, in which the complete transition from R^{-6} to R^{-7} behaviour takes place between 10-20nm; below 10nm and above 20nm we may assume the two limits.

The electric dipole-dipole interaction is a well-known result. In the near-zone we recognise the R^{-6} dispersion energy or van der Waals interaction. This force may be considered to arise from fluctuations in electron density and the R-dependence is obtained from second-order coupling of the electrostatic dipolar interaction term [45]. The deviation from perfect gas behaviour is due to this interaction. Similarly the other near-zone results may be obtained from electrostatic interactions using higher multipole terms. However, these interactions do not allow for retardation effects and the results are only valid at the molecular separations discussed above. Outside this range other effects, due to retardation, are observed and the interaction falls off to an R^{-7} dependence.

The result (4.2.15) extends previous works since it is both valid at all separations outside overlap and applies to the interaction between oriented molecules.

As noted, the interactions containing electric-quadrupole and magnetic-dipole coupling are 2-3 orders of magnitude smaller than the electric dipole-dipole result for each vertex which we replace and so are not the dominant terms. It is nevertheless useful the examine the various terms for their dependence on intermolecular separation.

At a glance Table 4.7.1 highlights a major physical dissimilarity between the electric-quadrupole and magnetic-dipole interactions. When the molecules are allowed to rotate there is no intermolecular force arising from dipole-quadrupole coupling at one centre, that is the mixed dipole-quadrupole polarizability A_{ijk} for a molecule vanishes

TABLE 4.7.1 SUMMARY OF THE CONTRIBUTIONS TO THE DISPERSION INTERACTION IN THE NEAR- AND FAR-ZONES: ROTATIONALLY AVERAGED RESULTS

Molecule A	Molecule B	R-dependence/ near-zone	R-dependence/ far-zone
$\alpha(0)$	$\alpha(0)$	R^{-6}	R^{-7}
$\alpha(0)$	$G(0)$	zero result	zero result
$\alpha(0)$	$A(0)$	zero result	zero result
$G(0)$	$G(0)$	R^{-6}	R^{-9}
$A(0)$	$A(0)$	zero result	zero result
$\alpha(0)$	$\chi(0)$	zero result	R^{-7}
$\alpha(0)$	$\langle \underset{\sim}{q}^2 \rangle$		
$\alpha(0)$	$\theta(0)$	R^{-8}	R^{-9}

with averaging. The polarizability G_{ij}, on the other hand, representing electric-dipole/magnetic-dipole coupling of a molecule remains and rotating molecules may be coupled in this way via the electromagnetic field provided that the interaction at the other centre is of the appropriate symmetry; the $\alpha_{ij}(A)$-$G_{ij}(B)$ coupling vanishes under rotation, whereas the $G_{ij}(A)$-$G_{ij}(B)$ interaction is non-zero and shows discrimination.

As discussed in Section 4.4(b) the latter interaction may be written in terms of the rotatory strengths R^{to} of each molecule, giving (4.4.28) and (4.4.29) for the near- and far-zones respectively. In the near-zone we observe an interaction proportional to R^{-6} and predict an inverse ninth dependence on separation in the far-zone. It was noted in the text that the rotatory strengths take opposite signs for enantiomers and hence both results show discriminatory effects. Thus the A(R)-B(R) and A(R)-B(S) interactions differ in sign; for chemically identical molecules like species repel and for opposite isomers ΔE [A(R)-A(S)] ≤ 0. Note though that the rotatory strengths may be positive or negative and so it is not possible to predict the absolute sign of an interaction if the molecules are different chemically.

The discriminatory results given in Table 4.7.1 for the near-zone and far-zone interactions have previously been determined [11,60]; the account here is an extension of those works, which assumed approximations appropriate to each case at the outset and hence did not determine the complete result. The far-zone dipole-dipole result, for example, may be determined from just four of the twelve time-ordered graphs shown in Fig 4.1, based on slightly different physical grounds; energy may be borrowed from the vacuum subject to the energy-time uncertainty relation $\Delta E \Delta t \geq \hbar$ and so the retarded result is obtained from those terms which contribute if the photon frequencies are very small. When intermolecular separation is small the photon energies must be much larger to satisfy the same principle, since the time-scale is short. Hence a different set of four graphs should be considered. It is only when the complete range of separations is required that the full set is included.

The results given in this account could also be obtained by choosing the Heisenberg form of QED, where the field operators, instead of the states, show the time dependence. The dispersion interactions are then determined by calculating the response of one molecule to the Maxwell field of the other. Such calculations have been done by Thirunamachandran [65] for the interaction of an electric-dipole polarizable molecule with a magnetic-dipole polarizable molecule and an electric-quadrupole polarizable molecule, applicable at all separations and allowing the molecules to rotate.

The results given here agree with those obtained by Thirunâmachandran for these cases and with the earlier work by Mavroyannis and Stephen [60], who presented only the limiting results. In the latter paper an alternative form of Hamiltonian was used in the calculation (the authors chose the Lorentz gauge instead of the Coulomb gauge). We find that, having confined the magnetic field interactions to molecule B (ie combining the diamagnetic interaction with the magnetic-dipole interactions), molecules with large susceptibilities will interact with an electric-dipole polarizable molecule with an R^{-7} dependence on intermolecular separation in the far-zone. The near-zone result vanishes. The near-zone result for the $\alpha(0)$-$\theta(0)$ interaction, however, (with molecule B assumed to have a large quadrupole polarizability) remains and shows R^{-8} behaviour. In the far-zone the interaction is retarded by a factor which approaches R^{-1} and so we predict a result proportional to R^{-9}. Whilst confirming the results in this form, this account presents, in addition, the general, oriented expressions.

In the following Section any additional identities which were used in previous Sections without explicit justification are given as an appendix. Further explanation of some of the steps used in the method of Section 4.2 is given and the derivation of the angular integral results is outlined.

4.8 Appendix

In this section some of the detail of the general method used throughout the previous sections is accounted, and the remaining definitions are given.

If we study the expression (4.2.3) we see that it results from summations over photon polarization vectors in expressions of the form

$$\Delta E\ (i)$$

$$= -\sum_{r,s}\ \sum_{\underset{\sim}{p}\underset{\sim}{p}'}\ \sum_{\lambda\lambda'} \left(\frac{\hbar cp}{2\varepsilon_0 V}\right)\left(\frac{\hbar cp'}{2\varepsilon_0 V}\right)\mu_i^{or}\mu_j^{ro}\mu_k^{os}\mu_l^{so}e^{i(\underset{\sim}{p}+\underset{\sim}{p}').\underset{\sim}{R}}$$

$$\times\ \bar{e}_i^{(\lambda)}(\underset{\sim}{p})e_k^{(\lambda)}(\underset{\sim}{p})\bar{e}_j^{(\lambda')}(\underset{\sim}{p}')e_l^{(\lambda')}(\underset{\sim}{p}')D_a^{-1} \quad . \qquad (4.8.1)$$

The appropriate sum is given by

$$\sum_{\lambda} e_i^{(\lambda)}(\underset{\sim}{k})\bar{e}_j^{(\lambda)}(\underset{\sim}{k}) = (\delta_{ij}-\hat{k}_i\hat{k}_j) \ . \qquad (4.8.2)$$

In the consideration of magnetic-dipole interactions, Section 4.4 also uses the results (4.8.3) and (4.8.4), overleaf, as discussed on page 102.

$$\sum_{\lambda} e_i^{(\lambda)}(\underset{\sim}{k})\bar{b}_j^{(\lambda)}(\underset{\sim}{k}) = \varepsilon_{ijk}\hat{k}_k \qquad (4.8.3)$$

$$\sum_{\lambda} b_i^{(\lambda)}(\underset{\sim}{k})\bar{b}_j^{(\lambda)}(\underset{\sim}{k}) = (\delta_{ij}-\hat{k}_i\hat{k}_j) \qquad (4.8.4)$$

The sums over $\underset{\sim}{p}$ and $\underset{\sim}{p}'$ in (4.2.3) are replaced by integrals in the limit $V \Rightarrow \infty$ of the volume of the quantization box for the electromagnetic field;

$$(1/V)\sum_{\underset{\sim}{p}} \xrightarrow[V\to\infty]{} (2\pi)^{-3}\int d^3\underset{\sim}{p} \qquad (4.8.5)$$

Hence (4.2.4).

The expression (4.2.8) is written down by separating the wavevector integrals in (4.2.4) into their radial and angular parts using the relation

$$d^3\underset{\sim}{p} = p^2 dp d\Omega \qquad (4.8.6)$$

and then performing the angular integrals. The latter are done using a combination of the identities (4.3.4) and (4.8.7), below.

$$\frac{1}{p}\nabla_i\int e^{\pm i\underset{\sim}{p}.\underset{\sim}{R}}d\Omega = \pm i\int\hat{p}_i e^{\pm i\underset{\sim}{p}.\underset{\sim}{R}}d\Omega \qquad (4.8.7)$$

Similarly, repeated use of (4.8.7) allows the integrals (4.3.7) and (4.3.8) to be evaluated and (4.3.5) is given directly. The quantities on the right hand side of these expressions have been defined in the text.

Finally this leaves a discussion of the evaluation of the p'-integral in (4.2.8), and the definitions of the quantities $\nu_{ijk}(pR)$

and $\Phi_{ijkl}(pR)$, resulting from similar integrals, which were used in the text. The relationship between the pair $\{\tau_{ij}(p'R),\omega_{ij}(pR)\}$ is given by (4.3.12), as stated. It is easily shown that this result may be obtained by using the standard integrals [67]

$$\int_{-\infty}^{\infty}\frac{\sin(ax)}{(x+\beta)}dx = \pi\cos(a\beta) \tag{4.8.8}$$

and

$$\int_{-\infty}^{\infty}\frac{\cos(ax)}{(x+\beta)}dx = \pi\sin(a\beta) \tag{4.8.9}$$

and their derivatives with respect to a. Similarly using (4.8.8/9) we obtain the analogous expressions (4.8.10-12)

$$\int_{-\infty}^{\infty}\frac{\eta_i(p'R)p'^3}{(p+p')}dp' = -p^3\pi\rho_i(pR) \ , \tag{4.8.10}$$

$$\int_{-\infty}^{\infty}\frac{\sigma_{ijk}(p'R)p'^4}{(p+p')}dp' = p^4\pi\nu_{ijk}(pR) \tag{4.8.11}$$

and

$$\int_{-\infty}^{\infty}\frac{\xi_{ijkl}(p'R)p'^5}{(p+p')}dp' = p^5\pi\Phi_{ijkl}(pR) \ . \tag{4.8.12}$$

The quantities $\nu_{ijk}(\mathrm{pR})$ and $\Phi_{ijk\ell}(\mathrm{pR})$ are given below.

$$\begin{aligned}\nu_{ijk}(\mathrm{pR}) = \Bigg\{&\hat{R}_i\hat{R}_j\hat{R}_k\left(-\frac{\sin pR}{pR} - 6\frac{\cos pR}{p^2R^2} + 15\frac{\sin pR}{p^3R^3} + 15\frac{\cos pR}{p^4R^4}\right)\\ &+(\delta_{ik}\hat{R}_j + \delta_{jk}\hat{R}_i)\left(\frac{\cos pR}{p^2R^2} - 3\frac{\sin pR}{p^3R^3} - 3\frac{\cos pR}{p^4R^4}\right)\\ &-\delta_{ij}\hat{R}_k\left(-\frac{\sin pR}{pR} - 2\frac{\cos pR}{p^2R^2} + 3\frac{\sin pR}{p^3R^3} + 3\frac{\cos pR}{p^4R^4}\right)\Bigg\}\end{aligned} \tag{4.8.13}$$

$$\begin{aligned}\Phi_{ijk\ell}(\mathrm{pR}) = \Bigg\{&-\hat{R}_i\hat{R}_j\hat{R}_k\hat{R}_\ell\left(\frac{\cos pR}{pR} -10\frac{\sin pR}{p^2R^2} -45\frac{\cos pR}{p^3R^3} +105\frac{\sin pR}{p^4R^4} +105\frac{\cos pR}{p^5R^5}\right)\\ &+(\delta_{ik}\delta_{j\ell} + \delta_{jk}\delta_{i\ell})\left(\frac{\cos pR}{p^3R^3} - 3\frac{\sin pR}{p^4R^4} - 3\frac{\cos pR}{p^5R^5}\right)\\ &-\delta_{ij}\delta_{k\ell}\left(-\frac{\sin pR}{p^2R^2} - 2\frac{\cos pR}{p^3R^3} + 3\frac{\sin pR}{p^4R^4} + 3\frac{\cos pR}{p^5R^5}\right)\\ &+ (\delta_{ik}\hat{R}_j\hat{R}_\ell + \delta_{i\ell}\hat{R}_j\hat{R}_k + \delta_{jk}\hat{R}_i\hat{R}_\ell + \delta_{j\ell}\hat{R}_i\hat{R}_k + \delta_{k\ell}\hat{R}_i\hat{R}_j)\\ &\times\left(-\frac{\sin pR}{p^2R^2} - 6\frac{\cos pR}{p^3R^3} + 15\frac{\sin pR}{p^4R^4} + 15\frac{\cos pR}{p^5R^5}\right)\\ &+ \delta_{ij}\hat{R}_k\hat{R}_\ell\left(\frac{\cos pR}{pR} - 4\frac{\sin pR}{p^2R^2} - 9\frac{\cos pR}{p^3R^3} + 15\frac{\sin pR}{p^4R^4} + 15\frac{\cos pR}{p^5R^5}\right)\Bigg\}\end{aligned} \tag{4.8.14}$$

In the text results were quoted in terms of the dynamic polarizability or magnetic susceptibility of the molecule and mixed electric-dipole/magnetic-dipole and dipole/quadrupole analogues. In Table 4.8.1 these quantities are defined together for reference.

Table 4.8.1: DEFINITIONS OF DYNAMIC AND MIXED DYNAMIC POLARIZABILITIES

Dynamic polarizability:

$$\alpha^{oo}_{ij}(icu) = 2\sum_{r} \frac{E_{ro}}{E_{ro}^{2}+(\hbar cu)^{2}}\, \mu^{or}_{i}\mu^{ro}_{j} \tag{4.8.15}$$

Electric/magnetic polarizability:

$$G^{oo}_{ij}(icu) = 2i\sum_{r} \frac{\hbar cu}{E_{ro}^{2}+(\hbar cu)^{2}}\, \mu^{or}_{i}m^{ro}_{j} \tag{4.8.16}$$

Dipole/quadrupole polarizability:

$$A^{oo}_{ijk}(icu) = 2\sum_{r} \frac{E_{ro}}{E_{ro}^{2}+(\hbar cu)^{2}}\, \mu^{or}_{i}Q^{ro}_{jk} \tag{4.8.17}$$

Magnetic susceptibility:

$$\chi^{oo}_{ij}(icu) = 2\sum_{r} \frac{E_{ro}}{E_{ro}^{2}+(\hbar cu)^{2}}\, m^{or}_{i}m^{ro}_{j} \tag{4.8.18}$$

Quadrupole polarizability:

$$\theta^{oo}_{ijkl}(icu) = 2\sum_{r} \frac{E_{ro}}{E_{ro}^{2}+(\hbar cu)^{2}}\, Q^{or}_{ij}Q^{ro}_{kl} \tag{4.8.19}$$

CHAPTER 5

ION-MOLECULE INTERACTIONS

5.1 Introduction

The multipolar Hamiltonian has been used in Chapter 4 to give a comprehensive account of dispersion interactions between neutral molecules in their ground states. Such interactions are fully retarded; the coupling proceeds entirely via exchange of transverse photons since all electrostatic interactions between the molecules were eliminated in the construction of the Hamiltonian. It is now of interest to relax this restriction on molecular neutrality and consider similar interactions where molecules carry a net charge. The Hamiltonian theory appropriate for such cases was developed in Chapter 2 and shall be applied here in the discussion of such ion-molecule interactions. This multipolar theory, however, is not suited to a discussion of the interactions of free electrons. A theory will be presented in the following chapter which deals specifically with this special case.

For the calculations here it is assumed that both ion and molecule are held fixed. The required interaction terms are recovered from the final form of the Hamiltonian given in Chapter 2, with the note that this condition eliminates those interaction terms which were dependent on the vector potential. The non-retarded results which are then determined here include all terms up to electric quadrupole. These terms may be added to the results of the previous chapter and the charge-octupole interaction is determined so that all terms up to a cut-off point of an R^{-6} dependence on separation have been taken into account. The minimal-coupling treatment of this interaction is also outlined as a contrast.

The molecular ion is also assumed to have a permanent dipole moment; this is a necessary assumption since there can be no intermediate state sum for the ion where the interaction is electrostatic. Consequently, the energy shift will depend on a molecular property of the neutral molecule, such as a polarizability, but simply on the charge and dipole moment of the ion.

We begin by considering charge-dipole electrostatic coupling and this is followed by the consideration of higher charge-multipole terms. Included also are combinations of these interactions and all multipolar interactions to the same order. The interactions are again described using time-ordered graphs.

5.2 Non-retarded electric-dipole interactions

We aim here to present for the first time the complete multipolar expression for the dispersion interaction between an ion, A, and a neutral molecule B. This requires the determination of those terms dependent on the ionic charge Q_A. The interaction Hamiltonian for the system is

$$\begin{aligned} H_{int} = & -\varepsilon_0^{-1}\underset{\sim}{\mu}(A).\underset{\sim}{d}^{\perp}(\underset{\sim}{R}_A) - \varepsilon_0^{-1}Q_{ij}(A)\nabla_j d_i^{\perp}(\underset{\sim}{R}_A) + W_{elec} \\ & -\varepsilon_0^{-1}\underset{\sim}{\mu}(B).\underset{\sim}{d}^{\perp}(\underset{\sim}{R}_B) - \varepsilon_0^{-1}Q_{ij}(B)\nabla_j d_i^{\perp}(\underset{\sim}{R}_B) \end{aligned} \qquad (5.2.1)$$

where W_{elec} is the electrostatic interaction term of the Hamiltonian (2.7.4) and is made up of the complete charge-multipole series. The first three terms of the multipolar expansion of W_{elec} are [68,69]

$$W_{\text{elec}} = -(Q_A/4\pi\varepsilon_0)\left\{\mu_i(B)\hat{R}_i/R^2 + Q_{ij}(B)\beta_{ij}/R^3 - 3\Omega_{ijk}(B)\hat{G}_{ijk}/R^4\right\} \tag{5.2.2}$$

$$= W_1 + W_2 + W_3 \ , \tag{5.2.3}$$

in which the interactions are charge-dipole, charge-quadrupole and charge-octupole respectively. In (5.2.2) β_{ij} takes its definition from (4.2.6) and in W_3 the component $\Omega_{ijk}(B)$ of the third-rank octupole moment tensor for B is

$$\Omega_{ijk}(B) = (1/3!)\sum_{\gamma} e_\gamma(\mathbf{q}_\gamma-\mathbf{R}_B)_i(\mathbf{q}_\gamma-\mathbf{R}_B)_j(\mathbf{q}_\gamma-\mathbf{R}_B)_k \ , \tag{5.2.4}$$

with γ to be summed over all electrons and nuclei, and the geometric factor $\hat{G}_{ijk}$ is

$$\hat{G}_{ijk} = (\delta_{ij}\hat{R}_k + \delta_{ki}\hat{R}_j + \delta_{jk}\hat{R}_i - 5\hat{R}_i\hat{R}_j\hat{R}_k) \ . \tag{5.2.5}$$

In this expansion the intermolecular vector $\mathbf{R}$ is defined as

$$\mathbf{R} = \mathbf{R}_B - \mathbf{R}_A \tag{5.2.6}$$

This section deals with those terms up to electric dipole which include the charge-dipole interaction. This includes the fully electrostatic interaction given by Fig 5.1, in which the horizontal dashed lines refer to interaction potentials, and interactions, given by the third-order perturbation result, which also proceed through an exchange of one transverse photon.

For dipoles favourably oriented with respect to $\mathbf{R}$ we expect the dominant contribution to the interaction to be the electrostatic charge-dipole term. From Fig 5.1 we obtain

$$\Delta E_1 = -(1/2)(1/4\pi\varepsilon_0)^2 Q_A^2 \alpha_{ij}^{oo}(B)\hat{R}_i\hat{R}_j R^{-4} \tag{5.2.7}$$

The R^{-4} dependence is well-known; the result is given here in terms of the static polarizability of the neutral molecule.

Those interactions which are part Coulombic and part transverse-photon exchange are next considered. Fig 5.2 shows the graphs for such a case. For example, in graph (i) the various states are given by

$$\begin{aligned}
|i\rangle &= |E_o(A);\ E_o(B);\ 0(\underset{\sim}{p},\lambda)\rangle \\
|I\rangle &= |E_o(A);\ E_o(B);\ 1(\underset{\sim}{p},\lambda)\rangle \\
|II\rangle &= |E_o(A);\ E_s(B);\ 0(\underset{\sim}{p},\lambda)\rangle \\
|f\rangle &= |E_o(A);\ E_o(B);\ 0(\underset{\sim}{p},\lambda)\rangle
\end{aligned} \tag{5.2.8}$$

There are six graphs in total, the three shown plus three for emission of the virtual photon by molecule B. The third-order perturbation result is straightforward. Summing over the wavevectors and polarizations of the virtual photon as is required and adding the various contributions using the simple result

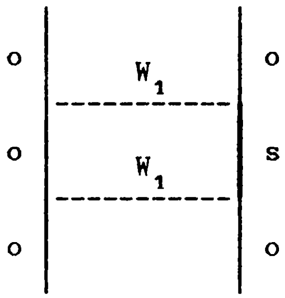
$$\frac{1}{(\hbar cp)E_{so}^{B}} + \frac{1}{E_{so}^{B}(E_{so}^{B}+\hbar cp)} + \frac{1}{(\hbar cp)(E_{so}^{B}+\hbar cp)} = \frac{2}{(\hbar cp)E_{so}^{B}} \tag{5.2.9}$$

gives an energy shift

$$\Delta E_2 = (1/4\pi\varepsilon_0)^2 Q_A \mu_k^{oo}(A)\alpha_{ij}^{oo}(B)\hat{R}_i\beta_{jk}R^{-5}\ , \tag{5.2.10}$$

which is of the form expected.

FIG 5.1 : ION-MOLECULE DISPERSION: THE COULOMB INTERACTION



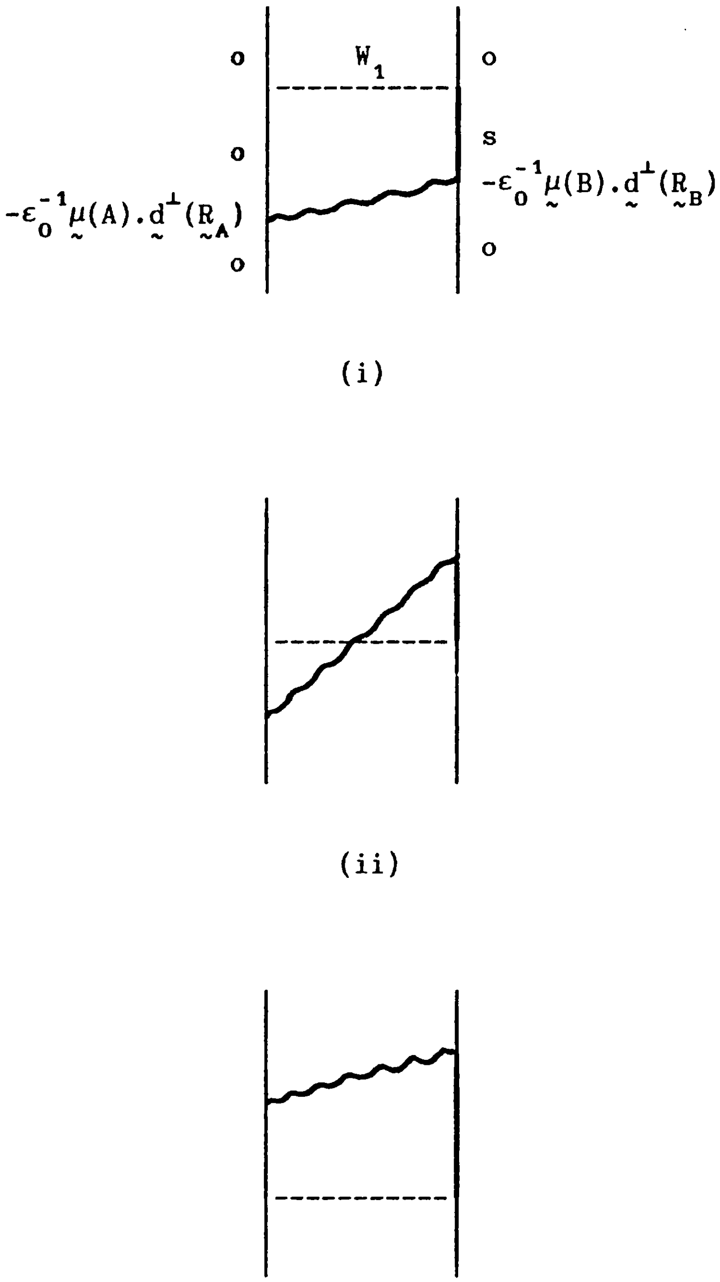
The result makes use of the identity

$$\frac{1}{V}\sum_{\underset{\sim}{p}} (\delta_{ij}-\hat{p}_i\hat{p}_j)e^{i\underset{\sim}{p}.\underset{\sim}{R}} = (2\pi)^{-3}\int(\delta_{ij}-\hat{p}_i\hat{p}_j)e^{i\underset{\sim}{p}.\underset{\sim}{R}}d^3\underset{\sim}{p} = -(4\pi R^3)^{-1}\beta_{ij} \tag{5.2.11}$$

which is obtained through the transverse delta dyadic. The shift contains an R^{-5} dependence on separation and requires the ion A to have a permanent moment. It is because of the fact that A interacts through its permanent moment that this interaction, which proceeds through the exchange of a virtual photon, leads to a non-retarded energy shift. The London result (Section 4.2) is obtained from here by replacing the charge dipole interaction with the exchange of a second transverse photon through electric dipole interaction. Intermediate states are required for A with the retarded interaction, giving a result dependent on its polarizability and which shows the R^{-6} behaviour.

This accounts for the first set of interactions, those up to electric dipole only. We now go on to consider higher-order terms; we

FIG 5.2 : ION-MOLECULE DISPERSION INTERACTION:
NON-RETARDED ELECTRIC-DIPOLE CONTRIBUTIONS



(i)

(ii)

(iii)

+ three graphs

include both the transverse field interaction with electric quadrupole vertices and the electrostatic charge-quadrupole and charge-octupole terms. The study gives all terms up to an R^{-6} interaction.

5.3 Higher multipole interactions

First we consider the remaining electrostatic contributions. These are shown in Fig 5.3. In (i) and (ii) a charge-quadrupole or a charge-octupole interaction occurs along with charge-dipole coupling. In Fig 5.3(iii) the interaction is described entirely by the charge-quadrupole potential. The corresponding energy shifts are easily determined and added to give

$$\Delta E_3 = -(Q_A/4\pi\varepsilon_0)^{-2}$$

$$\times\left\{A^{oo}_{ijk}(B)\hat{R}_i\beta_{jk}R^{-5} + (1/2)\theta^{oo}_{ijk\ell}(B)\beta_{ij}\beta_{k\ell}R^{-6} - 3E^{oo}_{ijk\ell}(B)\hat{R}_i\hat{G}_{jk\ell}R^{-6}\right\} \tag{5.3.1}$$

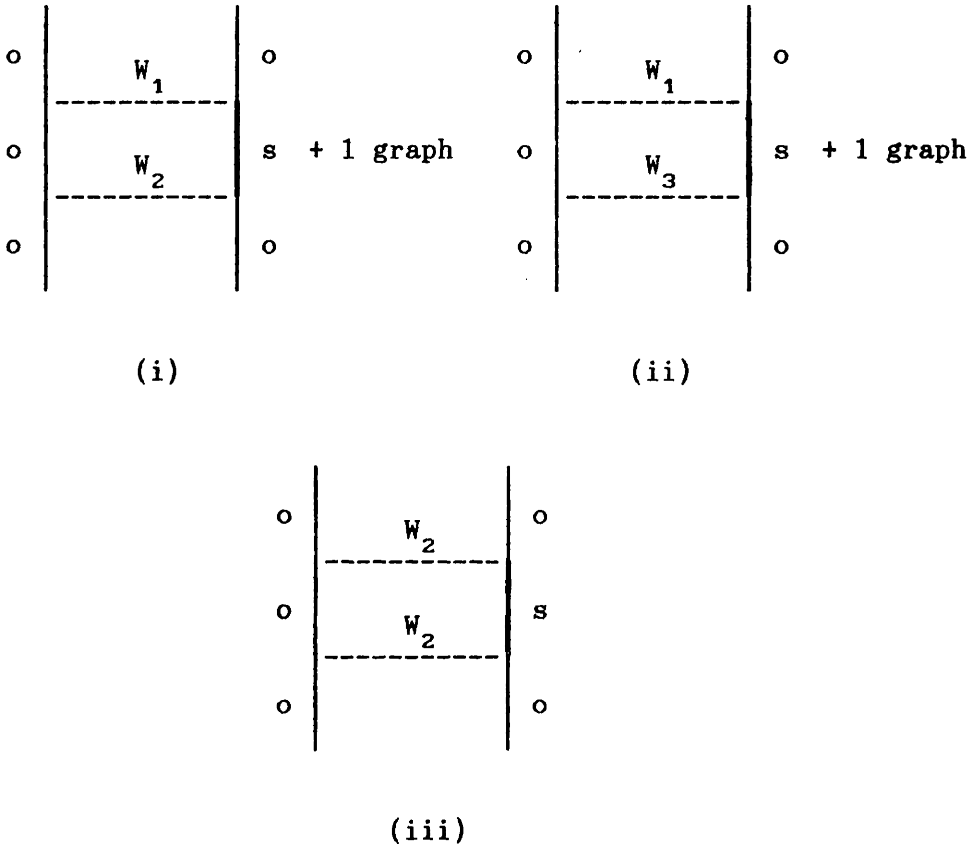
In (5.3.1) $\theta^{oo}_{ijk\ell}(B)$, the quadrupole-quadrupole polarizability, is the quadrupole analogue of the static polarizability and we have used the definition

$$E^{oo}_{ijk\ell}(B) = 2\sum_{s}\frac{\mu^{os}_i\Omega^{so}_{jk\ell}}{E_{so}} \tag{5.3.2}$$

for the static dipole-octupole polarizability. These terms are of the same order as the London expression and may be significant, depending on the symmetry of molecule B. $A^{oo}_{ijk}(B)$ is the static form of the dipole-quadrupole polarizability.

There remain two further contributions to the intermolecular energy shift; (a) the electrostatic interaction potential is of the charge-quadrupole type and both of the virtual photon interaction

FIG 5.3 : ION-MOLECULE DISPERSION:
HIGHER-ORDER COULOMB INTERACTIONS

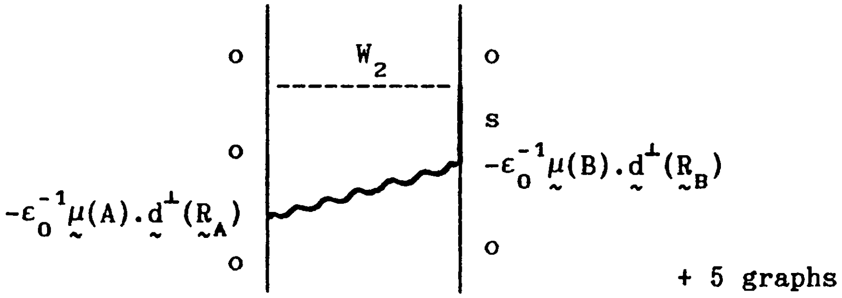


(i)

(ii)

(iii)

FIG 5.4 : ION-MOLECULE DISPERSION:
A TYPICAL CHARGE-QUADRUPOLE CONTRIBUTION



vertices are of the electric dipole type; and (b) the electrostatic interaction potential is charge-dipole and the virtual photon interaction is via a dipole vertex at one molecule and a quadrupole vertex at the other. An example of the type (a) interaction is shown in Fig 5.4. There are six such graphs. With the use of (5.2.9) the energy shift arising from these graphs may be evaluated to give

$$\Delta E_4 = (1/4\pi\varepsilon_0)^2 Q_A \mu_{k}^{\circ\circ}(A) A_{\ell ij}^{\circ\circ}(B) \beta_{ij} \beta_{k\ell} R^{-6} , \tag{5.3.3}$$

which we see falls off with the inverse sixth power of separation.

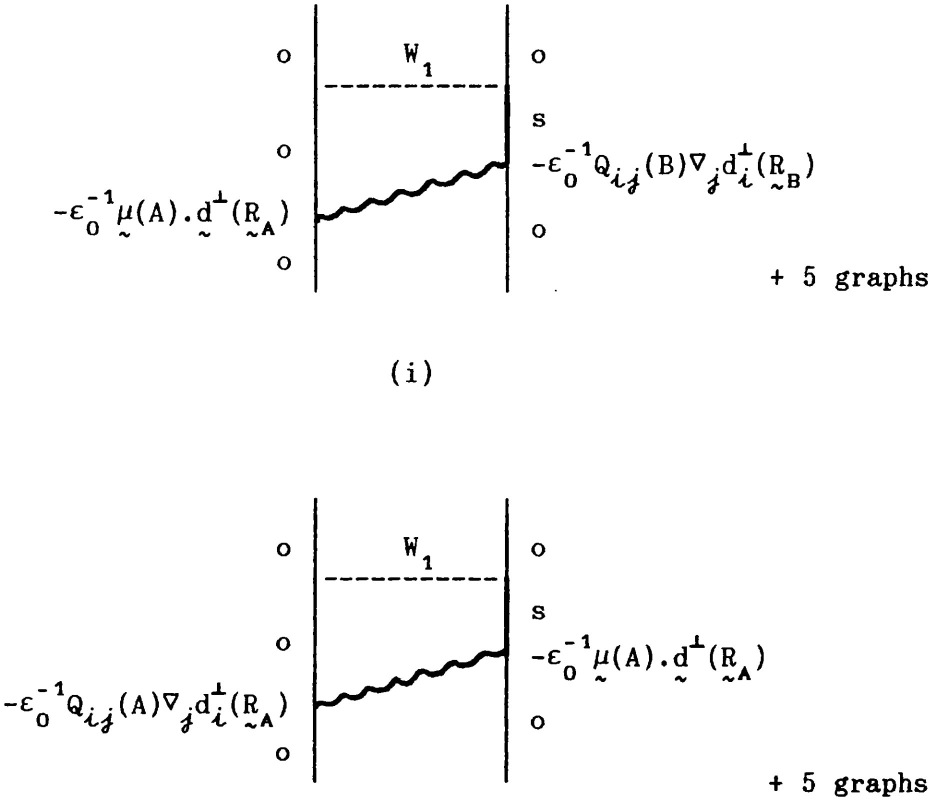
If we assume that selection rules allow the latter type of interaction, for example if the molecule or ion is optically active, then we must consider a further six graphs for the quadrupole interaction at each centre. Typical graphs are drawn in Fig 5.5.; the interactions should be of the same order as (5.3.3), above (coupling proceeds through charge, two electric dipoles and a quadrupole) and the form of the graphs again leads to the use of (5.2.9) in order to sum over the energy denominators in the third-order perturbation expression. In the final result the two sets of terms have been combined, giving

$$\Delta E_5 = -3Q_A (1/4\pi\varepsilon_0)^2 \left(\mu_{\ell}^{\circ\circ}(A) A_{ijk}^{\circ\circ}(B) + Q_{\ell k}^{\circ\circ}(A) \alpha_{ij}^{\circ\circ}(B) \right) \hat{R}_i \hat{G}_{jk\ell} R^{-6} . \tag{5.3.4}$$

This accounts for all interactions up to and including a cut-off point at an R^{-6} dependence on separation.

It is briefly shown below how the result to electric dipole may be obtained through the use of the minimal-coupling interaction terms, with a comment on the calculation of higher-order interactions.

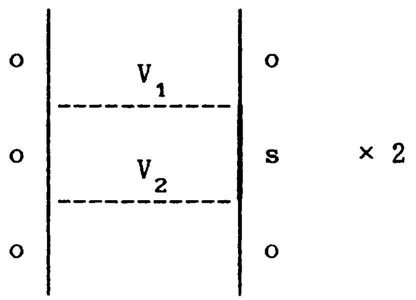
FIG 5.5 : ION-MOLECULE DISPERSION:
NON-RETARDED ELECTRIC-QUADRUPOLE CONTRIBUTIONS



(i)

(ii)

FIG 5.6 : ION-MOLECULE DISPERSION BY MINIMAL COUPLING:
ELECTROSTATIC CONTRIBUTIONS



5.4 The minimal-coupling result

This alternative method is not given in detail here. Attention is merely confined to those terms arising from the ionic charge: the equivalence of the dispersion terms for the neutral case is assumed. Even for results in the electric dipole approximation the inclusion of the $\underset{\sim}{a}^2(\underset{\sim}{R})$ term is warranted and the twelve multipolar graphs of Fig 4.1 are replaced by the well-known sum of twenty seven in the minimal-coupling method.

For the present problem the intermolecular potential energy V_{AB} in the minimal-coupling method is given by (5.4.1). The first term, V_1, of (5.4.1) is of course common to both formalisms. V_2 is then the familiar dipolar interaction.

$$V_{AB} = -(1/4\pi\varepsilon_0)\left\{Q_A\mu_i(B)\hat{R}_i/R^2 - \mu_i(A)\mu_j(B)\beta_{ij}/R^3\right\} \tag{5.4.1}$$

First note that since we are calculating an energy shift there will be no contribution from those interactions of the form of Fig 5.2 but with the $\underset{\sim}{p}.\underset{\sim}{a}(\underset{\sim}{R})$ coupling for the virtual photon. This follows since diagonal momentum matrix elements are zero. Next, of the electrostatic interactions left to consider, the first has been dealt with and is given by (5.2.7). We are left to consider the interaction given in Fig 5.6, where the factor 2 accounts for the interchange of V_1 and V_2. The combined energy shift gives

$$\Delta E_6 = (1/4\pi\varepsilon_0)^2 Q_A\mu_k^{00}(A)\alpha_{ij}^{00}(B)\hat{R}_i\beta_{jk}R^{-5}\ , \tag{5.4.2}$$

which equals the contribution (5.2.10) from the six graphs of Fig 5.2. Hence the total energy shift up to electric dipole has now been generated using the minimal-coupling interactions.

5.5 Summary

The multipolar Hamiltonian has been used to calculate the contributions towards the ion-molecule energy shift which depend on the net charge of the ion. All interactions up to R^{-6} have been calculated and each of the results depends on one of the forms of static polarizability (dipole-dipole, dipole-quadrupole etc) defined for the neutral molecule. As well as its dependence on the ionic charge, where the interaction includes exchange of a virtual photon the energy shift also requires the ion to have a permanent dipole or quadrupole moment.

An important point to note is that all of the results are non-retarded, even those for which the interaction included exchange of a virtual photon. This follows since in such cases the ion interacts through a permanent moment. The energy difference between initial and intermediate or intermediate and final states is then independent of a term for the ion and the resulting sum (5.2.9) leads to shifts which may be written in terms of the static molecular polarizabilities. Each shift therefore applies at all intermolecular separations.

The dominant term is that given by (5.2.7), where the interaction is of the charge-dipole type. The shift has an R^{-4} dependence on the intermolecular separation and, unless the molecule has a very small dipole-dipole static polarizability, this will always be the leading term. Two interaction terms have a magnitude which falls off as R^{-5}. These are the electrostatic charge-dipole/charge-quadrupole interaction and the charge-dipole interaction which is accompanied by exchange of a virtual photon through electric dipole coupling at both molecule and ion. The remaining R^{-6} terms, which require the higher-multipole static polarizabilities for B to be significant, are likely to be less important than the pure dipole term (4.2.15), although we note that their contribution will not fall off by a factor which is inversely proportional to R in the far-zone.

Note that we have excluded magnetic-dipole interactions. Just as there is no static interaction between a permanent electric dipole and a magnetic dipole, we find that there are no magnetic-dipole contributions to the energy shift arising from graphs of the types considered here. For example, when we replace the electric quadrupole vertex of Fig 5.5(i) with a magnetic dipole vertex we obtain an energy shift of zero. We were also able to neglect the terms of (2.7.8) and (2.7.9) in which the interaction is via the vector potential. This is a result of our constraint that the ion is held fixed; these interaction terms do not appear in the Hamiltonian if there is no ionic contribution to the current density.

The equivalence to the order shown in Section 5.4 is rather elementary and perhaps does not emphasize the advantages of the multipolar over the minimal-coupling treatment. As we consider the higher-order terms, however, the simplicity of the multipolar calculations becomes more apparent. In Chapter 3 the relative merits of the use of the two interaction Hamiltonians in the calculation of matrix elements was discussed. It was shown through the use of sum rules how the higher-order energy terms obtained in the minimal-coupling method from the expansion of the vector potential were equivalent to those written down directly from the expansions of the multipolar formalism; we concluded that the latter method was both easier to use and physically more suitable. The same conclusion should be reached here for the matrix elements which involve exchange of transverse photons.

However, the multipolar Hamiltonian has not previously been used, as it has here, to determine the interactions between charged species. We must therefore assess how much this treatment has benefited the calculations. The partial cancellation of the intermolecular potential energy term in the multipolar Hamiltonian has been discussed at length. The remaining electrostatic terms, given by W_{elec} in (5.2.1), all depend on the net charge of the ion A and form a series of charge-multipole interactions. We have cancelled all multipole-multipole interaction terms in the construction of the Hamiltonian so that there is no term of the form of V_2 in (5.4.1). Besides those terms which interact through the vector potential, however, the minimal-coupling interaction Hamiltonian boasts an intact intermolecular potential energy term V_{inter}. Only two terms were required here for the interactions to electric dipole but for the consideration of higher-order interactions we require the full multipole-multipole account. Each molecule will interact with the dipole potential, quadrupole potential etc of the other giving a rapidly expanding number of terms with increasing order of the interaction. For example, in the case under consideration here, to R^{-6} this would require the use of dipole-quadrupole (R^{-4}) interaction potentials.

The interaction Hamiltonian (5.2.1) is therefore of considerable use in the calculation of the interactions between ions and molecules. The non-retarded interactions are determined in a straightforward manner, improving considerably on the minimal-coupling method, and are obtained directly in terms of molecular properties; this then allows them to be compared with the retarded interactions determined by the conventional multipolar interactions.

CHAPTER 6

THE INTERACTION OF FREE ELECTRONS WITH MOLECULES

6.1 Introduction

The interaction of free electrons with atoms and molecules is of continuing interest both theoretically and experimentally [70-73], most notably in the investigation of elastic scattering. For example, Au [71,72] has calculated electron-atom interactions using the minimal-coupling formalism for all parts of his calculations. Now in this work we have already seen the benefit of applying the transformation to the multipolar formalism even for systems carrying net charge; in Chapter 5 ion-molecule dispersion interactions were derived in terms of the static polarizability of the neutral molecule. In such an important area of interest a similar study of the interaction between a free electron and a neutral molecule would be highly desirable. However, the theory presented in Chapter 2 assumes that all interacting species may be allocated a centre of mass or charge about which a multipole expansion is appropriate. Clearly this assumption is invalid in this case. The dynamics of the free electron are best described within the minimal-coupling formalism, with a suitable choice of wavefunction describing an associated momentum state. It is therefore appropriate that such a theory should be detailed which addresses this problem whilst preserving the multipolar description of the molecular interactions.

The transformation to the multipolar Hamiltonian is adapted here by considering the free electronic and molecular terms separately. Only the latter terms are transformed such that the new Lagrangian leads to a Hamiltonian in which the free electron interacts via the vector potential and the interactions of the bound electrons proceed through the electric displacement field. The electrostatic terms are unaffected by the transformation. The Hamiltonian is then used to determine the interaction of a free electron with a molecule. For convenience and without loss of generality the centre of mass of the latter is taken to be the origin. The interaction is found to be composed of both non-retarded contributions, and retarded terms for which we present both general results and results in the far-zone. All of the results apply for a given separation and in each case the electron is assumed to have a small initial momentum.

It was shown in Chapter 1 that there is considerable freedom regarding the exact function used in the transformation of the minimal-coupling Lagrangian. As an alternative to the transformation described above it is possible to add the time derivative of an additional term, thus transforming the free electron parts as well. Such a procedure is discussed briefly also and it is shown that the free electronic charge may contribute to a new transverse field, with which it interacts, thus eliminating the $\underset{\sim}{p}.\underset{\sim}{a}(\underset{\sim}{q})$ and $\underset{\sim}{a}^2(\underset{\sim}{q})$ interactions. However, as in the general Hamiltonian for ion-molecule systems it is not possible to eliminate the vector potential completely and the transformation was found to be less useful than was anticipated.

We begin with the presentation of the modified theory for an electron-molecule system, giving the two forms of transformation. The resulting Hamiltonians are then applied to the calculation of ion-molecule interaction energies, correct to e^4.

6.2 A new Lagrangian

The dynamical system consists of a free electron, defined by its coordinate $\mathbf{q}$ and momentum $\mathbf{p}$, a neutral molecule B and the quantized radiation field. The labels α and a are used for the electrons and nuclei, respectively, of the molecule, which may be considered at rest with the origin defined at its centre of mass.

Much of the development of the theory naturally follows that given earlier in the first two chapters. Hence it is sufficient to present here only the new features. Choosing the Coulomb gauge, the initial form of the Lagrangian is taken from (2.2.10), although its exact form is reliant on the choice of charge and current densities. The charge density is

$$\rho(\mathbf{r}) = -e\delta(\mathbf{r}-\mathbf{q}) - e\sum_{\alpha}\delta(\mathbf{r}-\mathbf{q}_{\alpha}) + e\sum_{a}Z_{a}\delta(\mathbf{r}-\mathbf{q}_{a}) \tag{6.2.1}$$

The transformation to the multipolar Lagrangian previously followed the partitioning of the current density in terms of the polarization and magnetization fields. These fields are again introduced for B, since we wish to describe its interactions in terms of its multipole moments. The free electron contribution to the current density is unaltered. Hence the total current density may be partitioned such that

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}(e^{-};\mathbf{r}) + \mathbf{j}(B;\mathbf{r}) , \tag{6.2.2}$$

with the composite terms taking the forms

$$\mathbf{j}(e^-;\mathbf{r}) = -e\dot{\mathbf{q}}\delta(\mathbf{r}-\mathbf{q}) \tag{6.2.3}$$

and

$$\mathbf{j}(B;\mathbf{r}) = \dot{\mathbf{p}}(B;\mathbf{r}) + \boldsymbol{\nabla}\times\mathbf{M}(B;\mathbf{r}) \ . \tag{6.2.4}$$

The fields in (6.2.4) take their previous definitions, except that we have put $\mathbf{R}_B = 0$, ie

$$\mathbf{p}(B;\mathbf{r}) = -e\sum_{\alpha(B)} \mathbf{q}_\alpha \int_0^1 \delta(\mathbf{r}-\lambda\mathbf{q}_\alpha)d\lambda + e\sum_{a(B)} Z_a\mathbf{q}_a \int_0^1 \delta(\mathbf{r}-\lambda\mathbf{q}_a)d\lambda \tag{6.2.5}$$

and

$$\mathbf{M}(B;\mathbf{r}) = -e\sum_{\alpha(B)} (\mathbf{q}_\alpha\times\dot{\mathbf{q}}_\alpha)\int_0^1 \lambda\delta(\mathbf{r}-\lambda\mathbf{q}_\alpha)d\lambda + e\sum_{a(B)} Z_a(\mathbf{q}_a\times\dot{\mathbf{q}}_a)\int_0^1 \lambda\delta(\mathbf{r}-\lambda\mathbf{q}_a)d\lambda. \tag{6.2.6}$$

The transformation of the Lagrangian, which follows next, is the important step in the formulation. The restrictions on the form of the function chosen for addition to the Lagrangian were given earlier. We may write

$$L_{new} = L_{min} - \frac{d}{dt}\int p_i^{\perp}(B;\mathbf{r})a_i(\mathbf{r})d^3\mathbf{r} \tag{6.2.7}$$

where the familiar transformation now includes only the polarization field for B. The interaction of the electron current (6.2.3) with the vector potential is thus left unaltered. Should we consider a system where the electron might interact with a number of molecules then the total molecular polarization field would be required in (6.2.7).

The new Lagrangian is again written as the sum of particle, field and interaction parts and the transformation follows the elimination of the scalar potential. The electrostatic terms formed by this are included in (6.2.8) with a partitioning into an intermolecular term, given below, and an intramolecular term for the molecule. In the particle Lagrangian (6.2.9) the nuclear terms are written separately; these are retained for completeness but it is recognised that in many problems, such as the scattering of electrons by atoms, they may be discarded. Thus

$$L_{new} = L_{part} + L_{rad} + L_{int} \tag{6.2.8}$$

with

$$L_{part} = (m_e/2)\dot{\mathbf{q}}^2 + (m_e/2)\sum_{\alpha}\dot{\mathbf{q}}_{\alpha}^2 + \sum_{a}(m_a/2)\dot{\mathbf{q}}_a^2 + V_{intra}(B)\ , \tag{6.2.9}$$

$$L_{rad} = (\varepsilon_0/2)\int\left\{\dot{\mathbf{a}}(\mathbf{r})^2 - c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r}\ , \tag{6.2.10}$$

and

$$\begin{aligned} L_{int} = &-\int p_i^{\perp}(B;\mathbf{r})\dot{a}_i(\mathbf{r})d^3\mathbf{r} + \int\left\{\nabla\times\mathbf{M}(B;\mathbf{r})\right\}_i a_i(\mathbf{r})d^3\mathbf{r} \\ &- e\int\dot{q}_j a_i(\mathbf{r})\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{q})d^3\mathbf{r} - V_{inter} \qquad . \end{aligned} \tag{6.2.11}$$

The intermolecular potential energy term is given by

$$V_{inter} = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\{\sum_{\alpha}\frac{1}{|\mathbf{q}-\mathbf{q}_{\alpha}|} - \sum_{a}\frac{Z_a}{|\mathbf{q}-\mathbf{q}_a|}\right\}. \tag{6.2.12}$$

From these expressions the canonical momenta may be written down directly. Note that the integration over $\mathbf{r}$ in the third term of (6.2.11) may be performed after first writing the integrand with the complete delta function, which is allowed since $\mathbf{a}(\mathbf{r})$ is transverse.

6.3 The canonical momenta

The canonical variables are given by $(\underset{\sim}{q},\underset{\sim}{p})$ for the electron, $(\underset{\sim}{q}_\alpha,\underset{\sim}{p}_\alpha)$ and $(\underset{\sim}{q}_a,\underset{\sim}{p}_a)$ for B and the field variables are given by the pair $(\underset{\sim}{a}(\underset{\sim}{r}),\underset{\sim}{\Pi}(\underset{\sim}{r}))$ as usual. The momenta, defined from the Lagrangian, are given by

$$p_i = m_e\dot{q}_i - ea_i(\underset{\sim}{q}) \tag{6.3.1}$$

$$p_{i(\alpha)} = m_e\dot{q}_{i(\alpha)} - \int\left(\underset{\sim}{n}_\alpha(B;\underset{\sim}{r})\times\underset{\sim}{b}(\underset{\sim}{r})\right)_i d^3\underset{\sim}{r} \tag{6.3.2}$$

$$p_{i(a)} = m_a\dot{q}_{i(a)} - \int\left(\underset{\sim}{n}_a(B;\underset{\sim}{r})\times\underset{\sim}{b}(\underset{\sim}{r})\right)_i d^3\underset{\sim}{r} \tag{6.3.3}$$

and

$$\Pi_i(\underset{\sim}{r}) = \varepsilon_0\dot{a}_i(\underset{\sim}{r}) - p_i^{\perp}(B;\underset{\sim}{r}) \quad . \tag{6.3.4}$$

Note the forms of the particle canonical momenta. For the electron, p_i appears in its minimal-coupling form whereas $p_{i(\alpha)}$ and $p_{i(a)}$ are written in their usual multipolar form in terms of the auxiliary fields $\underset{\sim}{n}_\alpha(B;\underset{\sim}{r})$ and $\underset{\sim}{n}_a(B;\underset{\sim}{r})$, which are redefined as

$$\underset{\sim}{n}_\alpha(B;\underset{\sim}{r}) = -e\sum_{\alpha(B)}\underset{\sim}{q}_\alpha\int_0^1\lambda\delta(\underset{\sim}{r}-\lambda\underset{\sim}{q}_\alpha)d\lambda \tag{6.3.5}$$

and

$$\underset{\sim}{n}_a(B;\underset{\sim}{r}) = +e\sum_{a(B)}Z_a\underset{\sim}{q}_a\int_0^1\lambda\delta(\underset{\sim}{r}-\lambda\underset{\sim}{q}_a)d\lambda \ . \tag{6.3.6}$$

A rearrangement of these expressions in order to obtain the velocities will precede the formation of the Hamiltonian.

6.4 The Hamiltonian

The Hamiltonian constructed from (6.2.8) is given below. The standard partitioning gives

$$H_{new} = H_{part} + H_{rad} + H^{(1)}_{int} + H^{(2)}_{int} + W_{elec} + H_{self} , \tag{6.4.1}$$

where each term is written out explicitly below. The particle Hamiltonian is simply given by

$$H_{part} = \underset{\sim}{p}^{2}/2m_{e} + \frac{1}{2m_{e}} \sum_{\alpha} \underset{\sim}{p}^{2}_{\alpha}(B) + (1/2) \sum_{a} \underset{\sim}{p}^{2}_{a}(B)/m_{a} + V_{intra}(B), \tag{6.4.2}$$

the radiation Hamiltonian by

$$H_{rad} = \frac{1}{2}\int\left\{\underset{\sim}{d}^{\perp 2}(\underset{\sim}{r})/\varepsilon_{0} + \varepsilon_{0}c^{2}(\underset{\sim}{\nabla}\times\underset{\sim}{a}(\underset{\sim}{r}))^{2}\right\}d^{3}\underset{\sim}{r} \tag{6.4.3}$$

and the interaction terms are given by

$$H^{(1)}_{int} = (e/m)\underset{\sim}{p}.\underset{\sim}{a}(\underset{\sim}{q}) -\varepsilon_{0}^{-1}\int\underset{\sim}{p}(B;\underset{\sim}{r}).\underset{\sim}{d}^{\perp}(\underset{\sim}{r})d^{3}\underset{\sim}{r} -\int\underset{\sim}{m}(B;\underset{\sim}{r}).\underset{\sim}{b}(\underset{\sim}{r})d^{3}\underset{\sim}{r} \tag{6.4.4}$$

and

$$H^{(2)}_{int} = (1/2m_{e}) \sum_{\alpha(B)} \left(\int\underset{\sim}{n}_{\alpha}(B;\underset{\sim}{r})\times\underset{\sim}{b}(\underset{\sim}{r})d^{3}\underset{\sim}{r}\right)^{2} + \sum_{a(B)} (1/2m_{a})\left(\int\underset{\sim}{n}_{a}(B;\underset{\sim}{r})\times\underset{\sim}{b}(\underset{\sim}{r})d^{3}\underset{\sim}{r}\right)^{2}$$

$$+ (e^{2}/2m_{e})\underset{\sim}{a}^{2}(\underset{\sim}{q}) \quad . \tag{6.4.5}$$

In contrast to the conventional transformation of the minimal-coupling to the multipolar Hamiltonian for neutral systems where all electrostatic terms are completely eliminated, V_{inter} given by

(6.2.12) remains after the transformation and forms part of the interaction Hamiltonian. The first terms of the Taylor expansion of V_{inter} about the origin are given by

$$W_{elec} = -\left(\frac{e}{4\pi\varepsilon_0}\right)\left\{\mu_i(B)\hat{q}_i/q^2 + Q_{ij}(B)(\delta_{ij}-3\hat{q}_i\hat{q}_j/q^3\right\} . \tag{6.4.6}$$

The remaining self-energy term is

$$H_{self} = \frac{1}{2\varepsilon_0}\int|\underset{\sim}{p}^{\perp}(B;\underset{\sim}{r})|^2 d^3\underset{\sim}{r} . \tag{6.4.7}$$

In (6.4.4) the magnetization of the neutral molecule $\underset{\sim}{m}(B;\underset{\sim}{r})$ assumes the definition used in Chapter 4, modified only by the choice of origin.

Let us consider the distinctive features of this new Hamiltonian. The field canonical momentum is the same as the electric displacement vector field (apart from sign) and the coupling of the molecule with the field is given by conventional multipolar interactions. The interaction of the free electron with the field, however, is given by the $\underset{\sim}{p}.\underset{\sim}{a}(\underset{\sim}{q})$ and $\underset{\sim}{a}^2(\underset{\sim}{q})$ terms. As mentioned earlier, one significant difference in contrast to the Hamiltonian of Chapter 2 is that now there is no corresponding intermolecular polarization product, a consequence of the transformation used. The partial cancellation of the intermolecular potential energy term in that case does not take place here and hence (6.2.12) is left intact.

These terms will be used shortly to consider the interaction of an electron with a neutral molecule. In addition to the electrostatic interaction between the pair there are terms arising from exchange of virtual photons. The constraint will be that both electron and molecule return from any intermediate state to their initial states.

First we extend the theory of the preceding sections by considering an alternative type of transformation.

6.5 An alternative transformation

In this alternative transformation the total time derivative which is added to L_{min} now includes a term for the electron as well. The explicit form of the transformation is

$$L_{new} = L_{min} - \frac{d}{dt}\int p_i^{\perp}(B;\underset{\sim}{r})a_i(\underset{\sim}{r})d^3\underset{\sim}{r} + e\frac{d}{dt}\int q_j a_j(\underset{\sim}{r})\delta(\underset{\sim}{r}-\underset{\sim}{q})d^3\underset{\sim}{r} \tag{6.5.1}$$

The first total time derivative has been dealt with; the multipolar form of interaction for B will not be considered further. The second term transforms the electronic parts. The form of this term was chosen specifically to maintain the similarities between the molecular and electron parts.

In the resulting Lagrangian new terms appear in L'_{int};

$$L'_{int} = e\int q_j \dot{a}_i(\underset{\sim}{r})\delta^{\perp}_{ij}(\underset{\sim}{r}-\underset{\sim}{q})d^3\underset{\sim}{r} + e\int q_j(\nabla_i a_j(\underset{\sim}{r}))\delta(\underset{\sim}{r}-\underset{\sim}{q})\dot{q}_i d^3\underset{\sim}{r} - V_{inter} \tag{6.5.2}$$

with the intermolecular potential energy term again given by (6.2.12). In writing the first term of the above expression it has been noted that the contribution from the longitudinal part of the total delta function is zero. The second term results from the total time derivative of the delta function and integration by parts. The new forms of the canonical momenta are then

$$p_i = m_e\dot{q}_i + e\int q_j(\nabla_i a_j(\mathbf{r}))\delta(\mathbf{r}-\mathbf{q})d^3\mathbf{r} \qquad (6.5.3)$$

and

$$\Pi_i(\mathbf{r}) = \varepsilon_0\dot{a}_i(\mathbf{r}) - p_i^{\perp}(B;\mathbf{r}) + eq_j\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{q}) \ . \qquad (6.5.4)$$

The new field canonical momentum is a modified form of the displacement vector field. Its cross term with $p_i^{\perp}(B;\mathbf{r})$ following the square of $\dot{a}_i(\mathbf{r})$ in the construction of the Hamiltonian will have the dimension of a polarization product and will thus partially cancel the electron-molecule potential energy V_{inter}.

Using these canonical momenta the Hamiltonian follows immediately. The new terms only are given below. Hence

$$H_{new} = H_{part} + H_{rad} + H_{int}^{(1)} + H_{int}^{(2)} + W_{elec} + H_{self} \qquad (6.5.5)$$

with H_{part} unchanged and H_{rad} given by

$$H_{rad} = \frac{1}{2}\int\left\{\mathbf{d}^{\perp 2}(\mathbf{r})/\varepsilon_0 + \varepsilon_0 c^2(\nabla\times\mathbf{a}(\mathbf{r}))^2\right\}d^3\mathbf{r} \ , \qquad (6.5.6)$$

where $\mathbf{d}^{\perp}(\mathbf{r})$ is a new transverse field to be defined shortly,

$$H_{int}^{(1)} = (e/\varepsilon_0)\mathbf{q}.\mathbf{d}^{\perp}(\mathbf{R}) - (e/2m_e)\left(p_i q_j + q_j p_i\right)\nabla_i a_j(\mathbf{R})$$
$$- \varepsilon_0^{-1}\int\mathbf{p}(B;\mathbf{r}).\mathbf{d}^{\perp}(\mathbf{r})d^3\mathbf{r} \ , \qquad (6.5.7)$$

$$H_{int}^{(2)} = (e^2/2m_e)\left(q_j\nabla_i a_j(\mathbf{R})\right)\left(q_k\nabla_i a_k(\mathbf{R})\right) \ , \qquad (6.5.8)$$

and the remaining electrostatic and self-energy terms are given by

$$W_{\text{elec}} = -(e/\varepsilon_0)\int q_j p^{\perp}_i(B;\mathbf{r})\delta^{\perp}_{ij}(\mathbf{r}-\mathbf{q})d^3\mathbf{r} + V_{\text{inter}} \, . \tag{6.5.9}$$

and

$$H_{\text{self}} = \frac{e^2}{2\varepsilon_0}\int q_j q_k \delta^{\perp}_{ij}(\mathbf{r}-\mathbf{R})\delta^{\perp}_{ik}(\mathbf{r}-\mathbf{R})d^3\mathbf{r} \, . \tag{6.5.10}$$

The molecular term has been included in (6.5.7) since it is written in terms of the new field. In the definition

$$\mathbf{d}(\mathbf{r}) = \varepsilon_0\mathbf{e}(\mathbf{r}) + \mathbf{p}(B;\mathbf{r}) - e\mathbf{q}\delta(\mathbf{r}-\mathbf{q}) \, , \tag{6.5.11}$$

an electronic as well as a molecular term contributes to this new field. This choice will then give

$$\mathbf{\Pi}_{\text{mult}}(\mathbf{r}) = -\mathbf{d}^{\perp}(\mathbf{r}) \tag{6.5.12}$$

by analogy, although $\mathbf{d}(\mathbf{r})$ given by (6.5.11) should not be mistaken for the displacement field, which uses the same symbol. Let us compare this Hamiltonian with (6.4.1) derived earlier. A new interaction term has been derived which describes how a free electron may interact through the exchange of transverse photons. However, the vector potential has not been eliminated; this is only possible for neutral systems and charged systems at rest. In fact, the transformation has produced a first-order term with the dimension of a magnetic interaction and a second-order term of a diamagnetic equivalent, neither of which is straightforward to use. Further, unlike in molecular interactions, where the dipole approximation may be used, each of these terms would have to be considered in the study of electron-molecule interactions since there can be no question of order with regard to magnitude. Likewise the electrostatic terms are complicated. It was easy to consider just V_{inter} in (6.4.1). The corresponding terms here would result from a simplification of (6.5.9). In Section 2.6, where the intermolecular polarization product contained integrals in closed form, W_{elec} was determined as a complete sum. In this case we could only determine these terms in the form of a series expansion. Of the two Hamiltonians (6.4.1) and (6.5.5), the former is the more suited for applications and is the one used in the following section.

6.6 Electron-molecule interactions

The Hamiltonian developed earlier in this chapter is used here to determine the interactions of a free electron with a neutral molecule. The use of perturbation theory gives the interactions in the form of energy shifts for a given separation. The interaction Hamiltonian for the system is

$$\begin{aligned} H_{int} = {} & (e/m_e)\underset{\sim}{p}.\underset{\sim}{a}(\underset{\sim}{q}) + (e^2/2m_e)\underset{\sim}{a}^2(\underset{\sim}{q}) - \varepsilon_0^{-1}\underset{\sim}{\mu}(B).\underset{\sim}{d}^{\perp}(\underset{\sim}{0}) \\ & - (e/4\pi\varepsilon_0)\mu_i(B)q_i/q^3 \end{aligned} \tag{6.6.1}$$

where the molecular centre of mass is defined as the origin. The position vector relative to this centre and the momentum of the electron are denoted by $\underset{\sim}{q}$ and $\underset{\sim}{p}$ respectively: the electron is described by the state $|\underset{\sim}{p}\rangle$ with an associated momentum $\underset{\sim}{p} = \hbar\underset{\sim}{\kappa}$. The electric dipole approximation is assumed for the interaction of the molecule with the electromagnetic field.

Typical time-ordered graphs showing the interactions between an electron and a molecule are drawn in Fig 6.1, where a vertical double line represents the molecule. The graphs characterise the type of interaction. Graphs (a) and (b) determine the non-retarded interaction whilst (d), (e) and (f) will account for the fully retarded contributions. In Fig 6.1(c) the interaction is partly Coulombic and partly due to transverse photon exchange. The graphs are used to calculate the interaction up to e^4 and the total energy shift is the sum of these results.

The electron is assumed to have a small momentum so that its change of kinetic energy upon interaction with the field is small compared with the spacing of the intermediate states of the molecule. For this case the addition of the energy denominators is greatly simplified and some of the results of Chapter 4 are used here. Further, in some cases the separation $\underset{\sim}{q}$ is sufficiently large (the far-zone limit) that the virtual photon energies are small. The molecule may also be assumed to be random oriented with respect to $\underset{\sim}{p}$.

We first consider those interactions which are purely electrostatic and thus clearly non-retarded.

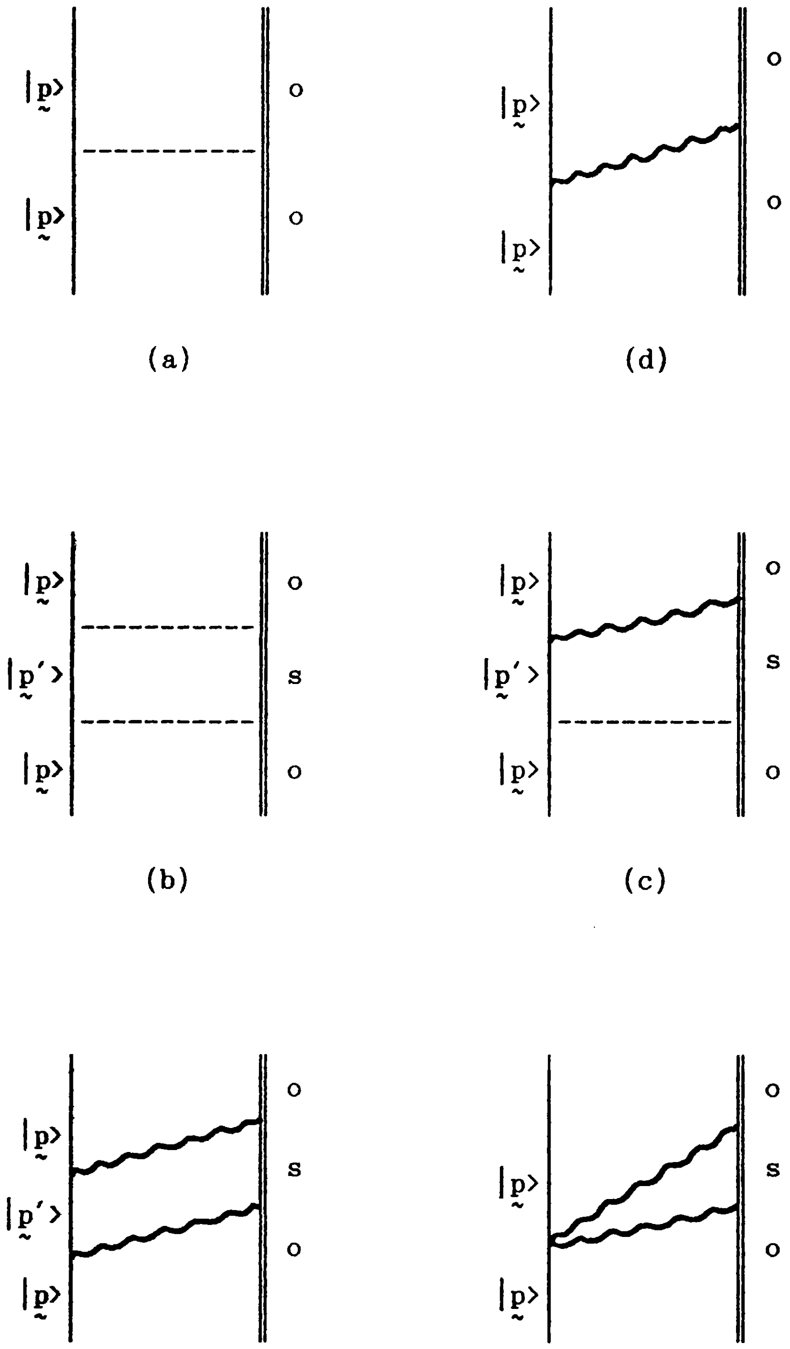
i) *Non-retarded interactions*

If the neutral molecule B has a permanent moment then the lowest order interaction is given by Fig 6.1(a). The energy shift for this case may be written down directly as

$$\Delta E(a) \;=\; (-e/4\pi\varepsilon_0)\mu_i^{oo}(B)\hat{q}_i q^{-2} \tag{6.6.2}$$

which is a simple charge-dipole interaction dependent on the inverse square of the separation. The higher-order electrostatic term, given by Fig 6.1(b), involves a sum over the free electronic and molecular intermediate states. Now the energy denominator for this case is given by $[E_{so}-(p^2-p'^2)/2m]$, where the second term is the difference in kinetic energy of the electron in the two momentum states. It is a good approximation to assume that this quantity is small compared with E_{so} if the electron is slowly moving. This allows us to make the

FIG 6.1: CONTRIBUTIONS TO ELECTRON-MOLECULE COUPLING IN QED



(a) (d)

(b) (c)

(e) (f)

expansion

$$\frac{1}{E_{so}-(p^2-p'^2)/2m} = \frac{1}{E_{so}} + \frac{(p^2-p'^2)/2m}{E_{so}^2} + \frac{[(p^2-p'^2)/2m]^2}{E_{so}^2[E_{so}-(p^2-p'^2)/2m]} \tag{6.6.3}$$

and assume that the major contribution comes from the first two terms of (6.6.3). The contribution from the third term of (6.6.3) may be neglected so that the remaining terms give the shift

$$\Delta E(b) \simeq \Delta E'(b) + \Delta E''(b) \quad . \tag{6.6.4}$$

The contribution with the first term as the denominator is straightforward; E_{so}^{-1} may be taken into the definition of the static electric dipole polarizability of molecule B. Effecting closure over $\underset{\sim}{p}'$ gives the non-retarded result

$$\Delta E'(b) = (-e^2/2)(4\pi\varepsilon_0)^{-2}\alpha_{ij}^{oo}(B)\hat{q}_i\hat{q}_j q^{-4} \tag{6.6.5}$$

which is independent of the electron momentum $\underset{\sim}{p}$.

In order to evaluate ΔE''(b) we make use of the relationship

$$[(p^2-p'^2)/2m]\langle \underset{\sim}{p}'|q_i q^{-3}|\underset{\sim}{p}\rangle = \langle \underset{\sim}{p}'|[q_i q^{-3},H_{elec}]|\underset{\sim}{p}\rangle \tag{6.6.6}$$

where H_{elec} is the Hamiltonian for the unperturbed electron, and the commutator

$$[q_i q^{-3},H_{elec}] = (i\hbar/2m)\left(\beta_{ij}q^{-3}p_j + p_j\beta_{ij}q^{-3}\right) \tag{6.6.7}$$

with

$$\beta_{ij} = (\delta_{ij} - 3\hat{q}_i\hat{q}_j) \quad . \tag{6.6.8}$$

It is then possible to effect closure over $\underset{\sim}{p}'$ and obtain

$$\Delta E''(b) = (e^2\hbar^2/2m)(4\pi\varepsilon_0)^{-2} \sum_s \frac{\mu_i^{os}\mu_j^{so}}{E_{so}^2}(\delta_{ij}+3\hat{q}_i\hat{q}_j)q^{-6} \; , \tag{6.6.9}$$

which is small compared with (6.6.5). Contributions from the third term of (6.6.3) are even smaller, with higher inverse powers of q-dependence, and are neglected.

Next we consider the interactions given by the six graphs of the type Fig 6.1(c), which include the exchange of a virtual photon in addition to the electrostatic interaction.

ii) *Coulomb interaction plus transverse-photon exchange*

An exact solution of the contribution from graphs of the type Fig 6.1(c) to the total energy shift is not possible. However, with the use of an expansion of the type (6.6.3) for each factor in the denominator we may consider the separate contributions individually. The first term after angular integration of the photon wavevector is

$$\begin{aligned}\Delta E'(c) = \; & i(2\pi)^{-3}(4\pi\varepsilon_0)^{-1}(e^2\hbar/2\varepsilon_0 m)p_i \sum_s \mu_j^{os}\mu_k^{so} \\ & \times(4\pi)\int_0^\infty [\tau_{ij}(kq) - \tau_{ij}(kq)]q_k q^{-3}D'(k)k^2 dk \; = \; 0\end{aligned} \tag{6.6.10}$$

where p_i is the component of the electron momentum along the direction i; $\tau_{ij}(kq)$ is defined by (4.2.7) and $D'(k)$ refers to the sum

$$D'(k) = \frac{1}{E_{so}(E_{so}+\hbar ck)} + \frac{1}{\hbar ck(E_{so}+\hbar ck)} + \frac{1}{E_{so}\hbar ck} \; . \tag{6.6.11}$$

So we need to consider the next term in order to obtain a contribution from this set. Upon integration the leading term gives

$$\Delta E''(c) = i(2\pi)^{-3}(e^2\hbar^3/2\varepsilon_0^2 m^2)p_i \sum_s \mu_j^{os}\mu_k^{so} \int_0^\infty \sigma_{ij\ell}(kq)\beta_{\ell k} q^{-3} D''(k) k^3 dk \tag{6.6.12}$$

with the now slightly more complicated sum over the energy factors given by

$$D''(k) = \frac{1}{E_{so}^2(E_{so}+\hbar ck)} + \frac{1}{(\hbar ck)^2(E_{so}+\hbar ck)} + \frac{(E_{so}+\hbar ck)}{E_{so}^2(\hbar ck)^2} \tag{6.6.13}$$

and $\sigma_{ij\ell}(kq)$ also assuming its earlier definition (4.3.9.). A useful result may be obtained from this expression in the far-zone, where $E_{so} \gg \hbar ck$. The sum reduces to

$$D''_{FZ}(k) = 2\left(E_{so}(\hbar ck)^2\right)^{-1} \tag{6.6.14}$$

which is then used in (6.6.12). To simplify the calculation we may choose one axis of the laboratory frame to be parallel to the electron momentum. For a freely rotating molecule we then obtain

$$\Delta E''(c) = i(3e^2\hbar/32\pi^2\varepsilon_0^2 m^2 c^2)\alpha(B)p(\underset{\sim}{\hat{q}}\cdot\underset{\sim}{\hat{p}})q^{-5} \tag{6.6.15}$$

where $\alpha(B)$ is the isotropic, static polarizability of B and $\underset{\sim}{\hat{p}}$ is a unit vector along the direction of the electron momentum. This term, in contrast to those of the previous sub-section, is dependent on the magnitude of the electron momentum.

iii) *Fully retarded interactions*

This final section considers all interactions which are fully retarded. Coupling may proceed via exchange of a single or two transverse photons and the interaction vertices are either linear or quadratic in the vector potential. To begin with, consider Fig 6.1(d). Two such graphs account for the exchange of a virtual photon. However, following angular integration we find that the two terms give equal and opposite contributions ie

$$\begin{aligned}\Delta E(d) &= i(2\pi e/\varepsilon_0 mc)p_i\mu_j^{oo}(B)\int_0^\infty[\tau_{ij}(kq) - \tau_{ij}(kq)]k\,dk\\ &= 0 \qquad\qquad (6.6.16)\end{aligned}$$

and so there are no contributions from this form of coupling.

The twelve graphs of Fig 6.1(e) may be used to determine the energy shift arising from an exchange of two virtual photons. The form of the graphs is familiar from the dispersion calculations of Chapter 4, except, of course, that here the electron interacts with the vector potential. The use of $\underset{\sim}{a}(\underset{\sim}{r})$ instead of $\underset{\sim}{d}(\underset{\sim}{r})$ at the electron vertices does not provide any difficulty, however, since we may make use of the results of Tables 4.3.1/2 to evaluate the sum over the energy denominators. The relevant sum is S_4 and an exact expression for $\Delta E(e)$ is

$$\Delta E(e) = (e\hbar/m\varepsilon_0 V)^2 p_i p_j \sum_s \mu_k^{os}\mu_l^{so} \sum_{\underset{\sim}{p}'}\sum_{\underset{\sim}{k}'}\sum_{\underset{\sim}{k}} \tilde{\alpha}_{ik}\tilde{\alpha}'_{jl}\langle \underset{\sim}{p}|e^{i\underset{\sim}{k}.\underset{\sim}{q}}|\underset{\sim}{p}'\rangle\langle \underset{\sim}{p}'|e^{i\underset{\sim}{k}'.\underset{\sim}{q}}|\underset{\sim}{p}\rangle$$

$$\times\frac{E_{so}+\hbar ck'-(p^2-p'^2)/2m}{[E_{so}-(p^2-p'^2)/2m][\hbar ck'-(p^2-p'^2)/2m][E_{so}+\hbar ck']}\left(\frac{1}{k+k'}-\frac{1}{k-k'}\right)(\hbar c)^{-1} \qquad (6.6.17)$$

in which $\tilde{\alpha}_{ik}$ is defined by (4.2.5). The evaluation of (6.6.17) requires an approximation; we again assume that for a slowly moving electron the quantity $(p^2-p'^2)/2m$ is negligible in comparison with the other energies. This allows closure over $\underset{\sim}{p}'$ so that a result may be quoted for a given q. Following angular integration the complete result reduces to

$$\Delta E(e) = (e/2\pi^2\varepsilon_0 mc)^2 p_i p_j \sum_s \frac{\mu_k^{os}\mu_\ell^{so}}{E_{so}}$$
$$\times\int_0^\infty\int_0^\infty \tau_{ik}(kq)\tau_{j\ell}(k'q)\left(\frac{1}{k+k'} - \frac{1}{k-k'}\right)k^2k'\,dk\,dk'. \tag{6.6.18}$$

Before proceeding note that the pre-integral factor is symmetric to the interchange of the indices $i \leftrightarrow j$ and/or $k \leftrightarrow \ell$. Integration over p′ gives

$$\Delta E(e) = \pi(e/2\pi^2\varepsilon_0 mc)^2 q^{-3} p_i p_j \sum_s \frac{\mu_k^{os}\mu_\ell^{so}}{E_{so}}$$
$$\times\int_0^\infty \tau_{ik}(kq)\Big\{\alpha_{j\ell}[(kq)^2\cos(kq)] + \beta_{j\ell}[1 - (kq)\sin(kq) - \cos(kq)]\Big\}dk. \tag{6.6.19}$$

Using (4.2.7) for $\tau_{ik}(kq)$ we may write each term in a symmetric form so that a suitable change of variable gives for the integral of (6.6.19)

$$(2q)^{-1}\int_0^\infty\Big\{2\alpha_{ik}\alpha_{j\ell}T_1(x) + (\alpha_{ik}\beta_{j\ell} + \beta_{ik}\alpha_{j\ell})T_2(x) + 2\beta_{ik}\beta_{j\ell}T_3(x)\Big\}dx \tag{6.6.20}$$

where the trigonometric functions $T_n(x)$ are

$$T_1(x) = (x/2)\sin(2x) \tag{6.6.21}$$

$$T_2(x) = \cos(2x) - \sin(2x)/x + \sin(x)/x \tag{6.6.22}$$

$$T_3(x) = [\sin(2x)-2x\cos(2x)]/2x^3 - \sin(2x)/2x - [\sin(x)-x\cos(x)]/x^3 \ , \tag{6.6.23}$$

and

$$kq = x \quad . \tag{6.6.24}$$

With the use of standard integrals [67] it is easily shown that the integral (6.6.20) is zero, so that

$$\Delta E(e) = 0 \quad . \tag{6.6.25}$$

Thus there is no contribution to the electron-molecule interaction from two-photon exchange with graphs of the type Fig 6.1(e), within the approximations used.

However, there is another type of two-photon exchange which needs to be considered. It occurs through quadratic coupling with the vector potential as shown in Fig 6.1(f). There are three such graphs. Summing the three terms with the use of Table 4.3.3 gives after angular integration

$$\Delta E(f) = -(e^2/16\pi^4\varepsilon_0^2 mc^2) \sum_s \mu_i^{os}\mu_j^{so} \int_0^\infty \frac{k'^2\tau_{jk}(k'q)}{k_s + k'} \int_{-\infty}^\infty \frac{k^2\tau_{ik}(kq)}{k + k'} dk dk' . \tag{6.6.26}$$

Integrating over k and dropping the primes gives

$$\Delta E(f) = -(e^2/16\pi^3\varepsilon_0^2 mc^2 q^2) \sum_s \mu_i^{os}\mu_j^{so} \int_0^\infty \frac{k^2\tau_{jk}(kq)}{k_s + k}$$
$$\times\Big(\alpha_{ik}[-kq\cos(kq)] + \beta_{ik}[\sin(kq) - (kq)^{-1} + \cos(kq)/(kq)]\Big)dk \ . \tag{6.6.27}$$

Now with limits 0 to ∞ a final evaluation of (6.6.27) cannot be done exactly. However, as for $\Delta E(c)$, we may determine the contribution in the far-zone; (6.6.27) is modified by the use of $k_s \gg k$ and the final result is found to be dependent on the static polarizability of B. The use of standard integrals gives an energy shift

$$\Delta E(f) \quad = \quad -(e^2\hbar/256\pi^3\varepsilon_0^2mc)\alpha^{oo}_{ij}(B)(\delta_{ij}+7\hat{q}_i\hat{q}_j)q^{-5} \tag{6.6.28}$$

which has the same q-dependence as the aforementioned term but does not depend on the electron momentum. This concludes the calculation of all interaction energies up to e^4.

6.7 Summary

It has been calculated here that the interaction between a free electron and a neutral molecule is made up of both electrostatic terms and terms which arise from transverse photon exchange and that the former are the more dominant, especially if the molecule is polar. The results are summarised below.

For molecules with a permanent moment the lowest order interaction is given by (6.6.2). This is the simple charge-dipole interaction and the inverse square dependence will dominate higher-order terms. Since there is no contribution from coupling involving the exchange of one virtual photon (6.6.16), the complete interaction to e^2 is entirely electrostatic.

The remaining interactions up to an order of e^4 have also been determined. The calculation of the second-order electrostatic coupling was made following the binomial expansion of the energy denominator, a step which took the assumption that the electron is slowly moving. The resulting terms then form an inverse power series in the separation q, such that the first two terms only need be considered. The first, which behaves as q^{-4} and depends on the static polarizability of the molecule, corresponds to the ion-molecule interaction (5.2.7) and is the dominant term for the interaction of a free electron with a non-polar molecule since it remains for all separations. This contrasts the dispersion interaction studied in Chapter 4, in which the London result falls off with increasing separation to give the Casimir-Polder interaction. The second term, which behaves as q^{-6}, is considered as a small correction term to the total electrostatic interaction.

We next considered the third-order interaction made up of the exchange of a virtual photon in addition to electrostatic coupling. The leading term was determined for the far-zone case and it was found that the energy shift was proportional to the electron momentum and the static, isotropic polarizability of the molecule, with a q^{-5} dependence on separation. A result with similar q-dependence was obtained in the far-zone for the leading term from the third-order interaction involving exchange of two photons (6.6.28). Unfortunately it was not possible to obtain an exact, general result in these cases. Where two-photon exchange proceeded through interactions linear in the vector potential it was found that there were no terms significant to the overall energy shift, although contributions from terms smaller in magnitude have yet to be calculated.

The new Hamiltonian developed here to study the interaction of free electrons with molecules is both ideal in its form (with multipolar expansions describing the molecular interactions and a momentum state representing the electron) and easy to apply. The results given may be compared with those of Au [71,72], whose calculations used the minimal-coupling Hamiltonian. As far as is comparable our results agree; he has obtained terms with the same q-dependence, although his work applied to the electron-atom rather than the electron-molecule interaction. The Hamiltonian itself was written down for a single electron and molecule, although a more general form for a collection of electrons and molecules follows naturally. The extension to a study of electron-ion interactions is also straightforward, since the multipolar Hamiltonian for the interactions involving ions has been developed here also.

The work presented in this chapter forms the basis for further studies on electron-molecule interactions. As well as the calculation of higher-order terms of the type dealt with here it would also be logical to relax some of the restrictions imposed on the nature of the interaction. The results given are in the form of an energy shift for a given separation q. If we were to consider more general cases, in which the momentum state for the electron may change, then perhaps we could consider scattering processes. For example, if we were to define initial and final momentum states for the electron as $|\underset{\sim}{p}\rangle$ and $|\underset{\sim}{p}'\rangle$ with $|\underset{\sim}{p}| = |\underset{\sim}{p}'|$ then an integration over all space would allow the results to be interpreted as contributions towards the elastic scattering of an electron.

REFERENCES

[1] Dirac P.A.M.: Proc. R. Soc. London A114, 243 (1927)

[2] Schwinger J. ed: *Selected papers on Quantum Electrodynamics* (Dover, New York, 1958)

[3] Power E.A.: *Introductory Quantum Electrodynamics* (Longmans, London, 1964)

[4] Loudon R.: *Quantum Theory of Light* (Oxford University Press, 1973)

[5] Moss R.E.: *Advanced Molecular Quantum Mechanics* (Chapman and Hall, London, 1973)

[6] Woolley R.G.: Adv. Chem. Phys. 33, 153 (1975)

[7] Stenholm S.: Phys. Reports C6, 1 (1973)

[8] Milonni P.W.: Phys. Reports C25, 1 (1976)

[9] Andrews D.L., Craig D.P., Thirunamachandran T.: Int. Rev. Phys. Chem. 8, 339 (1989)

[10] Healy W.P.: *Non-relativistic Quantum Electrodynamics* (Academic Press, London, 1982)

[11] Craig D.P., Thirunamachandran T.: *Molecular Quantum Electrodynamics* (Academic Press, London 1984)

[12] Lanczos C.: *The Variational Principles of Mechanics* (University of Toronto Press, Toronto, 1949)

[13] Landau L.D., Lifshitz E.M.: *Mechanics* (Pergamon, Oxford, 1960)

[14] Avery J.: *The Quantum Theory of Atoms, Molecules and Photons* (McGraw-Hill, London, 1972)

[15] Kibble T.W.B.: *Classical Mechanics* (McGraw-Hill, U.K.(Ltd), 2nd Ed 1973)

[16] Goldstein H.: *Classical Mechanics* (Addison-Wesley, Reading, Massachusetts, 1978)

[17] Belinfante F.J.: Physica 12, 1 (1946)

[18] Göppert-Mayer M.: Ann. der Physik 4, 273 (1931)

[19] Richards P.I.: Phys. Rev. 73, 254 (1948)

[20] Fiutak J.: Can. J. Phys. 41, 12 (1963)

[21] Babiker M., Power E.A., Thirunamachandran T.: Proc. R. Soc. London A338, 235 (1974)

[22] Healy W.P.: J. Phys. A10, 279 (1977)

[23] Healy W.P.: J. Phys. A11, 1899 (1978)

[24] Power E.A., Thirunamachandran T.: Proc. R. Soc. London A372, 265 (1980)

[25] Lamb JR W.E.: Phys. Rev. 85, 259 (1952)

[26] Yang K.H., Hirschfelder J.O., Johnson B.R.: J. Chem. Phys. 75, 2321 (1981)

[27] Lam Y.T.: PhD Thesis (University of London 1983)

[28] Jackson J.D.: *Classical Electrodynamics* (Wiley-Interscience, New York, 1962)

[29] de Groot S.R.: *The Maxwell Equations* (North-Holland, Amsterdam, 1969)

[30] de Groot S.R., Suttorp L.G.: *Foundations of Electrodynamics* (North-Holland, Amsterdam, 1972)

[31] Röntgen W.: Annln. Phys. Chem. 35, 264 (1888)

[32] Power E.A., Thirunamachandran T.: Mathematika 18, 240 (1971)

[33] Wilson JR. E.B., Decius J.C., Cross P.C.: *Molecular Vibrations* (McGraw-Hill, London, 1955)

[34] Babiker M., Power E.A., Thirunamachandran T.: Proc. R. Soc. London A332, 187 (1973)

[35] Power E.A., Zienau S.: Phil. Trans. R. Soc. London A251, 427 (1959)

[36] Woolley R.G.: Proc. R. Soc. London A321, 557 (1971)

[37] Power E.A., Thirunamachandran T.: Am. J. Phys. 46, 370 (1978)

[38] Power E.A., Thirunamachandran T.: Phys. Lett. A87, 449 (1982)

[39] Fried Z.: Phys. Rev. A8, 2835 (1973)

[40] Geltman S.: Phys. Lett. 4, 168 (1963)

[41] Slater J.C.: *Quantum Theory of Atomic Structure*
(McGraw-Hill, New York, 1960)

[42] Bates D.R. ed: *Quantum Theory Vol I*
(Academic Press, New York, 1961)

[43] Pantell R.H., Puthoff H.E.: *Fundamentals of Quantum Electronics*
(Wiley-Interscience, New York, 1969)

[44] Power E.A., Thirunamachandran T.: J. Phys. B8, L170 (1975)

[45] Power E.A. in: Adv. Chem. Phys. 12, (1967)
Intermolecular Forces ed Hirschfelder J.O.

[46] Raman C.V., Krishnan K.S.: Nature 121, 501 (1928)

[47] Kramers H.A., Heisenberg W.: Z. Phys. 31, 681 (1925)

[48] Louisell W.H.: *Quantum Statistical Properties of Radiation*
(Wiley-Interscience, New York, 1973)

[49] Lambropoulos P.: Ad. At. Mol. Phys. 12, 87 (1976)

[50] London F.: Trans. Faraday Soc. 33, 8 (1937)

[51] Margenau H., Kestner N.R.: *Theory of Intermolecular Forces*
(Pergamon Press, Oxford, 2nd Ed 1971)

[52] Casimir H.B.G., Polder D.: Phys. Rev. 73, 360 (1948)

[53] Leech J.W.: Phil. Mag. 46 1328 (1955)

[54] Aub M.R., Power E.A., Zienau S.: Phil. Mag. 2 571 (1957)

[55] Power E.A., Zienau S.: Nuovo Cim. 6 7 (1957)

[56] McClone R.R., Power E.A.: Proc. R. Soc. London A286, 573 (1965)

[57] Craig D.P., Thirunamachandran T.: Acc. Chem. Res. 19, 10 (1986)

[58] Verwey E.J.W., Overbeek J.T.G., van Nes K.:
Theory of the Stability of Lyophobic Colloids
(Elsevier, Amsterdam, 1948)

[59] Tabor D., Winterton R.H.S.:
Proc. R. Soc. London A312, 435 (1969)

[60] Mavroyannis C., Stephen M.J.: Mol. Phys. 5, 629 (1962)

[61] Power E.A., Thirunamachandran T.:
J. Chem. Phys. 60, 3695 (1974)

[62] Atkins P.W., Barron L.: Proc. R. Soc. Lond. A304, 303 (1968)

[63] Barron L., Buckingham A.D.: Mol. Phys. 20, 1111 (1971)

[64] Andrews D.L., Thirunamachandran T.: J. Chem. Phys. 67, 5026 (1977)

[65] Thirunamachandran T.: Physica Scripta T21, 123 (1988)

[66] Taylor M.D., Thirunamachandran T.: Mol. Phys. 49, 881 (1983)

[67] Gradshteyn I.S., Ryzhik I.M.: *Tables of Integrals Series and Products* (Academic Press, Moscow, 1965)

[68] Buckingham A.D. in: *Intermolecular Interactions: From Diatomics to Biopolymers* ed Pullman B. (Wiley, Bath, 1978)

[69] Stone A.J. in: *Theoretical Models of Chemical Bonding* ed Maksic Z.B. (Springer-Verlag, Berlin, 1988)

[70] Feinberg G., Sucher J.: Phys. Rev. A27, 1958 (1983)

[71] Au C.K.: Phys. Rev. A34, 3568 (1986)

[72] Au C.K.: Phys. Rev. A38, 7 (1988)

[73] Polley J.P., Bailey T.L.: Phys. Rev. A37, 733 (1988)