

Article

Electric Octupole-Dependent Contributions to Optical Binding Energy

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Abstract: Contributions to the radiation-induced dispersion energy shift between two interacting particles dependent on the electric octupole moment are calculated using a physical picture in which moments induced by applied fluctuating electromagnetic fields are coupled via retarded interaction tensors. The specific potentials evaluated include those found between an electric dipole-polarisable molecule and either a mixed electric dipole–octupole- or purely octupole-polarisable molecule, and those between two mixed electric dipole–octupole-polarisable molecules. Interaction energies are obtained for molecular and pair orientationally averaged situations. Terms dependent on the octupole weight-1 moment may be viewed as higher-order corrections to the leading dipole–dipole interaction energy as also found in energy transfer and dispersion forces. A comprehensive polarisation analysis is carried out for linearly and circularly polarised laser light incident parallel and perpendicular to the inter-particle axis. Contributions to the optical binding energy arising when one of the pair is polar and characterised by either a permanent electric dipole or octupole moment are also evaluated. Neither of these energy shifts survive orientational averaging.

Keywords: optical binding energy; coupling of induced moments; octupole-dependent terms; real and virtual photons



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1. Introduction

For quite a few decades, Franco Persico admirably led the theoretical physics division at the University of Palermo in Sicily. Together with his students and colleagues, he made notable advances in the areas of quantum optics, strong field–matter interactions, many-body forces and dressed states [1–4]. An often-employed theory that has yielded solutions to many fundamental problems, including those involving atoms and molecules, is quantum electrodynamics (QED) [5–8]. Electromagnetic radiation and matter are treated equally in this framework, with both being subject to the principles of quantum mechanics.

A particularly interesting phenomenon that has been successfully explained by QED theory is the radiation field-induced shift in the dispersion energy between two atoms or molecules, colloquially termed the optical binding energy [9–11]. Thirunamachandran first predicted this in 1980 [12]. He used QED to calculate the potential energy of a pair of interacting particles in the ground state when subject to an intense laser field. This process provides an example featuring both real and virtual photons. The former originate from the applied radiation field and are scattered by the two objects, which are themselves coupled through the exchange of a single virtual photon. Experimentally, this manifests as the mutual attraction of neutral polarisable particles located in the focal area of a beam of light, in the process generating optomechanical forces and torques via optical spanner or wrench techniques that lead to the manipulation of pairs of particles [13], extending the earlier trapping, control and movement of individual entities via optical tweezer methods which culminated in the award of the 2018 Nobel Prize in Physics to Ashkin [14].

The original calculation of the change in the energy shift was carried out using time-dependent perturbation theory and involved the summation over 48 diagrams of a so-called

“dynamic” mechanism, where off-resonant laser light is absorbed and emitted at different centres, and the later evaluation of an additional 48 diagrams required when the real photons are scattered at the same site in a second so-called “static” mechanism [15].

The QED theory of this effect has also been extended to describe the optical binding energy between a pair of optically active molecules [16–18]. To account for the discriminatory change in the potential of such a system required dropping the electric dipole approximation and including both the electric and magnetic dipole coupling terms. The interference term between these two moments yields a contribution to the energy shift that is dependent on the chirality of the molecule that changes sign on replacing one enantiomer with its mirror-image structure. A diagrammatic time-dependent perturbation theory calculation of the change in the energy shift is necessarily prohibitive for the case of two chiral molecules due to the large number (192) of diagrams that need to be drawn, individually evaluated and finally summed. The result was instead obtained by calculating the coupling of the dipoles induced at each site by the time-varying electromagnetic fields. Similar to London’s view of the origin of the dispersion force, this method was adopted by Power and Thirunamachandran to evaluate the Casimir–Polder potential [19] and applied later to the pair radiation-induced interaction energy [20,21], and the optical binding energy in three- and N -body systems in the electric dipole approximation [22].

An often-overlooked contribution to many processes is the electric octupole coupling term. While of a higher order relative to the magnetic dipole and electric quadrupole interaction terms, when the octupole moment, $E_{ijk}^{(3)}$, is decomposed into its irreducible components of weight-1 and weight-3, $E_{ijk}^{(3^1)}$ and $E_{ijk}^{(3^3)}$, respectively, the former has the properties of a vector and may be viewed as a higher-order correction to the electric dipole interaction term. Its effect on two- [23,24] and three- [25–27] body dispersion potentials and the rate of resonance energy transfer [28,29] has been shown previously.

This partitioning may be written as

$$E_{ijk}^{(3)} = E_{ijk}^{(3^1)} + E_{ijk}^{(3^3)}, \quad (1)$$

where

$$E_{ijk}^{(3^1)} = -\frac{e}{30} \vec{q}^{\rightarrow 2} [\vec{q}_i \delta_{jk} + \vec{q}_j \delta_{ik} + \vec{q}_k \delta_{ij}], \quad (2)$$

and

$$E_{ijk}^{(3^3)} = -\frac{e}{6} [\vec{q}_i \vec{q}_j \vec{q}_k - \frac{1}{5} \vec{q}^{\rightarrow 2} (\vec{q}_i \delta_{jk} + \vec{q}_j \delta_{ik} + \vec{q}_k \delta_{ij})], \quad (3)$$

with e denoting the elementary charge, \vec{q}_i being the i -th Cartesian component of the electron coordinate, and Einstein’s summation convention is employed for Latin indices in the space-fixed frame of reference or Greek subscripts in the molecular frame that repeat. δ_{ij} is the Kronecker delta.

We extend the coupling of fluctuating moments at each centre to calculate the radiation field-induced energy shift between a pair of molecules involving electric dipole and octupole coupling terms and compare results with purely electric dipole potentials obtained previously [6,11,12] to see if higher-order corrections occur and what explicit form they take. A complete polarisation analysis is also carried out for linearly and circularly polarised light propagating in directions parallel and perpendicular to the inter-nuclear separation distance vector to aid experimental investigation. Results are also obtained for fully isotropic situations applicable to species in the fluid phase.

Sections 2–5 contain results for changes in the potential energy for the various octupole-dependent molecules under study. Brief conclusions are proffered in Section 6.

2. Optical Binding Energy between an Electric Dipole-Polarisable Molecule and a Mixed Dipole–Octupole-Polarisable Molecule

The picture to be adopted in the calculation of field-induced inter-particle energy shifts involving molecules dependent upon the electric octupole coupling term is the one in which

an applied electric field induces an electric multipole moment at a specific centre. This depends on the polarisability characteristics of the reacting species. The induced moments interact via their mutual multipole–multipole coupling tensor. The energy shift is then obtained on taking the expectation value for both particles in the ground electronic state and the radiation field in a state corresponding to a laser containing N photons. Results for the Casimir–van der Waals dispersion potential are obtained immediately on letting $N \rightarrow 0$, which were previously calculated using diagrammatic perturbation theory techniques [30], serving as a useful check of the work.

The first octupole-dependent case to be considered is the radiation field-induced interaction energy between an electric dipole-polarisable molecule, A , positioned at \vec{R}_A , and a mixed electric dipole–octupole-polarisable molecule, B , located at \vec{R}_B . In the presence of a transverse electric displacement field, $\vec{d}^\perp(\vec{r})$, the electric dipole moment induced at A , $E_i^{(1)ind}(A)$, is

$$E_i^{(1)ind}(A) = \epsilon_0^{-1} \alpha_{ij}^{11}(A; k) d_j^\perp(\vec{R}_A), \tag{4}$$

(with ϵ_0 denoting the permittivity of the free space), where the dynamic pure electric dipole polarisability tensor of A , at the frequency $\omega = ck$, where k is the magnitude of the wave vector, is given by

$$\alpha_{ij}^{11}(A; k) = \sum_a \left\{ \frac{E_i^{(1)0a}(A) E_j^{(1)a0}(A)}{E_{a0} - \hbar ck} + \frac{E_j^{(1)0a}(A) E_i^{(1)a0}(A)}{E_{a0} + \hbar ck} \right\}. \tag{5}$$

In Equation (5), $E_i^{(1)0a}(A)$ is the transition electric dipole moment matrix element between the ground state $|0\rangle$ and the virtual state $|a\rangle$ of A , $\langle 0|E_i^{(1)}(A)|a\rangle$, with similar expressions for other transition multipole moments, with $|b\rangle$ denoting the virtual electronic states of B . In the denominator of Equation (5), the energy difference between states $|0\rangle$ and $|a\rangle$ is $E_{a0} = E_a - E_0$. Due to the polarisability characteristics of B , two different multipole moments are induced there, namely the electric dipole moment

$$E_q^{(1)ind}(B) = \epsilon_0^{-1} \alpha_{qrst}^{13}(B; k) \nabla_s \nabla_t d_r^\perp(\vec{R}_B), \tag{6}$$

and the electric octupole moment

$$E_{rst}^{(3)ind}(B) = \epsilon_0^{-1} \alpha_{qrst}^{13}(B; k) d_q^\perp(\vec{R}_B), \tag{7}$$

where the frequency-dependent mixed electric dipole–octupole polarisability tensor is defined as

$$\alpha_{qrst}^{13}(B; k) = \sum_b \left\{ \frac{E_q^{(1)0b}(B) E_{rst}^{(3)b0}(B)}{E_{b0} - \hbar ck} + \frac{E_{rst}^{(3)0b}(B) E_q^{(1)b0}(B)}{E_{b0} + \hbar ck} \right\}. \tag{8}$$

The multipole moments induced at each site couple via the relevant retarded multipole–multipole interaction tensor. For the coupling of an electric multipole moment of order m at A and order n at B , its generalised form is [29]

$$V_{i_1 j_1 \dots i_m j_n}(k, \vec{R}) = (-1)^m \frac{k^{m+n+1}}{4\pi\epsilon_0} F_{i_1 j_1 \dots i_m j_n}(kR), \tag{9}$$

where the tensor $F_{i_1 j_1 \dots i_m j_n}$ is

$$F_{i_1 j_1 i_2 \dots i_m j_2 \dots j_n}(kR) = \frac{1}{k^{m+n+1}} (-\nabla^2 \delta_{i_1 j_1} + \nabla_{i_1} \nabla_{j_1}) \nabla_{i_2} \dots \nabla_{i_m} \nabla_{j_2} \dots \nabla_{j_n} \frac{e^{ikR}}{R}, \tag{10}$$

with $\vec{R} = \vec{R}_B - \vec{R}_A$. Thus the two induced electric dipoles couple through the retarded electric dipole–dipole interaction tensor, $V_{ij}(k, \vec{R})$, and the induced dipole at A and the induced octupole at B interact via the retarded electric dipole–octupole coupling tensor, $V_{irst}(k, \vec{R})$, giving rise to the following formula for the energy shift:

$$\Delta E^{11;13} = E_i^{(1)ind}(A)E_q^{(1)ind}(B)\text{Re}V_{iq}(k, \vec{R}) + E_i^{(1)ind}(A)E_{rst}^{(3)ind}(B)\text{Re}V_{irst}(k, \vec{R}), \quad (11)$$

with

$$\begin{aligned} \text{Re}V_{ij}(k, \vec{R}) &= -\frac{k^3}{4\pi\epsilon_0}\text{Re}F_{ij}(kR) \\ &= \frac{1}{4\pi\epsilon_0R^3}[(\delta_{ij} - \hat{R}_i\hat{R}_j)k^2R^2 \cos kR - (\delta_{ij} - 3\hat{R}_i\hat{R}_j)(kR \sin kR + \cos kR)], \end{aligned} \quad (12)$$

and

$$\begin{aligned} \text{Re}V_{ijkl}(k, \vec{R}) &= -\frac{k^5}{4\pi\epsilon_0}\text{Re}F_{ijkl}(kR) \\ &= \frac{1}{4\pi\epsilon_0R^5}[(\delta_{ij} - \hat{R}_i\hat{R}_j)\hat{R}_k\hat{R}_l k^4R^4 \cos kR + [\delta_{ij}(\delta_{kl} - 3\hat{R}_k\hat{R}_l) - (\delta_{ij}\hat{R}_k\hat{R}_l + \delta_{ik}\hat{R}_j\hat{R}_l + \delta_{il}\hat{R}_j\hat{R}_k \\ &\quad + \delta_{jk}\hat{R}_i\hat{R}_l + \delta_{jl}\hat{R}_i\hat{R}_k + \delta_{kl}\hat{R}_i\hat{R}_j) + 10\hat{R}_i\hat{R}_j\hat{R}_k\hat{R}_l](k^3R^3 \sin kR + k^2R^2 \cos kR) \\ &\quad + [(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - 5(\delta_{ij}\hat{R}_k\hat{R}_l + \delta_{ik}\hat{R}_j\hat{R}_l + \delta_{il}\hat{R}_j\hat{R}_k + \delta_{jk}\hat{R}_i\hat{R}_l \\ &\quad + \delta_{jl}\hat{R}_i\hat{R}_k + \delta_{kl}\hat{R}_i\hat{R}_j) + 35\hat{R}_i\hat{R}_j\hat{R}_k\hat{R}_l](k^2R^2 \cos kR - 3kR \sin kR - 3 \cos kR)]. \end{aligned} \quad (13)$$

Substituting Equations (4), (6) and (7) into Equation (11) provides an expression of the energy shift explicitly in terms of the molecular polarisabilities (5) and (8) of A and B ,

$$\begin{aligned} \Delta E^{11;13} &= \epsilon_0^{-2}\alpha_{ij}^{11}(A;k)\alpha_{qrst}^{13}(B;k)[d_j^\perp(\vec{R}_A)\nabla_s\nabla_t d_r^\perp(\vec{R}_B)\text{Re}V_{iq}(k, \vec{R}) \\ &\quad + d_j^\perp(\vec{R}_A)d_q^\perp(\vec{R}_B)\text{Re}V_{irst}(k, \vec{R})]. \end{aligned} \quad (14)$$

Next, the expectation value of Formula (14) is taken over the state

$$|0^A, 0^B; N(\vec{k}, \lambda)\rangle, \quad (15)$$

corresponding to both molecules in the electronic ground state and the field containing N photons of mode \vec{k}, λ , where \vec{k} is the direction of propagation of the applied radiation field and λ is its index of polarisation. For the matter sub-system, this yields the ground state polarisabilities (5) and (8). For the radiation field, use is made of the microscopic second quantised transverse electric displacement field operator of QED [31,32], whose form for a specific mode is

$$d_i^\perp(\vec{r}) = i\left(\frac{\hbar c k \epsilon_0}{2V}\right)^{1/2} [e_i^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}} - \bar{e}_i^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}}], \quad (16)$$

where $\bar{e}^{(\lambda)}(\vec{k})$ is the complex unit electric polarisation vector, $a^{(\lambda)}(\vec{k})$ is the photon annihilation operator, $a^{\dagger(\lambda)}(\vec{k})$ is the creation operator and V is the volume of the quantisation box. Employing Equation (16) leads straightforwardly to the following expectation value for the product of the m -th- and n -th-order gradients of the electric displacement field evaluated at two spatially distinct points for a state containing $|N(\vec{k}, \lambda)\rangle$ photons:

$$\begin{aligned} &< N(\vec{k}, \lambda) | \nabla_{k_2} \dots \nabla_{k_m} d_{k_1}^\perp(\vec{R}_A) \nabla_{l_2} \dots \nabla_{l_n} d_{l_1}^\perp(\vec{R}_B) | N(\vec{k}, \lambda) \rangle \\ &= \left(\frac{\hbar c k \epsilon_0}{2V}\right) k_{k_2} \dots k_{k_m} k_{l_2} \dots k_{l_n} [i^m (-i)^n (N+1) e_{k_1}^{(\lambda)}(\vec{k}) \bar{e}_{l_1}^{(\lambda)}(\vec{k}) e^{-i\vec{k}\cdot\vec{R}} \\ &\quad + (-i)^m i^n N \bar{e}_{k_1}^{(\lambda)}(\vec{k}) e_{l_1}^{(\lambda)}(\vec{k}) e^{i\vec{k}\cdot\vec{R}}]. \end{aligned} \quad (17)$$

Concentrating on the first term of the energy shift (14), the expectation value of the field-dependent factor is readily obtained from Equation (17),

$$\begin{aligned} &< N(\vec{k}, \lambda) |d_j^\perp(\vec{R}_A) \nabla_s \nabla_t d_r^\perp(\vec{R}_B) |N(\vec{k}, \lambda) > \\ &= -\left(\frac{\hbar c k \epsilon_0}{2V}\right) k_s k_t [N \bar{e}_j^{(\lambda)}(\vec{k}) e_r^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{R}} + (N+1) e_j^{(\lambda)}(\vec{k}) \bar{e}_r^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}], \end{aligned} \tag{18}$$

which, after carrying out the polarisation sum using the identity [5]

$$\sum_\lambda e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k}) = \delta_{ij} - \hat{k}_i \hat{k}_j, \tag{19}$$

yields

$$-\left(\frac{\hbar c k}{2\epsilon_0 V}\right) \alpha_{ij}^{11}(A; k) \alpha_{qrst}^{13}(B; k) (\delta_{jr} - \hat{k}_j \hat{k}_r) k_s k_t [N e^{i\vec{k} \cdot \vec{R}} + (N+1) e^{-i\vec{k} \cdot \vec{R}}] \text{Re} V_{iq}(k, \vec{R}). \tag{20}$$

2.1. Orientationally Averaged Energy Shift

To obtain the isotropic interaction potential, a pair orientational average of the radiation field vectors relative to the inter-particle displacement vector must be performed. The contributing averages, denoted by angular brackets, may be extracted from the generalised relation

$$\langle (\delta_{i_1 j_1} - \hat{k}_{i_1} \hat{k}_{j_1}) k_{i_2} \dots k_{i_m} k_{j_2} \dots k_{j_n} e^{\pm i\vec{k} \cdot \vec{R}} \rangle = -\frac{k^{m+n-2}}{(\pm i)^{m+n}} \text{Im}[F_{i_1 j_1 i_2 \dots i_m j_2 \dots j_n}(kR)], \tag{21}$$

so that the average featuring in Equation (20) is

$$\langle (\delta_{jr} - \hat{k}_j \hat{k}_r) k_s k_t e^{\pm i\vec{k} \cdot \vec{R}} \rangle = -k^2 \text{Im}[F_{jrst}(kR)], \tag{22}$$

where from Equation (10)

$$\begin{aligned} \text{Im}[F_{ijkl}(kR)] = & [-(\delta_{ij} - \hat{R}_i \hat{R}_j) \hat{R}_k \hat{R}_l \frac{\sin kR}{kR} + [\delta_{ij}(\delta_{kl} - 3\hat{R}_k \hat{R}_l) - (\delta_{ij} \hat{R}_k \hat{R}_l + \delta_{ik} \hat{R}_j \hat{R}_l + \delta_{il} \hat{R}_j \hat{R}_k \\ & + \delta_{jk} \hat{R}_i \hat{R}_l + \delta_{jl} \hat{R}_i \hat{R}_k + \delta_{kl} \hat{R}_i \hat{R}_j) + 10\hat{R}_i \hat{R}_j \hat{R}_k \hat{R}_l] \left(\frac{\cos kR}{k^2 R^2} - \frac{\sin kR}{k^3 R^3}\right) \\ & + [(\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) - 5(\delta_{ij} \hat{R}_k \hat{R}_l + \delta_{ik} \hat{R}_j \hat{R}_l + \delta_{il} \hat{R}_j \hat{R}_k + \delta_{jk} \hat{R}_i \hat{R}_l \\ & + \delta_{jl} \hat{R}_i \hat{R}_k + \delta_{kl} \hat{R}_i \hat{R}_j) + 35\hat{R}_i \hat{R}_j \hat{R}_k \hat{R}_l] \left(-\frac{\sin kR}{k^3 R^3} - 3\frac{\cos kR}{k^4 R^4} + 3\frac{\sin kR}{k^5 R^5}\right)]. \end{aligned} \tag{23}$$

Thus, contribution (20) becomes

$$\left(\frac{Ik^2}{2\epsilon_0 c}\right) \alpha_{ij}^{11}(A; k) \alpha_{qrst}^{13}(B; k) \text{Im}[F_{jrst}(kR)] \text{Re}[V_{iq}(k, \vec{R})], \tag{24}$$

on defining the intensity of the incident field as $I = (2N + 1) \hbar c^2 k / V$. On substituting Equation (12), Equation (24) becomes

$$-\frac{Ik^5}{8\pi\epsilon_0^2 c} \alpha_{ij}^{11}(A; k) \alpha_{qrst}^{13}(B; k) \text{Re}[F_{iq}(kR)] \text{Im}[F_{jrst}(kR)]. \tag{25}$$

The rotational averages for the two particles are given by the formulae [33]

$$\langle \alpha_{ij}^{11}(A; k) \rangle = \frac{1}{3} \delta_{ij} \delta_{\lambda\mu} \alpha_{\lambda\mu}^{11}(A; k) = \delta_{ij} \alpha^{11}(A; k), \tag{26}$$

and

$$\langle \alpha_{qrst}^{13}(B; k) \rangle = \frac{2}{15} \delta_{qr} \delta_{st} \alpha_{\lambda\lambda\mu\mu}^{131}(B; k) = \delta_{qr} \delta_{st} \alpha^{131}(B; k). \tag{27}$$

Note that a factor of 2/15 has been absorbed into the isotropic mixed dipole–octupole polarisability, α^{131} . In these and subsequent results, Greek subscripts refer to Cartesian tensor components in the body-fixed frame of reference. Interestingly, there is no contribution to the orientationally averaged mixed electric dipole–octupole polarizability (8), due to the octupole weight-3 term (3). After contracting tensors (25) becomes

$$-\frac{Ik^5}{8\pi\epsilon_0^2c}\alpha^{11}(A;k)\alpha^{131}(B;k)\text{Re}[F_{ij}(kR)]\text{Im}[F_{ijkk}(kR)]. \tag{28}$$

Evaluating $\text{Re}[F_{ij}(kR)]$ and $\text{Im}[F_{ij}(kR)]$,

$$\begin{aligned} \text{Re}[F_{ij}(kR)] &= \frac{1}{k^3}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{\cos kR}{R} \\ &= [-(\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{\cos kR}{kR} + (\delta_{ij} - 3\hat{R}_i\hat{R}_j)(\frac{\sin kR}{k^2R^2} + \frac{\cos kR}{k^3R^3})], \end{aligned} \tag{29}$$

and

$$\begin{aligned} \text{Im}[F_{ij}(kR)] &= \frac{1}{k^3}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{\sin kR}{R} \\ &= [-(\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{\sin kR}{kR} + (\delta_{ij} - 3\hat{R}_i\hat{R}_j)(-\frac{\cos kR}{k^2R^2} + \frac{\sin kR}{k^3R^3})], \end{aligned} \tag{30}$$

noting that $F_{ijkk}(kR) = F_{ij}(kR)$, Equation (28) becomes

$$\begin{aligned} &-\frac{I}{8\pi\epsilon_0^2cR^5}\alpha^{11}(A;k)\alpha^{131}(B;k) \\ &\times [k^3R^3 \sin 2kR + 2k^2R^2 \cos 2kR - 5kR \sin 2kR - 6 \cos 2kR + \frac{3}{kR} \sin 2kR]. \end{aligned} \tag{31}$$

Returning to Equation (14) and calculating the second term, the field part from Equation (18) is

$$\begin{aligned} &\langle N(\vec{k}, \lambda) | d_j^\perp(\vec{R}_A) d_q^\perp(\vec{R}_B) | N(\vec{k}, \lambda) \rangle \\ &= \left(\frac{\hbar c k \epsilon_0}{2V}\right) [N e_j^{(\lambda)}(\vec{k}) e_q^{(\lambda)}(\vec{k}) e^{i\vec{k}\cdot\vec{R}} + (N+1) e_j^{(\lambda)}(\vec{k}) e_q^{(\lambda)}(\vec{k}) e^{-i\vec{k}\cdot\vec{R}}]. \end{aligned} \tag{32}$$

Substituting Equation (32) and employing Equation (19) produces

$$\left(\frac{\hbar ck}{2\epsilon_0 V}\right) \alpha_{ij}^{11}(A;k)\alpha_{qrst}^{13}(B;k)(\delta_{jq} - \hat{k}_j\hat{k}_q) [N e^{i\vec{k}\cdot\vec{R}} + (N+1) e^{-i\vec{k}\cdot\vec{R}}] \text{Re}V_{irst}(k, \vec{R}). \tag{33}$$

From Equation (21), the pair orientational average is

$$\langle (\delta_{jq} - \hat{k}_j\hat{k}_q) e^{\pm i\vec{k}\cdot\vec{R}} \rangle = \text{Im}[F_{jq}(kR)] = \frac{1}{k^3}(-\nabla^2\delta_{jq} + \nabla_j\nabla_q)\frac{\sin kR}{R}, \tag{34}$$

and is given by Equation (30). With $\text{Re}V_{irst}(k, \vec{R})$ given by Equation (13), Equation (33) becomes

$$-\frac{Ik^5}{8\pi\epsilon_0^2c}\alpha_{ij}^{11}(A;k)\alpha_{qrst}^{13}(B;k)\text{Im}[F_{jq}(kR)]\text{Re}[F_{irst}(kR)], \tag{35}$$

which, after deploying Equations (26) and (27), becomes

$$-\frac{Ik^5}{8\pi\epsilon_0^2c}\alpha^{11}(A;k)\alpha^{131}(B;k)\text{Im}[F_{ij}(kR)]\text{Re}[F_{ijkk}(kR)], \tag{36}$$

and a term identical to Equation (31) results. Hence, the isotropic energy shift induced by an external electric field between an electric dipole-polarisable molecule and a mixed electric dipole–octupole-polarisable one is twice expression (31),

$$\begin{aligned} \Delta E^{11;131} &= -\frac{I}{4\pi\epsilon_0^2cR^5}\alpha^{11}(A;k)\alpha^{131}(B;k) \\ &\times [k^3R^3 \sin 2kR + 2k^2R^2 \cos 2kR - 5kR \sin 2kR - 6 \cos 2kR + \frac{3}{kR} \sin 2kR]. \end{aligned} \tag{37}$$

It is interesting to compare expression (37) with the analogous result between a pair of electrically-polarisable molecules [12]:

$$\Delta E^{11;11} = -\frac{I}{8\pi\epsilon_0^2 c R^3} \alpha^{11}(A; k) \alpha^{11}(B; k) \times [kR \sin 2kR + 2 \cos 2kR - 5 \frac{\sin 2kR}{kR} - 6 \frac{\cos 2kR}{k^2 R^2} + 3 \frac{\sin 2kR}{k^3 R^3}]. \tag{38}$$

It can be seen that the coefficients of the terms within square brackets match each other and agree with those occurring in the Casimir–Polder dispersion potential, allowing Equation (37) to be viewed as a higher-order correction to the leading pure electric dipole contribution to the radiation-induced dispersion energy. Asymptotic limits of the result Equation (37) readily follow. In the near zone, $kR \ll 1$, yielding an inverse separation distance dependence

$$\Delta E_{NZ}^{11;13^1} \sim -\frac{11}{15} \frac{Ik^4}{\pi\epsilon_0^2 c R} \alpha^{11}(A; k) \alpha^{13^1}(B; k), \tag{39}$$

while at the opposite extreme of the far zone, $kR \gg 1$, resulting in a modulated inverse square behaviour on relative separation

$$\Delta E_{FZ}^{11;13^1} \sim -\frac{Ik^5}{4\pi\epsilon_0^2 c R^2} \alpha^{11}(A; k) \alpha^{13^1}(B; k) \sin 2kR. \tag{40}$$

2.2. Polarisation Analysis

It is possible to obtain expressions for the change in energy shift that illustrate the dependence on different polarisation states and configurations of the incoming radiation field. This offers enhanced possibilities for experimental control and detection. Going back to the first term of Equation (14) and inserting relation (18) produces

$$-\left(\frac{\hbar ck}{2\epsilon_0 V}\right) \alpha_{ij}^{11}(A; k) \alpha_{qrst}^{13}(B; k) [N \bar{e}_j^{(\lambda)}(\vec{k}) e_r^{(\lambda)}(\vec{k}) e^{i\vec{k}\cdot\vec{R}} + (N + 1) e_j^{(\lambda)}(\vec{k}) \bar{e}_r^{(\lambda)}(\vec{k}) e^{-i\vec{k}\cdot\vec{R}}] k_s k_t \text{Re} V_{iq}(k, \vec{R}). \tag{41}$$

For large occupation numbers of the photon field, it is sufficient to approximate $N + 1$ by N so that Equation (41) becomes, after molecular orientational averaging,

$$-\frac{Ik^5}{4\pi\epsilon_0^2 c} \alpha^{11}(A; k) \alpha^{13^1}(B; k) e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k}) \times [(\delta_{ij} - \hat{R}_i \hat{R}_j) \frac{\cos kR}{kR} - (\delta_{ij} - 3\hat{R}_i \hat{R}_j) (\frac{\sin kR}{k^2 R^2} + \frac{\cos kR}{k^3 R^3})] \cos(\vec{k} \cdot \vec{R}). \tag{42}$$

One possibility is for the propagation direction of the laser to be parallel to the inter-molecular join, resulting in the polarisation vector being perpendicular to \vec{R} . Then, $\vec{k} \cdot \vec{R} = kR$. A second possibility is for the laser to be oriented orthogonal to \vec{R} , in which case the polarisation vector is parallel to the inter-particle separation distance vector. This results in $\cos(\vec{k} \cdot \vec{R}) = 1$. In addition, the laser may be linearly or circularly polarised. We examine each of these four possible combinations for each of the examples considered.

(a) Linearly polarised light.

(i) $\hat{k} \parallel \hat{R}; \hat{e} \perp \hat{R}$: In this scenario, Equation (42) becomes

$$-\frac{I}{4\pi\epsilon_0^2 c R^5} \alpha^{11}(A; k) \alpha^{13^1}(B; k) [k^4 R^4 \cos^2 kR - k^3 R^3 \sin kR \cos kR - k^2 R^2 \cos^2 kR], \tag{43}$$

giving rise to near- and far-zone limiting forms

$$\frac{Ik^2}{4\pi\epsilon_0^2cR^3}\alpha^{11}(A;k)\alpha^{13^1}(B;k), \tag{44}$$

and

$$-\frac{Ik^4}{4\pi\epsilon_0^2cR}\alpha^{11}(A;k)\alpha^{13^1}(B;k)\cos^2kR, \tag{45}$$

displaying R^{-3} and $(\cos^2kR)/R$ dependences, respectively.

(ii) $\hat{k}\perp\hat{R}$; $\hat{e}\parallel\hat{R}$: Expression (42) then becomes

$$-\frac{I}{2\pi\epsilon_0^2cR^5}\alpha^{11}(A;k)\alpha^{13^1}(B;k)[k^3R^3\sin kR+k^2R^2\cos kR], \tag{46}$$

from which inverse cubic short-range and modulated inverse square long-range dependences on R are found.

(b) Circularly polarised light. To proceed, use is made of the relation

$$e_i^{(L/R)}(\vec{k})\bar{e}_j^{(L/R)}(\vec{k})=\frac{1}{2}[\delta_{ij}-\hat{k}_i\hat{k}_j\mp i\epsilon_{ijk}\hat{k}_k], \tag{47}$$

where the upper and lower signs refer to left (L)- and right (R)-handed circular polarisations, and ϵ_{ijk} is the Levi-Civita tensor. Note that only the ij -symmetric part of (47) persists, since the geometric tensor appearing in Equation (42) is ij -symmetric.

(i) $\hat{k}\parallel\hat{R}$; $\hat{e}\perp\hat{R}$: For this case, an identical contribution to that arising from this configuration with linearly polarised light is found, namely Equation (43). Identical asymptotic behaviour follows.

(ii) $\hat{k}\perp\hat{R}$; $\hat{e}\parallel\hat{R}$: In this scenario, Equation (42) results in

$$-\frac{I}{4\pi\epsilon_0^2cR^5}\alpha^{11}(A;k)\alpha^{13^1}(B;k)[k^4R^4\cos kR+k^3R^3\sin kR+k^2R^2\cos kR], \tag{48}$$

yielding modulated inverse R behaviour in the far zone and R^{-3} dependence in the near zone.

For the second term of Equation (14), substituting Equation (32), taking $N+1\sim N$ and carrying out the molecular rotational averages with relations (26) and (27), produces

$$\frac{I}{\epsilon_0c}\alpha^{11}(A;k)\alpha^{13^1}(B;k)e_i^{(\lambda)}(\vec{k})\bar{e}_j^{(\lambda)}(\vec{k})\text{Re}V_{ijkk}(k,\vec{R})\cos(\vec{k}\cdot\vec{R}). \tag{49}$$

Noting that

$$\text{Re}V_{ijkk}(k,\vec{R})=-\frac{k^5}{4\pi\epsilon_0}\text{Re}[F_{ijkk}(kR)]=\frac{k^5}{4\pi\epsilon_0}\text{Re}[F_{ij}(kR)], \tag{50}$$

Equation (49) is found to be identical to Equation (42). Hence, identical polarisation analysis results and limiting forms follow, with expressions (43)–(46) and (48) all doubling up.

3. Energy Shift between Two Mixed Electric Dipole–Octupole-Polarisable Molecules

The next dispersion potential induced by an electromagnetic field to be considered is that between two identical electric dipole–octupole-polarisable molecules A and B . At B , the two induced moments are given by Equations (6) and (7), with analogous formulae

applicable to particle A. Similar and dissimilar moments couple to each other, leading to an energy shift formula that is the sum of four terms:

$$\begin{aligned} \Delta E^{13;13} &= E_i^{(1)ind}(A)E_q^{(1)ind}(B)\text{Re}V_{iq}(k, \vec{R}) + E_i^{(1)ind}(A)E_{rst}^{(3)ind}(B)\text{Re}V_{irst}(k, \vec{R}) \\ &+ E_{jkl}^{(3)ind}(A)E_q^{(1)ind}(B)\text{Re}V_{jqkl}(k, \vec{R}) + E_{jkl}^{(3)ind}(A)E_{rst}^{(3)ind}(B)\text{Re}V_{jrklst}(k, \vec{R}) \\ &= \varepsilon_0^{-2}\alpha_{ijkl}^{13}(A;k)\alpha_{qrst}^{13}(B;k)[\nabla_k\nabla_l d_j^\perp(\vec{R}_A)\nabla_s\nabla_t d_r^\perp(\vec{R}_B)\text{Re}V_{iq}(k, \vec{R}) \\ &+ \nabla_k\nabla_l d_j^\perp(\vec{R}_A)d_q^\perp(\vec{R}_B)\text{Re}V_{irst}(k, \vec{R}) \\ &+ d_i^\perp(\vec{R}_A)\nabla_s\nabla_t d_r^\perp(\vec{R}_B)\text{Re}V_{jqkl}(k, \vec{R}) + d_i^\perp(\vec{R}_A)d_q^\perp(\vec{R}_B)\text{Re}V_{jrklst}(k, \vec{R})], \end{aligned} \tag{51}$$

where the mixed electric dipole–octupole polarisability is given by Equation (8).

3.1. Isotropic Potential

We begin by evaluating the first term of Equation (51). Inserting $m = n = 3$ into expression (17) produces

$$\begin{aligned} &\langle N(\vec{k}, \lambda) | \nabla_k \nabla_l d_j^\perp(\vec{R}_A) \nabla_s \nabla_t d_r^\perp(\vec{R}_B) | N(\vec{k}, \lambda) \rangle \\ &= \left(\frac{\hbar c \varepsilon_0}{2V}\right) k_k k_l k_s k_t [N \bar{e}_j^{(\lambda)}(\vec{k}) e_r^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{R}} + (N+1) e_j^{(\lambda)}(\vec{k}) \bar{e}_r^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}]. \end{aligned} \tag{52}$$

Substituting relation (52) into the first term of Equation (51), performing the polarisation sum using the identity (19) and carrying out the following pair orientational average using the result (21),

$$\begin{aligned} &\langle (\delta_{jr} - \hat{k}_j \hat{k}_r) k_k k_l k_s k_t e^{\pm i\vec{k} \cdot \vec{R}} \rangle = k^4 \text{Im}[F_{jrklst}(kR)] \\ &= \frac{1}{k^3} (-\nabla^2 \delta_{jr} + \nabla_j \nabla_r) \nabla_k \nabla_l \nabla_s \nabla_t \frac{\sin kR}{R}, \end{aligned} \tag{53}$$

we obtain

$$-\frac{\hbar c k^8}{8\pi \varepsilon_0^2 V} (2N+1) \alpha_{ijkl}^{13}(A;k) \alpha_{qrst}^{13}(B;k) \text{Re}[F_{iq}(kR)] \text{Im}[F_{jrklst}(kR)], \tag{54}$$

which, after molecular rotational averaging, becomes

$$-\frac{Ik^7}{8\pi \varepsilon_0^2 c} \alpha^{13^1}(A;k) \alpha^{13^1}(B;k) \text{Re}[F_{ij}(kR)] \text{Im}[F_{ijkkl}(kR)]. \tag{55}$$

Noting from Equation (10) that $F_{ijkkl}(kR) = F_{ij}(kR)$, Equation (55) becomes

$$\begin{aligned} &-\frac{I}{8\pi \varepsilon_0^2 c R^7} \alpha^{13^1}(A;k) \alpha^{13^1}(B;k) \\ &\times [k^5 R^5 \sin 2kR + 2k^4 R^4 \cos 2kR - 5k^3 R^3 \sin 2kR - 6k^2 R^2 \cos 2kR + 3kR \sin 2kR]. \end{aligned} \tag{56}$$

For the second term of Equation (51), its field-dependent factor is evaluated by inserting $m = 3$ and $n = 1$ into Equation (17), giving

$$\begin{aligned} &\langle N(\vec{k}, \lambda) | \nabla_k \nabla_l d_j^\perp(\vec{R}_A) d_q^\perp(\vec{R}_B) | N(\vec{k}, \lambda) \rangle \\ &= -\left(\frac{\hbar c \varepsilon_0}{2V}\right) k_k k_l [N \bar{e}_j^{(\lambda)}(\vec{k}) e_q^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{R}} + (N+1) e_j^{(\lambda)}(\vec{k}) \bar{e}_q^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}], \end{aligned} \tag{57}$$

along with the pair average (22) and rewriting $ReV_{jrst}(k, \vec{R})$ using relation (13), produces, after molecular averaging,

$$-\frac{Ik^7}{8\pi\epsilon_0^2c}\alpha^{13^1}(A;k)\alpha^{13^1}(B;k)Re[F_{ijkk}(kR)]Im[F_{ijll}(kR)], \tag{58}$$

which can be seen to be identical to result (55) on noting that $F_{ijkk}(kR) = -F_{ij}(kR)$. For the third term of Equation (51), substituting $m = 1$ and $n = 3$ into Equation (17) for the field-field spatial correlation function, similar evaluation steps used for the second term of Equation (51) lead to a contribution that is identical to expression (58). For the fourth and final term of Equation (51), substituting $m = n = 1$ into Equation (17) gives, for the expectation value of the product of displacement fields at A and B,

$$\begin{aligned} &< N(\vec{k}, \lambda) |d_i^\perp(\vec{R}_A)d_q^\perp(\vec{R}_B)|N(\vec{k}, \lambda) > \\ &= \left(\frac{\hbar ck\epsilon_0}{2V}\right) [N\bar{e}_i^{(\lambda)}(\vec{k})e_q^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{R}} + (N+1)e_i^{(\lambda)}(\vec{k})\bar{e}_q^{(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{R}}]. \end{aligned} \tag{59}$$

Carrying out the polarisation sum using Formula (19) and the angular average via the relation (34), and obtaining the following from Equations (9) and (10)

$$\begin{aligned} ReV_{jrkltst}(k, \vec{R}) &= -\frac{k^7}{4\pi\epsilon_0} Re[F_{jrkltst}(kR)] \\ &= -\frac{1}{4\pi\epsilon_0} (-\nabla^2\delta_{jr} + \nabla_j\nabla_r)\nabla_k\nabla_l\nabla_s\nabla_t\frac{\cos kR}{R}, \end{aligned} \tag{60}$$

the fourth term is found to be identical to Equation (56). Adding all four identical terms yields the following expression for the field-induced potential:

$$\begin{aligned} \Delta E^{13^1;13^1} &= -\frac{I}{2\pi\epsilon_0^2cR^7}\alpha^{13^1}(A;k)\alpha^{13^1}(B;k) \\ &\times [k^5R^5 \sin 2kR + 2k^4R^4 \cos 2kR - 5k^3R^3 \sin 2kR - 6k^2R^2 \cos 2kR + 3kR \sin 2kR], \end{aligned} \tag{61}$$

which may also be interpreted as a higher-order correction term to the leading pure electric dipole shift. Inverse R behaviour is predicted in the near zone

$$\Delta E_{NZ}^{13^1;13^1} \sim \frac{14}{15} \frac{Ik^6}{\pi\epsilon_0^2cR}\alpha^{13^1}(A;k)\alpha^{13^1}(B;k), \tag{62}$$

and modulated inverse R^2 dependence at very long range

$$\Delta E_{FZ}^{13^1;13^1} \sim -\frac{Ik^5}{2\pi\epsilon_0^2cR^2}\alpha^{13^1}(A;k)\alpha^{13^1}(B;k) \sin 2kR. \tag{63}$$

3.2. Polarisation Analysis

We consider the same polarisation and propagation directions as earlier. Inserting Equation (52) into the first term of Equation (51) gives

$$\begin{aligned} &\left(\frac{\hbar ck}{2\epsilon_0V}\right)\alpha_{ijkl}^{13}(A;k)\alpha_{qrst}^{13}(B;k)k_kk_lk_s k_t [N\bar{e}_j^{(\lambda)}(\vec{k})e_r^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{R}} \\ &+ (N+1)e_j^{(\lambda)}(\vec{k})\bar{e}_r^{(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{R}}]ReV_{iq}(k, \vec{R}). \end{aligned} \tag{64}$$

Approximating $N + 1$ by N , carrying out the molecular averages and substituting for $ReV_{iq}(k, \vec{R})$ from Equation (12) yields

$$\begin{aligned} &-\frac{Ik^7}{4\pi\epsilon_0^2c}\alpha^{13^1}(A;k)\alpha^{13^1}(B;k)e_i^{(\lambda)}(\vec{k})\bar{e}_j^{(\lambda)}(\vec{k}) \\ &\times [-(\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{\cos kR}{kR} + (\delta_{ij} - 3\hat{R}_i\hat{R}_j)(\frac{\sin kR}{k^2R^2} + \frac{\cos kR}{k^3R^3})] \cos(\vec{k} \cdot \vec{R}), \end{aligned} \tag{65}$$

with the three other terms of Equation (51) producing identical results to Equation (65).

(a) Linearly polarised light.

(i) $\hat{k} \parallel \hat{R}; \hat{e} \perp \hat{R}$: For this configuration, Equation (65) becomes

$$\frac{I}{\pi \epsilon_0^2 c R^7} \alpha^{13^1}(A; k) \alpha^{13^1}(B; k) \times [k^6 R^6 \cos^2 kR - k^5 R^5 \sin kR \cos kR - k^4 R^4 \cos^2 kR], \quad (66)$$

with inverse cubic separation distance behaviour found in the near zone and a $(\cos^2 kR)/R$ dependence in the far zone.

(ii) $\hat{k} \perp \hat{R}; \hat{e} \parallel \hat{R}$: In this scenario, Equation (65) becomes

$$\frac{2I}{\pi \epsilon_0^2 c R^7} \alpha^{13^1}(A; k) \alpha^{13^1}(B; k) [k^5 R^5 \sin kR + k^4 R^4 \cos kR], \quad (67)$$

with asymptotically limiting forms R^{-3} at very short range, and $(\sin kR)/R^2$ in the far zone.

(b) Circularly polarised radiation.

We again employ the ij -symmetric part of identity Equation (47) for chiral light.

(i) $\hat{k} \parallel \hat{R}; \hat{e} \perp \hat{R}$: Equation (65) becomes

$$\frac{I}{\pi \epsilon_0^2 c R^7} \alpha^{13^1}(A; k) \alpha^{13^1}(B; k) \times [k^6 R^6 \cos^2 kR - k^5 R^5 \sin kR \cos kR - k^4 R^4 \cos^2 kR], \quad (68)$$

which is identical to Equation (66).

(ii) $\hat{k} \perp \hat{R}; \hat{e} \parallel \hat{R}$: Equation (65) becomes

$$\frac{I}{2\pi \epsilon_0^2 c R^7} \alpha^{13^1}(A; k) \alpha^{13^1}(B; k) [k^6 R^6 \cos kR + k^5 R^5 \sin kR + k^4 R^4 \cos kR], \quad (69)$$

with $R^{-1} \cos kR$ behaviour in the far zone and an R^{-3} limit in the near zone.

4. Field-Induced Potential between an Electric Dipole-Polarisable Molecule and an Electric Octupole-Polarisable Molecule

The final radiation-induced energy shift to be calculated that depends on electric octupole coupling and involves the scattering of a real photon at different centres is that between an electric dipole-polarisable molecule, A , and its pure octupole analogue, B . This potential is of the same order of magnitude as that considered in the previous section, and therefore should be included for consistency. The electric dipole induced at A is given by Equation (4), with pure electric dipole polarisability (5). By dint of the polarisability characteristic of B , only an electric octupole moment is induced there,

$$E_{ijk}^{(3)ind}(B) = \epsilon_0^{-1} \alpha_{ijklmn}^{33}(B; k) \nabla_m \nabla_n d_l^\perp(\vec{R}_B), \quad (70)$$

with the electric octupole polarisability defined as

$$\alpha_{ijklmn}^{33}(B; k) = \sum_b \left\{ \frac{E_{ijk}^{(3)0b}(B) E_{lmn}^{(3)b0}(B)}{E_{b0} - \hbar ck} + \frac{E_{lmn}^{(3)0b}(B) E_{ijk}^{(3)b0}(B)}{E_{b0} + \hbar ck} \right\}. \quad (71)$$

The two moments couple via the tensor $\text{Re}V_{ijkl}(k, \vec{R})$ written in Equation (13), giving rise to an interaction energy of the form

$$\begin{aligned} \Delta E^{11,33} &= E_i^{(1)ind}(A)E_{klm}^{(3)ind}(B)\text{Re}V_{iklm}(k, \vec{R}) \\ &= \epsilon_0^{-2}\alpha_{ij}^{11}(A;k)\alpha_{klmpqr}^{33}(B;k)d_j^\perp(\vec{R}_A)\nabla_q\nabla_r d_p^\perp(\vec{R}_B)\text{Re}V_{iklm}(k, \vec{R}). \end{aligned} \tag{72}$$

Substituting relation (18), carrying out the polarisation sum using Equation (19) and performing the pair average via the result (22), and rewriting the coupling tensor using Equation (13), the energy shift expression (72) becomes

$$\begin{aligned} \Delta E^{11,33} &= -\frac{I}{8\pi\epsilon_0^2c}\alpha_{ij}^{11}(A;k)\alpha_{klmpqr}^{33}(B;k)\left[\frac{1}{k^3}(-\nabla^2\delta_{jp} + \nabla_j\nabla_p)\nabla_q\nabla_r\frac{\sin kR}{R}\right] \\ &\times\left[(-\nabla^2\delta_{ik} + \nabla_i\nabla_k)\nabla_l\nabla_m\frac{\cos kR}{R}\right]. \end{aligned} \tag{73}$$

To obtain the isotropic potential energy, use is made of the result (26) for the orientational average of the electric dipole polarisability, while for pure octupole polarisability, we employ the result [23,33]

$$\begin{aligned} \langle \alpha_{klmpqr}^{33}(B;k) \rangle &= \frac{14}{210}[\delta_{kp}\delta_{lm}\delta_{qr}\alpha_{\lambda\mu\nu\lambda\nu}^{33}(B;k) + 2(\delta_{kp}\delta_{lq}\delta_{mr} + \delta_{kp}\delta_{lr}\delta_{mq} \\ &+ \delta_{kq}\delta_{lp}\delta_{mr} + \delta_{kq}\delta_{lr}\delta_{mp} + \delta_{kr}\delta_{lp}\delta_{mq} + \delta_{kr}\delta_{lq}\delta_{mp})\alpha_{\lambda\mu\nu\lambda\nu}^{33}(B;k)]. \end{aligned} \tag{74}$$

Noting that [23]

$$\alpha_{\lambda\mu\mu\lambda\nu\nu}^{33}(B;k) = \alpha_{\lambda\mu\mu\lambda\nu\nu}^{3^13^1}(B;k), \tag{75}$$

and

$$\alpha_{\lambda\mu\nu\lambda\mu\nu}^{33}(B;k) = \frac{3}{5}\alpha_{\lambda\mu\mu\lambda\nu\nu}^{3^13^1}(B;k) + \alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^33^3}(B;k), \tag{76}$$

the energy shift expression (73) becomes

$$\begin{aligned} \Delta E^{11,33} &= -\frac{2Ik^7}{6720 \times 8\pi\epsilon_0^2c}\alpha^{11}(A;k)\left\{\frac{7}{5}\text{Re}[F_{ijkk}(kR)]\text{Im}[F_{ijll}(kr)]\alpha_{\lambda\mu\mu\lambda\nu\nu}^{3^13^1}(B;k) \right. \\ &+ [-\text{Re}[F_{ijkk}(kR)]\text{Im}[F_{ijll}(kr)] + 5\text{Re}[F_{ijkl}(kR)]\text{Im}[F_{ijkl}(kr)] \\ &\left. + 10\text{Re}[F_{ijkl}(kR)]\text{Im}[F_{ikjl}(kr)]\right\}\alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^33^3}(B;k). \end{aligned} \tag{77}$$

Evaluating the product of geometric tensors finally results in

$$\begin{aligned} \Delta E^{11,33} &= -\frac{I}{19200\pi\epsilon_0^2cR^7}\alpha^{11}(A;k)\alpha_{\lambda\mu\mu\lambda\nu\nu}^{3^13^1}(B;k) \\ &\times [k^5R^5 \sin 2kR + 2k^4R^4 \cos 2kR - 5k^3R^3 \sin 2kR - 6k^2R^2 \cos 2kR + 3kR \sin 2kR] \\ &- \frac{I}{6720\pi\epsilon_0^2cR^7}\alpha^{11}(A;k)\alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^33^3}(B;k) \\ &\times [k^5R^5 \sin 2kR + 12k^4R^4 \cos 2kR - 90k^3R^3 \sin 2kR - 486k^2R^2 \cos 2kR \\ &+ 1863kR \sin 2kR + 4950 \cos 2kR - \frac{8755}{kR} \sin 2kR - \frac{9450}{k^2R^2} \cos 2kR + \frac{4725}{k^3R^3} \sin 2kR] \end{aligned} \tag{78}$$

Inspection of expression (78) shows that this contribution to the optical binding energy depends on both octupole weight-1 and weight-3 terms. As in the previous examples considered, the weight-1-dependent term may be viewed as a higher-order correction to the leading pure electric dipole contribution, the coefficients preceding each term in square brackets being identical. The second term of Equation (78) is proportional to $E_{\lambda\mu\nu}^{3^3}$, which is a third-rank tensor with 27 independent components. The coefficients within square brackets of this term are identical to that found in the dispersion potential between an electric dipole-polarisable molecule and an octupole-polarisable one [23].

Polarisation Analysis

Substituting relation (18) into Equation (72) and performing the molecular orientational averages yields

$$\begin{aligned} \Delta E^{11;33} = & -\frac{I}{105\epsilon_0 c} \alpha^{11}(A; k) \left\{ \frac{7}{5} e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k}) k_l k_l \text{Re} V_{ijkk}(k, \vec{R}) \alpha_{\lambda\mu\lambda\nu\nu}^{3^1 3^1}(B; k) \right. \\ & + [-e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k}) k_l k_l \text{Re} V_{ijkk}(k, \vec{R}) + 5e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k}) k_k k_l \text{Re} V_{ijkl}(k, \vec{R}) \\ & \left. + 10e_i^{(\lambda)}(\vec{k}) \bar{e}_k^{(\lambda)}(\vec{k}) k_j k_l \text{Re} V_{ijkl}(k, \vec{R}) \right] \alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k) \Big\} \cos(\vec{k} \cdot \vec{R}). \end{aligned} \tag{79}$$

(a) Linearly polarised beam.

(i) $\hat{k} \parallel \hat{R}; \hat{e} \perp \hat{R}$: Inserting the geometric tensors produces

$$\begin{aligned} \Delta E_{lin}^{11;33(\parallel)} = & \frac{I}{420\pi\epsilon_0^2 c R^7} \alpha^{11}(A; k) \left\{ \frac{7}{5} \alpha_{\lambda\mu\lambda\nu\nu}^{3^1 3^1}(B; k) \right. \\ & \times [k^4 R^4 \cos^2 kR + k^5 R^5 \sin kR \cos kR - k^6 R^6 \cos^2 kR] \\ & - 4\alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k) [k^6 R^6 \cos^2 kR - 6k^5 R^5 \sin kR \cos kR - 21k^4 R^4 \cos^2 kR \\ & \left. + 45k^3 R^3 \sin kR \cos kR + 45k^2 R^2 \cos^2 kR] \right\}, \end{aligned} \tag{80}$$

with asymptotic limits

$$\Delta E_{lin}^{11;33(\parallel)}(FZ) = -\frac{Ik^6}{420\pi\epsilon_0^2 c R} \alpha^{11}(A; k) \left\{ \frac{7}{5} \alpha_{\lambda\mu\lambda\nu\nu}^{3^1 3^1}(B; k) + 4\alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k) \right\}, \tag{81}$$

and

$$\Delta E_{lin}^{11;33(\parallel)}(NZ) = -\frac{3Ik^2}{7\pi\epsilon_0^2 c R^5} \alpha^{11}(A; k) \alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k), \tag{82}$$

with the last of these limits independent of $E_{\lambda\mu\nu}^{3^1}$.

(ii) $\hat{k} \perp \hat{R}; \hat{e} \parallel \hat{R}$: Now,

$$\begin{aligned} \Delta E_{lin}^{11;33(\perp)} = & -\frac{I}{420\pi\epsilon_0^2 c R^7} \alpha^{11}(A; k) \left\{ \frac{14}{5} \alpha_{\lambda\mu\lambda\nu\nu}^{3^1 3^1}(B; k) [k^4 R^4 \cos kR + k^5 R^5 \sin kR] \right. \\ & \left. - 12\alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k) [k^5 R^5 \sin kR + 6k^4 R^4 \cos kR - 15k^3 R^3 \sin kR - 15k^2 R^2 \cos kR] \right\}, \end{aligned} \tag{83}$$

with limiting forms

$$\Delta E_{lin}^{11;33(\perp)}(FZ) = -\frac{Ik^5}{420\pi\epsilon_0^2 c R^2} \alpha^{11}(A; k) \left\{ \frac{14}{5} \alpha_{\lambda\mu\lambda\nu\nu}^{3^1 3^1}(B; k) - 12\alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k) \right\}, \tag{84}$$

and

$$\Delta E_{lin}^{11;33(\perp)}(NZ) = \frac{180Ik^2}{420\pi\epsilon_0^2 c R^5} \alpha^{11}(A; k) \alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k). \tag{85}$$

(b) Circularly polarised radiation.

(i) $\hat{k} \parallel \hat{R}; \hat{e} \perp \hat{R}$: For this arrangement, $\Delta E_{L/R}^{11;33(\parallel)} = \Delta E_{lin}^{11;33(\parallel)}$, given by Equation (80), and with identical asymptotic limits (81) and (82).

(ii) $\hat{k} \perp \hat{R}; \hat{e} \parallel \hat{R}$: This results in

$$\begin{aligned} \Delta E_{L/R}^{11;33(\perp)} = & -\frac{I}{840\pi\epsilon_0^2 c R^7} \alpha^{11}(A; k) \left\{ \frac{7}{5} \alpha_{\lambda\mu\lambda\nu\nu}^{3^1 3^1}(B; k) \right. \\ & \times [k^4 R^4 \cos kR + k^5 R^5 \sin kR + k^6 R^6 \cos kR] \\ & - \alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B; k) [k^6 R^6 \cos kR - 14k^5 R^5 \sin kR + 31k^4 R^4 \cos kR \\ & \left. - 135k^3 R^3 \sin kR - 135k^2 R^2 \cos kR] \right\}, \end{aligned} \tag{86}$$

with far- and near-zone asymptotes

$$\Delta E_{L/R}^{11;33(\perp)}(FZ) = -\frac{Ik^6}{840\pi\epsilon_0^2 cR} \alpha^{11}(A;k) \left\{ \frac{7}{5} \alpha_{\lambda\mu\nu\lambda\nu\nu}^{3^3 3^1}(B;k) - \alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B;k) \right\}, \tag{87}$$

and

$$\Delta E_{L/R}^{11;33(\perp)}(NZ) = -\frac{135Ik^2}{840\pi\epsilon_0^2 cR^5} \alpha^{11}(A;k) \alpha_{\lambda\mu\nu\lambda\mu\nu}^{3^3 3^3}(B;k). \tag{88}$$

The last expression is again independent of the octupole weight-1 term.

5. Octupole-Dependent Contributions to Optical Binding Arising from the Static Mechanism

The three examples presented thus far involve the scattering of the real photon at different molecular sites. This is frequently referred to as the dynamic mechanism. We now consider the situation in which the incident laser light is emitted and absorbed by the same particle, either *A* or *B*. This is often termed the static mechanism. As well as the static electric dipole moment, higher-order response tensors participate in the induction of multipole moments. In the case of the induced electric dipole moment, this is given by

$$E_i^{(1)ind}(\xi) = E_i^{1(s)}(\xi) + \epsilon_0^{-1} \alpha_{ij}^{11}(\xi;k) d_j^\perp(\vec{R}_\xi) + \epsilon_0^{-1} \alpha_{ijkl}^{13}(\xi;k) \nabla_k \nabla_l d_j^\perp(\vec{R}_\xi) + \epsilon_0^{-2} \beta_{ijk}^{111}(\xi;k,k') d_j^\perp(\vec{R}_\xi) d_k^\perp(\vec{R}_\xi) + \epsilon_0^{-2} \beta_{ijklm}^{113}(\xi;k,k') d_j^\perp(\vec{R}_\xi) \nabla_l \nabla_m d_k^\perp(\vec{R}_\xi) + \dots \tag{89}$$

where $E_i^{1(s)}$ is the static electric dipole moment, $\alpha_{ij}^{11}(\xi;k)$ is the pure electric dipole polarisability and given earlier by Equation (5), $\alpha_{ijkl}^{13}(\xi;k)$ is the mixed electric dipole–octupole polarisability tensor defined by Equation (8), $\beta_{ijk}^{111}(\xi)$ is the pure electric dipole first hyperpolarisability tensor and $\beta_{ijklm}^{113}(\xi)$ is the electric dipole–dipole–octupole first hyperpolarisability tensor of molecule ξ . Similarly, for the induced octupole moment,

$$E_{ijk}^{(3)ind}(\xi) = E_{ijk}^{3(s)}(\xi) + \epsilon_0^{-1} \alpha_{ijk}^{13}(\xi;k) d_l^\perp(\vec{R}_\xi) + \epsilon_0^{-1} \alpha_{lmnij}^{33}(\xi;k) \nabla_m \nabla_n d_l^\perp(\vec{R}_\xi) + \epsilon_0^{-2} \beta_{mlijk}^{113}(\xi;k,k') d_m^\perp(\vec{R}_\xi) d_l^\perp(\vec{R}_\xi) + \epsilon_0^{-2} \beta_{pqrlmijk}^{333}(\xi;k,k') \nabla_q \nabla_r d_p^\perp(\vec{R}_\xi) \nabla_m \nabla_n d_l^\perp(\vec{R}_\xi) + \dots \tag{90}$$

where $\alpha_{lmnij}^{33}(\xi;k)$ is the pure electric octupole polarisability (71) and $\beta_{pqrlmijk}^{333}(\xi)$ is the pure electric octupole first hyperpolarisability tensor.

Let *A* be purely electric dipole-hyperpolarisable and *B* be described by a permanent electric octupole moment. From Equations (89) and (90), the interaction energy coupling the electric dipole induced at *A* and the octupole induced at *B* can be written as

$$\begin{aligned} \Delta E^{111;3} &= E_i^{(1)ind}(A) E_{jkl}^{(3)ind}(B) V_{ijkl}(k, \vec{R}) \\ &= \epsilon_0^{-2} \beta_{ijk}^{111}(A) E_{lmn}^{3(s)}(B) d_j^\perp(\vec{R}_A) d_k^\perp(\vec{R}_A) V_{ilmn}(0, \vec{R}). \end{aligned} \tag{91}$$

On account of *B* being polar, with its ground state permanent octupole moment appearing to leading order, the static coupling tensor $V_{ilmn}(0, \vec{R})$ features in Equation (91). A corresponding term arises on interchanging *A* and *B*, so that

$$\begin{aligned} \Delta E^{111;3} &= \frac{1}{2} \epsilon_0^{-2} [\beta_{ijk}^{111}(A) E_{lmn}^{3(s)}(B) d_j^\perp(\vec{R}_A) d_k^\perp(\vec{R}_A) V_{ilmn}(0, \vec{R}) \\ &\quad + E_{ijk}^{3(s)}(A) \beta_{lmn}^{111}(B) d_m^\perp(\vec{R}_B) d_n^\perp(\vec{R}_B) V_{iljk}(0, \vec{R})], \end{aligned} \tag{92}$$

with the factor of ½ due to index symmetry, allowing for *A* and *B* to be identical or distinct.

Taking the expectation value of Equation (92) over the ground state of both particles and the radiation field with state $|N(\vec{k}, \lambda)\rangle$ photons as before, noting that

$$\begin{aligned} & \langle N(\vec{k}, \lambda) | d_i^\perp(\vec{R}_\xi) d_j^\perp(\vec{R}_\xi) | N(\vec{k}, \lambda) \rangle \\ &= \left(\frac{\hbar c k \epsilon_0}{2V} \right) [N \bar{e}_i^{(\lambda)}(\vec{k}) e_j^{(\lambda)}(\vec{k}) + (N + 1) e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k})] \sim \frac{N \hbar c k \epsilon_0}{V} e_i^{(\lambda)}(\vec{k}) \bar{e}_j^{(\lambda)}(\vec{k}), \end{aligned} \tag{93}$$

on taking $N \gg 1$, the first term of expression (92) is

$$\left(\frac{N \hbar c k}{2 \epsilon_0 V} \right) e_j^{(\lambda)}(\vec{k}) \bar{e}_k^{(\lambda)}(\vec{k}) \beta_{ijk}^{111}(A) E_{lmn}^{(3)00}(B) V_{ilmn}(0, \vec{R}). \tag{94}$$

The molecular factors are averaged using the results [33] for a third-rank Cartesian tensor

$$\langle \beta_{ijk}^{111}(A) \rangle = \frac{1}{6} \epsilon_{ijk} \epsilon_{\lambda\mu\nu} \beta_{\lambda\mu\nu}^{111}(A), \tag{95}$$

and

$$\langle E_{lmn}^{(3)00}(B) \rangle = \frac{1}{6} \epsilon_{lmn} \epsilon_{\rho\sigma\tau} E_{\rho\sigma\tau}^{(3)00}(B), \tag{96}$$

yielding the isotropic potential

$$\frac{1}{36} \frac{I}{2 \epsilon_0 c} \epsilon_{ijk} \epsilon_{lmn} \epsilon_{\lambda\mu\nu} \epsilon_{\rho\sigma\tau} e_j^{(\lambda)}(\vec{k}) \bar{e}_k^{(\lambda)}(\vec{k}) \beta_{\lambda\mu\nu}^{111}(A) E_{\rho\sigma\tau}^{(3)00}(B) V_{ilmn}(0, \vec{R}). \tag{97}$$

This vanishes because the laser polarisation factor is symmetric in j, k while the Levi-Civita tensor is antisymmetric in this pair. The second term of Equation (92) similarly vanishes. Hence,

$$\langle \Delta E_{static}^{\beta^{111}-E^3} \rangle = 0. \tag{98}$$

A second situation occurs when A is electric dipole–dipole–octupole–first-hyperpolarisable and B is characterised by a permanent electric dipole moment. From Equations (89) and (90), coupling of an induced electric octupole at A with an induced electric dipole at B , and between induced electric dipoles at each centre, leads to

$$\begin{aligned} \Delta E^{113;1} &= E_{ijk}^{(3)ind}(A) E_l^{(1)ind}(B) V_{iljk}(k, \vec{R}) + E_p^{(1)ind}(A) E_q^{(1)ind}(B) V_{pq}(k, \vec{R}) \\ &= \frac{1}{2} \epsilon_0^{-2} [\beta_{ijkmn}^{113}(A) E_l^{1(s)}(B) d_m^\perp(\vec{R}_A) d_n^\perp(\vec{R}_A) V_{iljk}(0, \vec{R}) \\ &+ \beta_{ijkps}^{113}(A) E_q^{1(s)}(B) d_s^\perp(\vec{R}_A) \nabla_j \nabla_k d_i^\perp(\vec{R}_A) V_{pq}(0, \vec{R}) + A \leftrightarrow B]. \end{aligned} \tag{99}$$

Examining the first term of Equation (99), substituting the relation (93) produces

$$\left(\frac{N \hbar c k}{2 \epsilon_0 V} \right) e_m^{(\lambda)}(\vec{k}) \bar{e}_n^{(\lambda)}(\vec{k}) \beta_{ijkmn}^{113}(A) E_l^{(1)00}(B) V_{iljk}(0, \vec{R}). \tag{100}$$

Now,

$$\begin{aligned} & \langle N(\vec{k}, \lambda) | d_r^\perp(\vec{R}_A) \nabla_m \nabla_n d_l^\perp(\vec{R}_A) | N(\vec{k}, \lambda) \rangle \\ &= - \left(\frac{\hbar c k \epsilon_0}{2V} \right) k_m k_n [N \bar{e}_r^{(\lambda)}(\vec{k}) e_l^{(\lambda)}(\vec{k}) + (N + 1) e_r^{(\lambda)}(\vec{k}) \bar{e}_l^{(\lambda)}(\vec{k})] \\ &\sim - \left(\frac{N \hbar c k \epsilon_0}{V} \right) k_m k_n e_r^{(\lambda)}(\vec{k}) \bar{e}_l^{(\lambda)}(\vec{k}), \end{aligned} \tag{101}$$

on taking $N + 1 \sim N$, so that the second term of Equation (99) is

$$- \left(\frac{N \hbar c k}{2 \epsilon_0 V} \right) e_s^{(\lambda)}(\vec{k}) \bar{e}_i^{(\lambda)}(\vec{k}) k_j k_k \beta_{ijkps}^{113}(A) E_q^{(1)00}(B) V_{pq}(0, \vec{R}). \tag{102}$$

Both Equations (100) and (102) vanish on orientational averaging because [34] (p. 66)

$$\langle E_i^{(1)00}(\xi) \rangle = 0. \quad (103)$$

Hence,

$$\langle \Delta E_{static}^{\beta^{113}-E^1} \rangle = 0. \quad (104)$$

To this order of approximation, no term dependent on a single octupole moment contributes to the static optical binding mechanism.

6. Conclusions

While the dominant contribution to the change in energy shift between two interacting neutral polarisable molecules induced by an intense radiation field is that proportional to the electric dipole polarisability of each species, interesting effects arise when higher multipole moment terms are accounted for. When magnetic dipole coupling terms are included, for instance, the contribution to the potential that is dependent on both transition electric and magnetic dipole moments of either or both species is discriminatory, changing sign when one enantiomer is switched to its isomer of opposite handedness. In this work, new terms contributing to the optical binding energy that are dependent upon one or two electric octupole moments at each centre were calculated. These include the field-induced energy shift between an electric dipole-polarisable molecule and a second that is either mixed electric dipole–octupole-polarisable or purely electric octupole-polarisable, and between two mixed electric dipole–octupole-polarisable molecules.

Results were obtained for both particles randomly oriented relative to each other, and for all directions of propagation of the incident beam relative to the inter-nuclear displacement vector. The first and third examples mentioned above were found to depend only on the octupole weight-1 moment, which has three independent components and the properties of a vector. They may be viewed as higher-order corrections to the leading electric dipole–dipole energy shift. The second system's potential depended on both octupole weight-1 and weight-3 terms, with the former also interpreted as a higher-order correction. All three of these examples fell under the dynamic mechanism classification of the process as the laser beam is absorbed at one site and emitted at the other. Also examined were two examples that belong to the static mechanism categorisation. In this case, the beam of light is absorbed and emitted at the same centre. This necessitates one molecule—the one emitting or absorbing only a virtual photon—being polar, and possessing a static multipole moment. In one case, this was a permanent electric dipole moment so that the other particle was characterised by its mixed electric dipole–dipole–octupole first hyperpolarisability. In the second case, the polar molecule was described by its ground state permanent octupole moment while the other molecule possessed purely electric dipole first hyperpolarisability. Both energy shifts vanished after orientational averaging. For the surviving isotropic potentials, a complete polarisation analysis was also performed. Linearly and circularly polarised incident radiation propagating parallel and perpendicular to the inter-nuclear axis were four scenarios considered that could stimulate possible experimental detection.

Instead of perturbation theory, which is prohibitive when considering higher-order multipole moments due to the excessive number of diagrams that need to be drawn and summed to yield the matrix element or energy shift for a process, especially one like optical binding that is intrinsically higher-order in its number of light–matter couplings, an alternative computational method was employed. This involved first calculating the multipole moments induced at each centre by the applied electromagnetic field based on the polarisability characteristics of the responder. These moments then couple via their respective retarded multipole–multipole interaction tensor. An expectation value taken over the ground electronic state of each molecule with the radiation field in the state containing N photons yielded the field-induced energy shift. The respective dispersion potential readily follows on letting $N = 0$.

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