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van der Waals Dispersion Potential between Excited Chiral Molecules via the Coupling of Induced Dipoles

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Abstract: The retarded van der Waals dispersion potential between two excited chiral molecules was calculated using an approach, in which electric and magnetic dipole moments are induced in each particle by fluctuations in the vacuum electromagnetic field. An expectation value of the coupling of the moments at different centres to the dipolar interaction tensors was taken over excited matter states and the ground state radiation field, the former yielding excited molecular polarisabilities and susceptibilities, and the latter field–field spatial correlation functions. The dispersion potential term proportional to the mixed dipolar polarisability is discriminatory, dependent upon molecular handedness, and contains additional terms due to transitions that de-excite each species as well as the usual u -integral term over imaginary frequency, which applies to both upward and downward transitions. Excited state dispersion potentials of a comparable order of magnitude involving paramagnetic and diamagnetic couplings were also computed. Pros and cons of the method adopted are compared to other commonly used approaches.

Keywords: dispersion forces; excited states; vacuum fluctuations; molecular chirality; quantum electrodynamics

1. Introduction

Classic examples of phenomena that are attributed to vacuum fluctuations of the electromagnetic field [1] include spontaneous emission [2] and the Lamb shift [3,4]. In the case of inter-particle interactions, a fundamental coupling that arises from the zero-point energy associated with the ground state of the radiation field is the well-known Casimir-van der Waals dispersion force between two or more particles [5–8]. For atoms and non-polar molecules, this is the only interaction contributing to the inter-particle energy shift, and is responsible for the manifestation of solid and liquid phases of such forms of matter at low temperature.

The $\frac{1}{2}\hbar\omega$ of energy per mode possessed by the vacuum field, where ω is the circular frequency, albeit infinite in magnitude since there are an infinite number of oscillatory modes, is a direct consequence of quantising electromagnetic radiation, and is a quintessential feature of quantum electrodynamics (QED) theory [9–15], rigorously accounting for the photon. Here \hbar is the reduced Planck constant. The exchange of such gauge bosons between electrons, whether free or bound, mediates the interaction between particles of matter. For instance, the propagation of a single virtual photon, originating due to spontaneous emission by an excited entity undergoing decay, and whose excitation energy is captured on absorption of the photon by an acceptor species in close proximity, describes a multitude of processes involving the migration of energy between various types of chromophoric units, processes commonly collected under the umbrella term “excitation energy transfer” [16–19]. This is another example of a vacuum field-induced effect since there are no photons prior to or after the coupling between particles.

By way of contrast, in a perturbative calculation of the dispersion interaction, in which both species are in the ground electronic state and no photons are present, the energy shift



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is viewed as arising from the exchange of two virtual photons between the pair of atoms or molecules [12,13]. Additional computational difficulties arise when using perturbation theory if one or both of the particles are in excited electronic states [20]. These centre around the proper identification of terms associated with real photon emission and whether excitation energy is localised or is in fact exchanged between centres in a reversible manner. Quite a few recent publications have dealt with these aspects in an attempt to arrive at the correct functional form for the potential [21–26].

Other calculational techniques have been adopted to further understand the nature of the dispersion force when not all of the interacting particles are in their ground state. One approach is to evaluate the quantum electrodynamical radiation fields in the neighbourhood of a charged source and then calculate the response of the second particle, via its polarisability, to the electromagnetic field emanating from the first particle, with appropriate expectation values taken over ground and/or excited states of matter, yielding the pertinent multipolar contribution to the dispersion energy shift [27,28]. An advantage of employing this physical picture and calculational method is its straightforward extension to obtain the result for the N-body electric dipole polarisable [29] or N-body arbitrarily electric multipole polarisable [30] dispersion potentials.

An especially physically intuitive approach to calculate the Casimir–Polder interaction energy, in that it highlights the key role played by the vacuum electromagnetic field, is to consider the energy shift as arising from the coupling of electric dipole moments induced at each atom or molecule by the ground state of the field to the retarded electric dipole–dipole interaction tensor [31]. Because this last quantity features in the amplitude for resonance energy transfer, the method may be employed to readily evaluate the additional contribution to the dispersion potential that is due to real photon emission when one or both species are electronically excited. This approach will be employed below to calculate the dispersion energy shift between two excited chiral molecules, and two other potentials of a similar order of magnitude. For these cases, the usual electric dipole approximation needs to be relaxed, and higher multipole moment terms such as the magnetic dipole have to be included in the treatment. This is because optically active molecules possess fewer or no elements of symmetry relative to achiral compounds and consequently have less restrictive spectroscopic selection rules apply to them.

One interesting aspect of the dispersion interaction energy between chiral molecules is that it is discriminatory, depending on the handedness of the interacting pair. The chirality dependent ground state dispersion potential has been previously evaluated using the three methods described above, namely, the perturbation and response theories, and the induced moment method [32–35], with excited state energies only evaluated using response theory [36]. Recently, perturbation theory has been employed within the framework of macroscopic QED theory [6] to calculate the dispersion interactions between one or two chiral molecules in the presence of a chiral plate [37], or when situated in a magnetodielectric medium [38], with novel features emerging as a result of placing bodies in complex environments such as altering the sign of the dispersion force as the relative separation distances are varied. The results obtained will enable an assessment to be made of the feasibility of applying the fluctuating moment method to systems in excited electronic states that are characterised by multipoles higher than the electric dipole relative to more conventional approaches. These results will also complement other studies dealing with interactions amongst enantiomers.

The paper is organised as follows. A brief overview of the induced moment method applicable to chiral molecules is presented in Section 2. The calculation of the excited state dispersion potential between two chiral molecules is detailed in Section 3. An energy shift of a similar order of magnitude is then obtained in Section 4, that between an electric dipole polarisable molecule and a paramagnetically susceptible one. The diamagnetic counterpart to this last contribution, also of an identical order of magnitude to the two previous potentials, is evaluated in Section 5. A brief summary is given in Section 6.

2. Moments Induced in a Chiral Molecule by Electromagnetic Radiation

Consider a chiral molecule, ξ , located at the position \vec{R}_ξ . Lacking an improper axis of rotation, such species may belong to one of the following molecular point groups: C_1 , C_n , D_n , T , and O , with $n \geq 2$. In the first point group listed, spectroscopic selection rules permit transitions to all orders of multipole moment distributions between electronic states. Often, it is sufficient to invoke the dipole approximation to describe chiral molecules since the vector dot product of an electric dipole moment ($\vec{\mu}$) and a magnetic dipole moment (\vec{m}) vector yields a pseudoscalar quantity, which changes sign when substituting one enantiomer by its mirror-image structure. In what follows, only these two multipole moments are retained and the electric quadrupole moment, \vec{Q} , is neglected. Although \vec{Q} is of a comparable order of magnitude to \vec{m} , with both a factor of the fine structure constant smaller than $\vec{\mu}$, mixed electric dipole-quadrupole dependent contributions to the dispersion interaction vanish for freely tumbling systems, and are not considered henceforth.

Thus, within the dipolar approximation, the electric and magnetic dipole moments induced in a chiral molecule by electromagnetic radiation of mode \vec{k}, λ , where \vec{k} is the wave vector and λ is the index of polarisation of the propagating radiation fields, are:

$$\mu_i^{ind}(\xi; \vec{k}, \lambda) = \epsilon_0^{-1} \alpha_{ij}(\xi; k) d_j^\perp(\vec{k}, \lambda; \vec{R}_\xi) + G_{ij}(\xi; k) b_j(\vec{k}, \lambda; \vec{R}_\xi), \tag{1}$$

and

$$m_j^{ind}(\xi; \vec{k}, \lambda) = \epsilon_0^{-1} G_{ij}(\xi; k) d_i^\perp(\vec{k}, \lambda; \vec{R}_\xi) + \chi_{ij}(\xi; k) b_i(\vec{k}, \lambda; \vec{R}_\xi), \tag{2}$$

where the Latin letter subscripts denote Cartesian tensor components in the space-fixed frame of reference, and the Einstein summation rule is in effect for indices that repeat. Here, ϵ_0 denotes the permittivity of free space. In the relations (1) and (2), $\alpha_{ij}(\xi; k)$ is the dynamic electric dipole polarisability tensor, $G_{ij}(\xi; k)$ is the mixed electric-magnetic dipole analogue, and $\chi_{ij}(\xi; k)$ is the magnetic dipole polarisability tensor or the paramagnetic susceptibility tensor. Their explicit forms are given by

$$\alpha_{ij}(\xi; k) = \sum_t \left\{ \frac{\mu_i^{st}(\xi) \mu_j^{ts}(\xi)}{E_{ts} - \hbar ck} + \frac{\mu_j^{st}(\xi) \mu_i^{ts}(\xi)}{E_{ts} + \hbar ck} \right\}, \tag{3}$$

$$G_{ij}(\xi; k) = \sum_t \left\{ \frac{\mu_i^{st}(\xi) m_j^{ts}(\xi)}{E_{ts} - \hbar ck} + \frac{m_j^{st}(\xi) \mu_i^{ts}(\xi)}{E_{ts} + \hbar ck} \right\}, \tag{4}$$

and

$$\chi_{ij}(\xi; k) = \sum_t \left\{ \frac{m_i^{st}(\xi) m_j^{ts}(\xi)}{E_{ts} - \hbar ck} + \frac{m_j^{st}(\xi) m_i^{ts}(\xi)}{E_{ts} + \hbar ck} \right\}, \tag{5}$$

where $\mu_i^{st}(\xi) = \langle s | \mu_i(\xi) | t \rangle$ and $m_i^{st}(\xi) = \langle s | m_i(\xi) | t \rangle$ are the transition electric and magnetic dipole moment matrix elements between electronic states $|s\rangle$ and $|t\rangle$, with energies E_s and E_t , respectively, and $E_{ts} = E_t - E_s$ symbolizing the energy differences between these states. Here c stands for the speed of light.

For a specific mode \vec{k}, λ , the second quantised microscopic Maxwell field operators appearing in Equations (1) and (2) are the familiar Fourier series mode expansions for the transverse electric displacement field, $\vec{d}^\perp(\vec{r})$, and the magnetic field, $\vec{b}(\vec{r})$,

$$\vec{d}^\perp(\vec{k}, \lambda; \vec{r}) = i \left(\frac{\hbar ck \epsilon_0}{2V} \right)^{1/2} \left[\vec{e}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \vec{e}^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \right], \tag{6}$$

and

$$\vec{b}(\vec{k}, \lambda; \vec{r}) = i \left(\frac{\hbar k}{2\epsilon_0 c V} \right)^{1/2} [\vec{b}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \vec{b}^{(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}}]. \quad (7)$$

These radiation fields are linear functions of the bosonic annihilation and creation operators for a \vec{k}, λ -mode photon, $a^{(\lambda)}(\vec{k})$ and $a^{\dagger(\lambda)}(\vec{k})$, respectively, with $\vec{e}^{(\lambda)}(\vec{k})$ and $\vec{b}^{(\lambda)}(\vec{k})$ as the complex unit electric and magnetic polarisation vectors, and V is the quantisation volume of the box.

The leading contribution to the interaction energy, ΔE , between two molecules, A and B, arises from the coupling of the induced electric dipole moments at each centre. Keeping only the first term of Equation (1),

$$\Delta E = \sum_{\vec{k}, \lambda} \mu_i^{ind}(A; \vec{k}, \lambda) \mu_j^{ind}(B; \vec{k}, \lambda) \text{Re} V_{ij}(k, \vec{R}), \quad (8)$$

where the sum is executed over all radiation field modes, the inter-nuclear displacement, $R = |\vec{R}_B - \vec{R}_A|$, and $V_{ij}(k, \vec{R})$ is the retarded electric dipole–dipole tensor that couples the two induced dipoles. It is given by the familiar expression [12,13]

$$V_{ij}(k, \vec{R}) = \frac{1}{4\pi\epsilon_0 R^3} [(\delta_{ij} - 3\hat{R}_i \hat{R}_j)(1 - ikR) - (\delta_{ij} - \hat{R}_i \hat{R}_j)k^2 R^2] e^{ikR}, \quad (9)$$

where δ_{ij} is the Kronecker delta.

Power and Thirunamachandran showed [31] how Equation (8) led to the Casimir–Polder potential between two ground state atoms or molecules as well as to the energy shift when one of the pair is in an excited electronic state. In this paper, their method is extended to chiral molecules and other magnetic systems.

3. Dispersion Potential between Two Excited Chiral Molecules

Let us start with employing the fluctuating moment method to calculate the dispersion interaction energy between two optically active molecules. Species A is initially in the excited electronic state $|p\rangle$ and may undergo upward or downward virtual transitions to level $|n\rangle$, with B undergoing similar transitions from $|r\rangle \leftarrow |q\rangle$. In addition to the coupling between two induced electric dipoles as given in Equation (8), there is an analogous term involving the coupling of two magnetic dipoles, which also interact via the retarded interaction tensor (9). Furthermore, an electric dipole induced at one site may interact with an induced magnetic dipole of the second particle. This time coupling occurs through the interaction tensor [12,13]

$$U_{ij}(k, \vec{R}) = -\frac{ik}{4\pi\epsilon_0 c} \epsilon_{ijk} \nabla_k \frac{e^{ikR}}{R} = \frac{1}{4\pi\epsilon_0 c R^3} \epsilon_{ijk} \hat{R}_k [ikR + k^2 R^2] e^{ikR}, \quad (10)$$

where ϵ_{ijk} is the Levi–Civita tensor. Hence, the energy shift may be expressed as

$$\begin{aligned} \Delta E = \sum_{\vec{k}, \lambda} \{ & [\mu_i^{ind}(A) \mu_j^{ind}(B) + c^{-2} m_i^{ind}(A) m_j^{ind}(B)] \text{Re} V_{ij}(k, \vec{R}) \\ & + [\mu_i^{ind}(A) m_j^{ind}(B) + m_i^{ind}(A) \mu_j^{ind}(B)] \text{Im} U_{ij}(k, \vec{R}) \}. \end{aligned} \quad (11)$$

Equation (11) is the starting point in the evaluation of energy shifts dependent upon magnetic dipole coupling including chiral molecules to leading order. For terms proportional to the handedness of the two molecules, manifested by the mixed electric-magnetic dipole polarisability (4), substituting for the second term of Equation (1) and the first term of Equation (2), yields:

$$\begin{aligned} \Delta E = & \sum_{\vec{k}, \lambda} \{ [G_{ik}(A; k)G_{jl}(B; k)b_k(\vec{k}, \lambda; \vec{R}_A)b_l(\vec{k}, \lambda; \vec{R}_B) \\ & + \varepsilon_0^{-2}c^{-2}G_{ki}(A; k)G_{ij}(B; k)d_k^\perp(\vec{k}, \lambda; \vec{R}_A)d_l^\perp(\vec{k}, \lambda; \vec{R}_B)] \text{Re}V_{ij}(k, \vec{R}) \\ & + \varepsilon_0^{-1}[G_{ik}(A; k)G_{ij}(B; k)b_k(\vec{k}, \lambda; \vec{R}_A)d_l^\perp(\vec{k}, \lambda; \vec{R}_B) \\ & + G_{ki}(A; k)G_{jl}(B; k)d_k^\perp(\vec{k}, \lambda; \vec{R}_A)b_l(\vec{k}, \lambda; \vec{R}_B)] \text{Im}U_{ij}(k, \vec{R}) \}. \end{aligned} \tag{12}$$

To evaluate the dispersion potential between two electronically excited chiral molecules, with the electromagnetic field in the vacuum state, the expectation value of Equation (12) is taken over the state $|p^A, q^B; 0(\vec{k}, \lambda)\rangle$. The molecular factors yielded excited state mixed electric-magnetic dipole polarisabilities of the form given by Equation (4). From Equation (12), it can be seen that for the radiation field part, four separate field-field spatial correlation functions need to be evaluated over the ground state of the electromagnetic field. These are straightforwardly obtained from the Maxwell field operators (6) and (7), and have earlier been given [39] for an N-photon state of the radiation field, $|N(\vec{k}, \lambda)\rangle$, in the calculation of the modification of the ground state dispersion force between two chiral molecules due to an intense radiation field. For the vacuum electromagnetic field, these correlation functions are:

$$\langle 0(\vec{k}, \lambda) | d_k^\perp(\vec{R}_A) d_l^\perp(\vec{R}_B) | 0(\vec{k}, \lambda) \rangle = \left(\frac{\hbar c k \varepsilon_0}{2V} \right) e_k^{(\lambda)}(\vec{k}) \bar{e}_l^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}, \tag{13}$$

$$\langle 0(\vec{k}, \lambda) | b_k(\vec{R}_A) b_l(\vec{R}_B) | 0(\vec{k}, \lambda) \rangle = \left(\frac{\hbar k}{2\varepsilon_0 c V} \right) b_k^{(\lambda)}(\vec{k}) \bar{b}_l^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}, \tag{14}$$

$$\langle 0(\vec{k}, \lambda) | d_k^\perp(\vec{R}_A) b_l(\vec{R}_B) | 0(\vec{k}, \lambda) \rangle = \left(\frac{\hbar k}{2V} \right) e_k^{(\lambda)}(\vec{k}) \bar{b}_l^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}, \tag{15}$$

$$\langle 0(\vec{k}, \lambda) | b_k(\vec{R}_A) d_l^\perp(\vec{R}_B) | 0(\vec{k}, \lambda) \rangle = \left(\frac{\hbar k}{2V} \right) b_k^{(\lambda)}(\vec{k}) \bar{e}_l^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}. \tag{16}$$

3.1. Contribution from Upward and Downward Transitions

For ease of presentation, contributions from both upward and downward transitions that have identical functional form were distinguished from contributions that solely arise from downward transitions. We considered the former type of term first. Examining the first term of Equation (12), substituting Equation (14) produces

$$\sum_{\vec{k}, \lambda} \left(\frac{\hbar k}{2\varepsilon_0 c V} \right) G_{ik}(A; k)G_{jl}(B; k)b_k^{(\lambda)}(\vec{k})\bar{b}_l^{(\lambda)}(\vec{k})e^{-i\vec{k} \cdot \vec{R}} \text{Re}V_{ij}(k, \vec{R}). \tag{17}$$

It is worth pointing out that the radiation field part is similar to that featured in the evaluation of the Casimir–Polder potential [31], with magnetic rather than electric polarisation vectors appearing in Equation (17). To proceed further, the sum over photon modes must be performed. For the polarization index sum, the following identities may be employed:

$$\sum_{\lambda} e_i^{(\lambda)}(\vec{k})\bar{e}_j^{(\lambda)}(\vec{k}) = \sum_{\lambda} b_i^{(\lambda)}(\vec{k})\bar{b}_j^{(\lambda)}(\vec{k}) = \delta_{ij} - \hat{k}_i\hat{k}_j, \tag{18}$$

while the wave vector sum is converted to an integral via

$$\frac{1}{V} \sum_{\vec{k}} \rightarrow \frac{1}{(2\pi)^3} \int d^3\vec{k}. \tag{19}$$

In spherical polar coordinates, $d^3\vec{k} = k^2 dk d\Omega$, with $d\Omega$ an element of the solid angle. Thus, Equation (17) reads:

$$\frac{\hbar}{16\pi^3\epsilon_0c} \int dk d\Omega k^3 G_{ik}(A;k) G_{jl}(B;k) (\delta_{kl} - \hat{k}_k \hat{k}_l) e^{-i\vec{k}\cdot\vec{R}} \text{Re} V_{ij}(k, \vec{R}). \tag{20}$$

The angular average is carried out using

$$\frac{1}{4\pi} \int d\Omega (\delta_{ij} - \hat{k}_i \hat{k}_j) e^{\pm i\vec{k}\cdot\vec{R}} = (\delta_{ij} - \hat{R}_i \hat{R}_j) \frac{\sin kR}{kR} + (\delta_{ij} - 3\hat{R}_i \hat{R}_j) \left(\frac{\cos kR}{k^2 R^2} - \frac{\sin kR}{k^3 R^3} \right). \tag{21}$$

After substituting $\text{Re} V_{ij}(k, \vec{R})(9)$, Equation (20) reads:

$$\frac{\hbar}{16\pi^3\epsilon_0^2c^3} \int_0^\infty dk k^3 G_{ik}(A;k) G_{jl}(B;k) \left[(\delta_{kl} - \hat{R}_k \hat{R}_l) \frac{\sin kR}{kR} + (\delta_{kl} - 3\hat{R}_k \hat{R}_l) \left(\frac{\cos kR}{k^2 R^2} - \frac{\sin kR}{k^3 R^3} \right) \right] \times [(\delta_{ij} - 3\hat{R}_i \hat{R}_j) (\cos kR + kR \sin kR) - (\delta_{ij} - \hat{R}_i \hat{R}_j) k^2 R^2 \cos kR], \tag{22}$$

which holds for A and B in fixed mutual orientation. The isotropic contribution to the potential may be obtained by applying the result for the random orientational averaging of the tensor Equation (4) [40]

$$\langle G_{ij}(\xi;k) \rangle = \frac{1}{3} \delta_{ij} \delta_{\lambda\mu} G_{\lambda\mu}(\xi;k) = \delta_{ij} G(\xi;k), \tag{23}$$

where $\frac{1}{3} \delta_{\lambda\mu} G_{\lambda\mu}(\xi;k) = G(\xi;k)$ is the isotropic polarisability, and Greek letter subscripts denote the Cartesian tensor components in the body-fixed frame of reference. Contracting the geometric factors in Equation (22) gives:

$$-\frac{\hbar}{16\pi^3\epsilon_0^2cR^2} \int_0^\infty dk k^4 G(A;k) G(B;k) \left\{ \sin 2kR \left(1 - \frac{5}{k^2 R^2} + \frac{3}{k^4 R^4} \right) + \cos 2kR \left(\frac{2}{kR} - \frac{6}{k^3 R^3} \right) \right\} = -\frac{\hbar}{16\pi^3\epsilon_0^2R^2} \int_0^\infty dk k^4 G(A;k) G(B;k) \text{Im} \left[1 + \frac{2i}{kR} - \frac{5}{k^2 R^2} - \frac{6i}{k^3 R^3} + \frac{3}{k^4 R^4} \right] e^{2ikR}. \tag{24}$$

Finally, transforming to the complex variable $k = iu$, taking the integral into the complex plane by rotating the line of integration by $\pi/2$, yields:

$$-\frac{\hbar}{16\pi^3\epsilon_0^2cR^2} \int_0^\infty du u^4 e^{-2uR} G(A;iu) G(B;iu) \left[1 + \frac{2}{uR} + \frac{5}{u^2 R^2} + \frac{6}{u^3 R^3} + \frac{3}{u^4 R^4} \right]. \tag{25}$$

where $G(\xi;iu)$ is the isotropic dynamic mixed electric-magnetic dipole polarisability evaluated at the imaginary frequency, $\omega = icu$. The second term of Equation (12) produces a contribution identical to Equation (25), which therefore doubles up.

Considering the third term of Equation (12), substituting Equation (16) gives:

$$\sum_{\vec{k}, \lambda} \left(\frac{\hbar k}{2\epsilon_0 V} \right) G_{ik}(A;k) G_{lj}(B;k) b_k^{(\lambda)}(\vec{k}) \bar{e}_l^{(\lambda)}(k) e^{-i\vec{k}\cdot\vec{R}} \text{Im} U_{ij}(k, \vec{R}). \tag{26}$$

Use is now made of the polarisation sum,

$$\sum_{\lambda} e_i^{(\lambda)}(\vec{k}) \bar{b}_j^{(\lambda)}(\vec{k}) = \epsilon_{ijk} \hat{k}_k, \tag{27}$$

along with the continuum approximation to the wave vector sum (19). The required angular integration is given by

$$\frac{1}{4\pi} \int \hat{k}_k e^{\pm i\vec{k}\cdot\vec{R}} d\Omega = \mp i \left(\frac{\cos kR}{kR} - \frac{\sin kR}{k^2 R^2} \right) \hat{R}_k, \tag{28}$$

so that Equation (26) becomes, after inserting $\text{Im} U_{ij}(k, \vec{R})$ from Equation (10):

$$-\frac{i\hbar}{16\pi^3\epsilon_0^2cR^3}\epsilon_{ijm}\epsilon_{klm}\hat{R}_m\hat{R}_n\int_0^\infty dk k^3 G_{ik}(A;k)G_{lj}(B;k)\left[\frac{\cos kR}{kR}-\frac{\sin kR}{k^2R^2}\right][kR\cos kR+k^2R^2\sin kR]. \tag{29}$$

Performing a tumbling average using Equation (23) and contracting tensors, Equation (29) becomes:

$$\begin{aligned} &-\frac{i\hbar}{16\pi^3\epsilon_0^2cR^2}\int_0^\infty dk k^4 G(A;k)G(B;k)\left\{\sin 2kR+\frac{2}{kR}\cos 2kR-\frac{1}{k^2R^2}\sin 2kR\right\} \\ &= -\frac{i\hbar}{16\pi^3\epsilon_0^2cR^2}\int_0^\infty dk k^4 G(A;k)G(B;k)\text{Im}\left[1+\frac{2i}{kR}-\frac{1}{k^2R^2}\right]e^{2ikR}. \end{aligned} \tag{30}$$

Substituting the complex variable $k = iu$ and rotating the line of integration as above yields:

$$\frac{\hbar}{16\pi^3\epsilon_0^2cR^2}\int_0^\infty du u^4 e^{-2uR}G(A;iu)G(B;iu)\left[1+\frac{2}{uR}+\frac{1}{u^2R^2}\right]. \tag{31}$$

Recognising that the fourth term of Equation (12) produces an identical contribution to Equation (31), the u -integral contribution to the excited state dispersion potential between two chiral (c) molecules is given by twice the sum of Equations (25) and (31),

$$\Delta E_{c-c}^u = -\frac{\hbar}{8\pi^3\epsilon_0^2cR^2}\int_0^\infty du u^4 e^{-2uR}G(A;iu)G(B;iu)\left[\frac{4}{u^2R^2}+\frac{6}{u^3R^3}+\frac{3}{u^4R^4}\right], \tag{32}$$

which is applicable to both upward and downward transitions in A and B since there are no limitations on the intermediate state sums over levels $|n\rangle$ and $|r\rangle$ in the excited state polarisabilities, $G(\zeta;iu)$, $\zeta = A, B$.

3.2. Additional Contribution from Downward Transitions

Let us now examine the terms contributing to the energy shift due to the emission of a real photon from the excited electronic states of A and B . These are in addition to the upward transitions captured in the u -integral term (32). The total contribution arising from de-excitation in each molecule can be written as

$$\Delta E^{RES} = \Delta E^{A-RES} + \Delta E^{B-RES}. \tag{33}$$

The starting expressions for each of the two terms are easily obtained from Equation (12). For species A , one has:

$$\begin{aligned} \Delta E^{A-RES} &= \sum_{\vec{k},\lambda} \{[G_{ik}(A;k)G_{jl}(B;k)b_k(\vec{R}_A)b_l(\vec{R}_B) \\ &+ \epsilon_0^{-2}c^{-2}G_{ki}(A;k)G_{lj}(B;k)d_k^\perp(\vec{R}_A)d_l^\perp(\vec{R}_B)]V_{ij}^{RES}(k_{pn},\vec{R}) \\ &+ \epsilon_0^{-1}[G_{ik}(A;k)G_{lj}(B;k)b_k(\vec{R}_A)d_l^\perp(\vec{R}_B) \\ &+ G_{ki}(A;k)G_{jl}(B;k)d_k^\perp(\vec{R}_A)b_l(\vec{R}_B)]U_{ij}^{RES}(k_{pn},\vec{R})\}, \end{aligned} \tag{34}$$

where $V_{ij}^{RES}(k_{pn},\vec{R})$ and $U_{ij}^{RES}(k_{pn},\vec{R})$ are the resonant contributions of the coupling tensors (9) and (10), respectively, evaluated at the wave vector of the downward transition occurring in A , $k_{pn} = \omega_{pn}/c$. An expression similar to Equation (34) may be written for ΔE^{B-RES} with $V_{ij}^{RES}(k_{qr},\vec{R})$ and $U_{ij}^{RES}(k_{qr},\vec{R})$ appearing instead, reflecting de-excitation in B at the resonant frequency $\omega_{qr} = ck_{qr}$ for the transition $|r\rangle \leftarrow |q\rangle$. Similar to the evaluation of the u -integral term, an expectation value was taken over Equation (33) with the state $|p^A, q^B; 0(\vec{k}, \lambda)\rangle$. Use was made of the vacuum field-field spatial correlation functions (13)–(16) for the radiation field part. For species A and B , excited state molecular

polarisabilities $G_{ij}(\xi; k)$ featured. Examining the first term of Equation (34), and following similar steps that led to Equation (20), yields:

$$\frac{1}{8\pi^3\epsilon_0c^2} \sum_n \int dk d\Omega k^4 \frac{\mu_i^{pn}(A)m_k^{np}(A)}{k_{np}^2 - k^2} G_{jl}(B; k)(\delta_{kl} - \hat{k}_k\hat{k}_l) e^{-i\vec{k}\cdot\vec{R}} V_{ij}^{RES}(k_{pn}, \vec{R}), \tag{35}$$

after substituting $G_{ik}(A; k)$ (4). Instead of Equation (21), it is convenient to use the following form for the integration over the solid angle $d\Omega$:

$$\frac{1}{4\pi} \int d\Omega (\delta_{ij} - \hat{k}_i\hat{k}_j) e^{\pm i\vec{k}\cdot\vec{R}} = \frac{1}{2ik^3} (-\nabla^2\delta_{ij} + \nabla_i\nabla_j) \frac{1}{R} (e^{ikR} - e^{-ikR}). \tag{36}$$

Equation (35) then becomes, after carrying out the integral over k ,

$$\begin{aligned} & \frac{1}{4\pi\epsilon_0c^2} \sum_{\substack{n \\ E_p > E_n}} \mu_i^{pn}(A)m_k^{np}(A) G_{jl}(B; k_{pn}) (-\nabla^2\delta_{kl} + \nabla_k\nabla_l) \frac{e^{-ik_{pn}R}}{R} V_{ij}^{RES}(k_{pn}, \vec{R}) \\ &= -\frac{1}{16\pi^2\epsilon_0^2c^2} \sum_{\substack{n \\ E_p > E_n}} \mu_i^{pn}(A)m_k^{np}(A) G_{jl}(B; k_{pn}) [(-\nabla^2\delta_{ij} + \nabla_i\nabla_j) \frac{e^{ik_{pn}R}}{R}] [(-\nabla^2\delta_{kl} + \nabla_k\nabla_l) \frac{e^{-ik_{pn}R}}{R}], \end{aligned} \tag{37}$$

where in the last line, $V_{ij}^{RES}(k_{pn}, \vec{R})$ (9) is inserted. Interestingly, B responds through its polarisability, $G_{jl}(B; k_{pn})$, to the excitation energy of the downward transition in A at the frequency $\omega_{pn} = ck_{pn}$. The energy shift term (37) applies for A and B in fixed relative orientation and the sum is restricted to states for which $E_{pn} > 0$. Performing an orientational average, absorbing the constant 1/3 into each molecular factor, and contracting, produces

$$-\frac{1}{8\pi^2\epsilon_0^2c^2R^6} \sum_{\substack{n \\ E_p > E_n}} [\vec{\mu}^{pn}(A) \cdot \vec{m}^{np}(A)] G(B; k_{pn}) [3 + k_{pn}^2R^2 + k_{pn}^4R^4]. \tag{38}$$

Let us now evaluate the fourth term of Equation (34), this time with the help of Equation (15), which yields

$$\frac{1}{8\pi^3\epsilon_0c} \epsilon_{klm} \sum_n \int dk d\Omega k^4 \frac{\mu_k^{pn}(A)m_i^{np}(A)}{k_{np}^2 - k^2} G_{jl}(B; k) \hat{k}_m e^{-i\vec{k}\cdot\vec{R}} U_{ij}^{RES}(k_{pn}, \vec{R}). \tag{39}$$

Employing an alternative form for the angular average (28),

$$\frac{1}{4\pi} \int d\Omega \hat{k}_k e^{\pm i\vec{k}\cdot\vec{R}} = \mp \frac{1}{2k^2} \nabla_k \frac{1}{R} (e^{ikR} - e^{-ikR}), \tag{40}$$

and performing the k -integration, Equation (39) becomes:

$$\begin{aligned} & -\frac{i}{4\pi\epsilon_0c} \sum_{\substack{n \\ E_p > E_n}} \mu_k^{pn}(A)m_i^{np}(A) G_{jl}(B; k_{pn}) k_{pn} \epsilon_{klm} \nabla_m \frac{e^{-ik_{pn}R}}{R} U_{ij}^{RES}(k_{pn}, \vec{R}) \\ &= -\frac{1}{(4\pi\epsilon_0c)^2} \sum_{\substack{n \\ E_p > E_n}} \mu_k^{pn}(A)m_i^{np}(A) G_{jl}(B; k_{pn}) k_{pn}^2 \epsilon_{ijn} \epsilon_{klm} \nabla_m \frac{e^{-ik_{pn}R}}{R} \nabla_n \frac{e^{ik_{pn}R}}{R}, \end{aligned} \tag{41}$$

where in the last line $U_{ij}^{RES}(k_{pn}, \vec{R})$ is substituted. After random averaging, accounting for the factor $(1/3)^2$ that arises, Equation (41) becomes:

$$-\frac{1}{8\pi^2\epsilon_0^2c^2R^6} \sum_{\substack{n \\ E_p > E_n}} [\vec{\mu}^{pn}(A) \cdot \vec{m}^{np}(A)] G(B; k_{pn}) [k_{pn}^2R^2 + k_{pn}^4R^4]. \tag{42}$$

Noting that the second and third terms of Equation (34) produce contributions identical to Equations (38) and (42), respectively, adding these two terms and doubling, results in the additional contribution arising from downward transitions having the form,

$$\Delta E_{c-c}^{A-RES} = -\frac{1}{4\pi^2 \epsilon_0^2 c^2 R^6} \sum_{E_p > E_n} [\vec{\mu}^{pn}(A) \cdot \vec{m}^{np}(A)] G(B; k_{pn}) [3 + 2k_{pn}^2 R^2 + 2k_{pn}^4 R^4]. \quad (43)$$

From Equation (43), the additional contribution arising from downward transitions in excited B, the second term of Equation (33), can be written down immediately as

$$\Delta E_{c-c}^{B-RES} = -\frac{1}{4\pi^2 \epsilon_0^2 c^2 R^6} \sum_{E_q > E_r} G(A; k_{qr}) [\vec{\mu}^{qr}(B) \cdot \vec{m}^{rq}(B)] [3 + 2k_{qr}^2 R^2 + 2k_{qr}^4 R^4], \quad (44)$$

where now species A responds via its excited state polarisability, $G(A; k_{qr})$, to the decay occurring due to the emission in B at the frequency $\omega_{qr} = ck_{qr}$. Just like the u -integral (32), the two terms of ΔE^{RES} are discriminatory, dependent upon the chirality of A and B, changing sign when a mirror-image counterpart replaces one enantiomer. The two contributions (43) and (44), are added to Equation (32) to give the total dispersion potential between two excited chiral molecules, namely,

$$\Delta E_{c-c} = \Delta E_{c-c}^u + \Delta E_{c-c}^{A-RES} + \Delta E_{c-c}^{B-RES}. \quad (45)$$

The result of Equation (45) agrees with an earlier evaluation using response theory [36].

4. Dispersion Energy Shift between an Electric Dipole Polarisable Molecule and a Paramagnetically Susceptible One

For the leading order, chirality in a molecule is characterised by the presence of electric and magnetic dipole moments. A contribution to the dispersion potential of an identical order of magnitude to that between two chiral molecules considered in the previous section is that between an electric dipole polarisable molecule and a magnetic dipole susceptible one. Both of these interaction energies contain a total of two electric and two magnetic dipole moments across the two sites. On letting A be an excited electrically polarisable species and B an excited paramagnetically susceptible entity, the relevant induced dipoles from Equations (1) and (2) to be used in the method deployed arise from the first term of Equation (1) and the second term of Equation (2), which couple to the interaction tensor (10), producing an energy shift:

$$\begin{aligned} \Delta E &= \sum_{\vec{k}, \lambda} \mu_i^{ind}(A; \vec{k}, \lambda) m_j^{ind}(B; \vec{k}, \lambda) \text{Im} U_{ij}(k, \vec{R}) \\ &= \sum_{\vec{k}, \lambda} \epsilon_0^{-1} \alpha_{ik}(A; k) \chi_{jl}(B; k) d_k^\perp(\vec{k}, \lambda; \vec{R}_A) b_l(\vec{k}, \lambda; \vec{R}_B) \text{Im} U_{ij}(k, \vec{R}). \end{aligned} \quad (46)$$

Taking the expectation value of Equation (46) over the state $|p^A, q^B; 0(\vec{k}, \lambda)\rangle$, and making use of the field-field correlation function (15), one obtains:

$$\Delta E = \sum_{\vec{k}, \lambda} \left(\frac{\hbar k}{2\epsilon_0 V} \right) \alpha_{ik}(A; k) \chi_{jl}(B; k) e_k^{(\lambda)}(\vec{k}) \bar{b}_l^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}} \text{Im} U_{ij}(k, \vec{R}). \quad (47)$$

Performing the polarisation sum using Equation (27), converting the \vec{k} -sum to an integral using Equation (19), and carrying out the angular integral using Equation (28), one arrives at

$$\begin{aligned} \Delta E &= \frac{i\hbar}{4\pi^2\epsilon_0} \epsilon_{klm} \hat{R}_m \int_0^\infty dk k^3 \alpha_{ik}(A;k) \chi_{jl}(B;k) \left[\frac{\cos kR}{kR} - \frac{\sin kR}{k^2 R^2} \right] \text{Im} U_{ij}(k, \vec{R}) \\ &= \frac{i\hbar}{16\pi^3 \epsilon_0^2 c R^3} \epsilon_{ijn} \epsilon_{klm} \hat{R}_m \hat{R}_n \int_0^\infty dk k^3 \alpha_{ik}(A;k) \chi_{jl}(B;k) \left[\frac{\cos kR}{kR} - \frac{\sin kR}{k^2 R^2} \right] [kR \cos kR + k^2 R^2 \sin kR], \end{aligned} \tag{48}$$

by inserting Equation (10) for $\text{Im} U_{ij}(k, \vec{R})$. This result holds for a pair of anisotropic molecules. To obtain the isotropic potential, we make use of the orientational averages for the second rank tensors,

$$\langle X_{ij}(\vec{\xi}; k) \rangle = \frac{1}{3} \delta_{ij} \delta_{\lambda\mu} X_{\lambda\mu}(\vec{\xi}; k) = \delta_{ij} X(\vec{\xi}; k), \tag{49}$$

for $X(\vec{\xi}; k) = \alpha(\vec{\xi}; k)$ or $\chi(\vec{\xi}; k)$. Contracting the tensors and simplification using trigonometric identities relating single and double angle arguments yields:

$$\begin{aligned} \Delta E &= \frac{i\hbar}{16\pi^3 \epsilon_0^2 R^2} \int_0^\infty dk k^4 \alpha(A;k) \chi(B;k) \left\{ \sin 2kR + \frac{2}{kR} \cos 2kR - \frac{1}{k^2 R^2} \sin 2kR \right\} \\ &= \frac{i\hbar}{16\pi^3 \epsilon_0^2 c R^2} \int_0^\infty dk k^4 \alpha(A;k) \chi(B;k) \text{Im} \left[1 + \frac{2i}{kR} - \frac{1}{k^2 R^2} \right] e^{2ikR} \end{aligned} \tag{50}$$

Rotating the integral from the real to the imaginary axis and substituting the complex variable $k = iu$, Equation (50) results in the u -integral contribution to the dispersion potential between an excited electric dipole polarisable molecule and an excited magnetic dipole susceptible molecule being given by

$$\Delta E_{e-m}^u = \frac{\hbar}{16\pi^3 \epsilon_0^2 c R^2} \int_0^\infty du u^4 e^{-2uR} \alpha(A;iu) \chi(B;iu) \left[1 + \frac{2}{uR} + \frac{1}{u^2 R^2} \right], \tag{51}$$

where $\alpha(A;iu)$ and $\chi(B;iu)$ are the excited state polarisabilities evaluated at the imaginary frequency $\omega = icu$ and is straightforwardly obtained from expressions (3) and (5), respectively. The result (51) is identical in form to the expression obtained previously for the ground state interaction energy using perturbation and response theories [34,41,42], and is likewise repulsive.

The resonant terms are evaluated from

$$\begin{aligned} \Delta E_{e-m}^{RES} &= \Delta E_{e-m}^{A-RES} + \Delta E_{e-m}^{B-RES} \\ &= \sum_{\vec{k}, \lambda} \epsilon_0^{-1} \alpha_{ik}(A;k) \chi_{jl}(B;k) d_k^\perp(\vec{k}, \lambda; \vec{R}_A) b_l(\vec{k}, \lambda; \vec{R}_B) [U_{ij}^{RES}(k_{pn}, \vec{R}) + U_{ij}^{RES}(k_{qr}, \vec{R})]. \end{aligned} \tag{52}$$

The evaluation of Equation (52) in a manner similar to the chiral–chiral example, using Equation (40) for the angular average, leads to the isotropic contributions,

$$\begin{aligned} \Delta E_{e-m}^{RES} &= -\frac{1}{8\pi^2 \epsilon_0^2 c^2 R^6} \sum_{E_p > E_n} |\vec{\mu}^{pn}(A)|^2 \chi(B; k_{pn}) [k_{pn}^2 R^2 + k_{pn}^4 R^4] \\ &\quad - \frac{1}{8\pi^2 \epsilon_0^2 c^2 R^6} \sum_{E_q > E_r} |\vec{m}^{qr}(B)|^2 \alpha(A; k_{qr}) [k_{qr}^2 R^2 + k_{qr}^4 R^4], \end{aligned} \tag{53}$$

neither of which, like the u -integral, are discriminatory. The two terms in Equation (53) apply only to downward transitions from the excited state. Each susceptibility responds to the emission frequency of the other particle, with the energy shift exhibiting inverse square dependent far-zone behaviour. The total excited state dispersion potential between electric and magnetic dipole polarisable systems is given by the sum of Equations (51) and (53),

$$\Delta E_{e-m} = \Delta E_{e-m}^u + \Delta E_{e-m}^{RES}, \tag{54}$$

agreeing with an earlier study [36].

5. Contribution from Diamagnetic Coupling

In Section 4, the paramagnetic contribution to the excited state dispersion interaction between an electric dipole polarisable molecule and a magnetic dipole susceptible molecule was studied. No account, however, was taken of the diamagnetic coupling term, which produces a contribution of identical order of magnitude to both the potentials evaluated thus far. This contribution is now considered. As previously stated, particle A is let to be an excited electric dipole polarisable species. However, here, B is selected to be an excited diamagnetic molecule. In the multipolar coupling scheme of non-relativistic QED [12–15,43,44], the diamagnetic coupling term of particle ξ is

$$H^d(\xi) = \frac{e^2}{8m} \sum_a \{(\vec{q}_a(\xi) - \vec{R}_\xi) \times \vec{b}(\vec{R}_\xi)\}^2, \tag{55}$$

where $\vec{q}_a(\xi)$ is the position of electron a relative to the centre of molecule ξ , \vec{R}_ξ . For an isotropic diamagnetic source located at the origin, Equation (55) reduces to $\frac{e^2}{12m} \sum_a q_a^2(\xi) \vec{b}^2(0)$. Therefore, in the presence of a magnetic field, the induced electronic coordinate of molecule B is given by

$$q_j^{ind}(B) = \chi_{jl}^d(B;0)b_l(0), \tag{56}$$

where the isotropic frequency independent excited state diamagnetic susceptibility is defined as

$$\chi^d(\xi;0) = -\frac{e^2}{12m} \sum_a \langle q_a^2(\xi) \rangle^{qq}, \tag{57}$$

where the excited state matrix element of $q_a^2(\xi)$ over the state $|q\rangle$ is $\langle q | \langle q_a^2(\xi) | \langle q \rangle = \langle q_a^2(\xi) \rangle^{qq}$. The induced electric dipole moment arising from the first term of Equation (1) and Equation (56) couple, yielding an energy shift,

$$\begin{aligned} \Delta E &= \sum_{\vec{k}, \lambda} \mu_i^{ind}(A; \vec{k}, \lambda) q_j^{ind}(B) \text{Im} U_{ij}(\vec{k}, \vec{R}) \\ &= \sum_{\vec{k}, \lambda} \epsilon_0^{-1} \alpha_{ik}(A; k) \chi_{jl}^d(B;0) d_k^\perp(\vec{k}, \lambda; \vec{R}_A) b_l(\vec{k}, \lambda; \vec{R}_B) \text{Im} U_{ij}(\vec{k}, \vec{R}). \end{aligned} \tag{58}$$

Next, the expectation value of Equation (58) was taken over the state $|p^A, q^B; 0(\vec{k}, \lambda)\rangle$, giving the p -th and q -th excited state electric dipole polarisability and diamagnetic susceptibility, respectively, and the electric-magnetic field-field spatial correlation function (15):

$$\Delta E = \sum_{\vec{k}, \lambda} \left(\frac{\hbar k}{2\epsilon_0 V} \right) \alpha_{ik}(A; k) \chi_{jl}^d(B;0) e_k^{(\lambda)}(\vec{k}) \bar{b}_l^{(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}} \text{Im} U_{ij}(\vec{k}, \vec{R}), \tag{59}$$

after omitting the molecular state labels. The remainder of the calculation follows that given in Section 4 when evaluating the paramagnetic contribution to the dispersion energy. For A and B in fixed relative orientation,

$$\Delta E = \frac{i\hbar}{16\pi^3 \epsilon_0^2 c R^3} \epsilon_{ijn} \epsilon_{klm} \hat{R}_m \hat{R}_n \int_0^\infty dk k^3 \alpha_{ik}(A; k) \chi_{jl}^d(B;0) \left[\frac{\cos kR}{kR} - \frac{\sin kR}{k^2 R^2} \right] [kR \cos kR + k^2 R^2 \sin kR]. \tag{60}$$

Utilising the result for the rotationally averaged diamagnetic susceptibility, $\langle \chi_{jl}^d(B;0) \rangle = \delta_{jl} \chi^d(B;0)$, the isotropic diamagnetic contribution to the dispersion potential is

$$\Delta E_{e-d}^u = \frac{\hbar}{16\pi^3 \epsilon_0^2 c R^2} \int_0^\infty du u^4 e^{-2uR} \alpha(A; iu) \chi^d(B;0) \left[1 + \frac{2}{uR} + \frac{1}{u^2 R^2} \right], \tag{61}$$

when expressed in terms of the complex variable $k = iu$.

Combining the diamagnetic u -integral term (61) with the corresponding paramagnetic term (51), gives:

$$\Delta E_{p+d}^u = \frac{\hbar}{16\pi^3 \epsilon_0^2 c R^2} \int_0^\infty du u^4 e^{-2uR} \alpha(A; iu) \chi^m(B; iu) \left[1 + \frac{2}{uR} + \frac{1}{u^2 R^2} \right], \quad (62)$$

where the magnetic susceptibility tensor, χ^m , is a sum of paramagnetic (p) and diamagnetic (d) components, recalling that the latter is frequency independent,

$$\chi^m(B; iu) = \chi^p(B; iu) + \chi^d(B; 0), \quad (63)$$

with the isotropic paramagnetic susceptibility given by

$$\chi^p(B; iu) = \frac{2}{3} \sum_r \frac{|\vec{m}^{qr}(B)|^2 E_{rq}}{E_{rq}^2 + (\hbar c u)^2}, \quad (64)$$

and with the diamagnetic susceptibility $\chi^d(B; 0)$ given by (57). A functional form similar to Equation (62) was obtained using perturbation and response theories for the ground state dispersion potential [13,34,41,45].

For the additional contributions to the u -integral term arising solely from de-excitation, diamagnetic B does not respond to the downward transitions in A, $|n\rangle \leftarrow |p\rangle$, so that from the first term of Equation (53),

$$\Delta E_{e-d}^{A-RES} = -\frac{1}{8\pi^2 \epsilon_0^2 c^2 R^6} \sum_{\substack{n \\ E_p > E_n}} |\vec{\mu}^{pn}(A)|^2 \chi^d(B; 0) [k_{pn}^2 R^2 + k_{pn}^4 R^4]. \quad (65)$$

Particle A, on the other hand, responds to the downward transitions occurring in B, $|r\rangle \leftarrow |q\rangle$, modifying the second term of Equation (53) to give for diamagnetic B the contribution,

$$\Delta E_{e-d}^{B-RES} = -\frac{e^2}{48\pi^2 \epsilon_0^2 c^2 m R^6} \sum_{\substack{r \\ E_q > E_r}} \langle |q^{qr}(B)|^2 \rangle \alpha(A; k_{qr}) [k_{qr}^2 R^2 + k_{qr}^4 R^4], \quad (66)$$

with

$$\Delta E_{e-d}^{RES} = \Delta E_{e-d}^{A-RES} + \Delta E_{e-d}^{B-RES}, \quad (67)$$

a sum of Equations (65) and (66). Hence, the total dispersion potential between an excited electric dipole polarisable molecule and an excited diamagnetic one is given by

$$\Delta E_{e-d} = \Delta E_{e-d}^u + \Delta E_{e-d}^{RES} \quad (68)$$

with ΔE_{e-d}^u given by Equation (61).

6. Summary

Within a quantum field framework, retarded van der Waals dispersion potentials between atoms or molecules in the ground state are commonly evaluated using diagrammatic time-dependent perturbation theory. This method, however, gives rise to computational difficulties when one or both of the pair are electronically excited, since resonant terms have to be accounted for. An alternative treatment of this problem involved employing response theory, in which each particle responds, through its electric or magnetic susceptibility, to the source Maxwell fields of the other entity. However, this method requires first calculating the second quantised electric and magnetic radiation fields in the vicinity of a source multipole moment before the energy shift can be evaluated, with the additional burden that fields second order in the moments are needed at the very least [27,34,46].

To overcome some of these problems, in this paper, the excited state dispersion potential between optically active molecules is examined from a different physical point of view, one that was previously considered for the calculation of the Casimir–Polder potential. Fluctuations in the vacuum electromagnetic field induce multipole moments in atoms or molecules, which in turn couple through pertinent retarded interaction tensors. Expectation values are taken over excited matter states and the ground state of the radiation field. The latter yielded known expressions for the field–field spatial correlation functions and serve to highlight the prominent role played by the electromagnetic vacuum when calculating dispersion forces.

For two excited chiral molecules characterised by electric and magnetic dipole moments, all three terms contributing to the dispersion interaction energy—the familiar u -integral term involving excited state mixed electric-magnetic dipole polarisabilities of each particle, and two extra contributions arising from downward only transitions in each species—are found to be discriminatory, depending on the handedness of molecules A and B. Two other dispersion potentials involving magnetic interactions that were of a similar order of magnitude to the chiral–chiral energy shift are also computed. These included the potential between an electric dipole polarisable molecule and a second that is either paramagnetically or diamagnetically susceptible. Neither energy shift contribution changes sign on interchanging enantiomers, with the second coupling term being independent of frequency, but which may be combined with the paramagnetic part to produce an overall magnetically susceptible contribution, as found earlier for the ground state [34,38,42].

Interest in dispersion energies between chiral molecules lies in their discriminatory behaviour as well as in outlining the role played by magnetic and diamagnetic coupling. It complements other research areas that involve optically active species such as chiral light–matter interactions, analytical based methods for achieving enantiomer excess and separation, and the synthesis of chiral compounds and drugs in organic chemistry and the pharmaceutical industry [35–38].

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