On the manifestation of Casimir effects in intermolecular interactions via the method of induced moments

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Abstract. A versatile, alternative method for calculating long-range interactions between atomic and molecular systems within the framework of non-relativistic quantum electrodynamics is the induced multipole moment approach. In the present contribution it is employed to compute the dispersion energy shift between a pair of neutral polarizable molecules in either ground or excited electronic states, and the change in mutual interaction energy caused by the action of an intense external radiation field. In this method the moments induced at each centre are coupled to each other via the resonant electric dipole-electric dipole interaction tensor, giving rise to an energy shift. On evaluating the expectation values for states corresponding to (i) both molecules in the ground state and the field in the vacuum state, (ii) both species excited and the field containing no photons, and (iii) both molecules in the ground state with the field containing $N$ photons, respectively result in energy shifts for each of the three processes described above. For the modification of the dispersion interaction by laser light, two distinct mechanisms are identified. One, the dynamic contribution, is proportional to the polarizability of each molecule, and a second, the static term, involves the product of the static moment at one centre and the molecular first hyperpolarizability of the other entity. In both cases the energy shift has a linear dependence on radiation field intensity. After molecular averaging, the static contribution is found to vanish.

1. Background

Sixty years ago Casimir and Polder [1] performed their seminal calculation of the van der Waals dispersion interaction between two neutral polarizable molecules in the ground electronic state. A novel aspect of their approach was the application of the techniques of quantum field theory to the problem at hand. A characteristic feature of this fundamental methodology when applied to the interactions occurring between charged particles, which are known to be electromagnetic in origin, is that the radiation field, in addition to matter, is subject to the rules of quantum mechanics – the formulation being more commonly known as quantum electrodynamics (QED) [2]. A particular consequence of a second quantized description is that the electron emerges from quantization of the matter field, and the photon from quantization of the electromagnetic field.
More specifically, Casimir and Polder employed the minimal-coupling Hamiltonian [3] for the non-relativistic interaction of charged particles with electromagnetic radiation together with time-dependent perturbation theory to evaluate the dispersion energy shift. In this coupling scheme the total Hamiltonian operator for the system of interest comprises a sum of molecular Hamiltonians for the two particles A and B, the radiation field Hamiltonian, and the interaction Hamiltonian coupling the molecules to the electromagnetic field. This last component is given explicitly in minimal-coupling by

\[ H_{\text{int}}^\text{min} = -\sum_\xi \sum_\alpha \frac{e_\alpha}{m_\alpha} \hat{p}_\alpha(\xi) \cdot \hat{a}(\hat{q}_\alpha(\xi)) + \sum_\xi \sum_\alpha \frac{e_\alpha^2}{2m_\alpha} \hat{a}^2(\hat{q}_\alpha(\xi)) + V_{\text{inter}}, \tag{1.1} \]

where \( e_\alpha \) is the charge of particle \( \alpha \), of mass \( m_\alpha \), whose position vector is \( \hat{q}_\alpha(\xi) \) and linear momentum vector is \( \hat{p}_\alpha(\xi) \), belonging to molecule \( \xi = A, B \), with \( \hat{a}(\hat{r}) \) the vector potential at field point \( \hat{r} \) in the Coulomb gauge. The final term appearing in Eq. (1.1) is the intermolecular potential energy between molecules \( \xi \) and \( \xi' \), \( V_{\text{inter}} = \sum_\xi V(\xi,\xi') \). The intra-molecular part, \( \sum_\xi V(\xi) \), of the total electrostatic potential energy, \( V \), is included in the molecular Hamiltonian [3]. This partitioning of the potential energy is facilitated by the choice of gauge, namely the one in which the divergence of the vector potential vanishes, allowing the Coulombic and solenoidal fields to be completely separated. In the leading electric dipole approximation, which is employed throughout this work, the third term of Eq. (1.1) is given by the static dipolar Coulomb interaction

\[ V_{\text{inter}} = \frac{1}{4\pi\varepsilon_0 R^3} \mu_i(A)\mu_j(B)(\delta_{ij} - 3\hat{R}_i\hat{R}_j), \tag{1.2} \]

where \( \mu_i(\xi) \) is the \( i \)-th Cartesian component of the electric dipole moment operator of species \( \xi \), with Einstein summation convention being adopted for repeated suffixes, and \( \hat{R} \) is the unit separation distance vector between bodies \( A \) and \( B \), \( \hat{R} = \hat{R}_B - \hat{R}_A \). A consequence of the long-wavelength approximation is that there are no spatial variations of the vector potential over the extent of the molecules, so that it is convenient to replace \( \hat{a}(\hat{q}(\xi)) \) by \( \hat{a}(\hat{R}_A) \). In a technically involved computation in which all terms correct to the fourth power of electronic charge were retained, and which necessitated contributions of second, third and fourth order in perturbation theory, the energy shift was calculated by Casimir and Polder for the state in which both molecules were in the ground electronic level, \( |0^\xi\rangle \), \( \xi = A, B \), with no radiation field present [1,4]. The resulting dispersion potential, which now bears their name, has the functional form

\[ \Delta E = \frac{\hbar c}{16\pi\varepsilon_0^2} \int_0^\infty du e^{-2uR^3} \alpha(A;icu)\alpha(B;icu) \left[ \frac{1}{u^2R^2} + \frac{2}{u^3R^3} + \frac{5}{u^4R^4} + \frac{6}{u^5R^5} + \frac{3}{u^6R^6} \right] \tag{1.3} \]

and which holds for all \( R \) beyond overlap of molecular charge distributions for isotropic \( A \) and \( B \) as indicated by the presence of the rotationally averaged electric dipole polarizability of species \( \xi \) at imaginary frequency \( \omega = icu \),

\[ \alpha(\xi;icu) = \frac{2}{3} \sum_\xi \frac{\mu_0^2(\xi)}{E_{icu}} \frac{E_{icu}}{E_{icu} + (icu)^3}. \tag{1.4} \]
It is interesting that when $R$ is much less than reduced characteristic molecular transition wavelengths, the energy shift Eq. (1.3) may be approximated in the near-zone to

$$\Delta E^{\text{NZ}} = -\frac{1}{24\pi^2\varepsilon_0^2 R^6} \sum_{r,s} \frac{|\mu^0(r)\mu^0(s)|^2}{E_{r0}E_{s0}}, \quad (1.5)$$

which is instantly recognizable as the London dispersion energy formula [5], having $R^6$ dependence. This is the result predicted by semi-classical theory in which the dipolar coupling potential Eq. (1.2) is evaluated in second order of perturbation theory. In this description, light signals are taken to propagate instantaneously between the pair – which is clearly unphysical. Of much greater significance is the asymptotic behaviour of Eq. (1.3) at large intermolecular separation distances. In the far-zone the potential has the limiting form

$$\Delta E^{\text{FZ}} = -\frac{23hc}{64\pi^2\varepsilon_0^2 R^7} \alpha(A;0)\alpha(B;0), \quad (1.6)$$

exhibiting an inverse seventh power distance dependence, and which is proportional to the product of static ($\omega \to 0$) polarizabilities of each molecule. The weakening of the potential in the wave-zone relative to the near-zone limit was attributed to the effect of retardation. Electromagnetic signals due to dipolar fluctuations in the charge distribution at one centre propagate at the correct speed of $c$ in the QED treatment, and arrive at the second site after a time delay $t-R/c$, by which further time the dipole moment in the first species will have reoriented itself compared with its configuration at some initial time. This is one key aspect of phenomena said to exhibit “Casimir effects”. Another, more widely known feature beautifully illustrated by the calculation of the dispersion force, and also a consequence of quantization of the radiation field, is the interpretation of the dispersion interaction as due to fluctuations of the vacuum electromagnetic field. This is the state of the radiation field in which there is an absence of photons. Yet the energy of the field in such a situation is non-zero, there being a zero-point energy of $\frac{1}{2}\hbar\omega$ associated with each mode of the radiation field of circular frequency $\omega$.

While the sum over zero-point energies of all modes is infinite in any finite volume, differences in the zero-point energy of the electromagnetic vacuum with and without the presence of a polarizable body lead to finite results and observable phenomena. Hence the concept of quantum vacuum fluctuations [6] has been a powerful one in atomic, molecular and optical physics, having been used to explain spontaneous emission from systems in excited electronic states and the Lamb shift, in addition to dispersion forces.

In an effort to bypass many of the complications associated with the use of the interaction Hamiltonian in minimal-coupling framework Eq. (1.1) in the calculation of Eq. (1.3), alternative physical viewpoints and simpler computational techniques have been put forward instead. Even though many of the new methods led to the Casimir-Polder potential being derived more easily, the most successful among them retained the key ingredients that give rise to Casimir effects, namely zero-point energy of the field and electromagnetic influences travelling at the speed of light. Chief among these alternatives is the multipolar Hamiltonian [7,8] of molecular QED, whose interaction Hamiltonian is expressed in the electric dipole approximation as

$$H_{\text{int}}^{\text{mult}} = -\varepsilon_0^{-1} \hat{\mu}(A) \cdot \hat{d}^+(\hat{R}_A) - \varepsilon_0^{-1} \hat{\mu}(B) \cdot \hat{d}^+(\hat{R}_B). \quad (1.7)$$

In this framework molecules couple directly to the radiation field as exemplified by the interaction of the electric dipole moment with the transverse electric displacement vector field operator $\hat{d}^+(\vec{r})$ in Eq. (1.7). The latter is typically expanded as a sum over radiation field modes $(\vec{k},\lambda)$ in terms of
annihilation and creation operators $a^{(\lambda)}(\vec{k})$ and $a^{\dagger(\lambda)}(\vec{k})$ that decrease and increase by one the number of photons with direction of propagation vector $\vec{k}$ and index of polarization $\lambda$, respectively, according to

$$d^{\perp}(\vec{r}) = i \sum_{k,\lambda} \left( \frac{\hbar c \epsilon_0}{2V} \right)^{1/2} \left[ \tilde{\epsilon}^{(\lambda)}(\vec{k}) a^{(\lambda)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} - \tilde{\epsilon}^{*(\lambda)}(\vec{k}) a^{\dagger(\lambda)}(\vec{k}) e^{-i\vec{k} \cdot \vec{r}} \right],$$  \hspace{1cm} (1.8)

where $\tilde{\epsilon}^{(\lambda)}(\vec{k})$ is the unit electric polarization vector, and $V$ is the quantization volume. Employing Eq. (1.7) greatly simplifies the calculation of the Casimir-Polder potential. Not only is the intermolecular Coulomb term absent, but $H_{\text{int}}^{\text{mult}}$ is retarded at the outset, since $d^{\perp}(\vec{r})$ in explicitly time dependent form is causal, and no static terms contribute. Further, the dispersion potential is understood as being mediated by the exchange of two virtual photons between $A$ and $B$, and to leading order requires only the fourth order perturbation theory term for its evaluation [3,9].

Another prominent method within the framework of non-relativistic QED for computing interactions between molecules, in particular dispersion forces, is response theory [10-14]. In this approach, the electronic charge distribution associated with an atomic or molecular particle is expanded as a sum of multipole moments and viewed as a source of electromagnetic radiation. The quantum electrodynamical Maxwell field operators in the proximity of the source are calculated in the Heisenberg representation as a series expansion in powers of the multipole moments. A second, test body then responds via its polarizability to the fields of the first species at the position of the second particle, and vice versa. For isotropic source and test molecules in the electric dipole approximation, the interaction energy is calculated from

$$\Delta E = -\frac{1}{2e_0} \sum_{\alpha} \alpha(A;\omega) d^{12}(B;\vec{R}_B) - \frac{1}{2e_0} \sum_{\alpha} \alpha(B;\omega) d^{12}(A;\vec{R}_A),$$  \hspace{1cm} (1.9)

where the expansion of the electric dipole dependent source field is of the form [11]

$$d^{\perp}(\xi;\vec{r}) = d^{(0)}(\xi;\vec{r}) + d^{(1)}(\xi;\vec{r};\vec{\mu}) + d^{(2)}(\xi;\vec{r};\vec{\mu}\vec{\mu}) + ..., \hspace{1cm} (1.10)$$

where the first term of the series is the vacuum field, independent of the source moment and is given by the interaction picture analogue of Eq. (1.8) with the boson operators specified at the initial time, $d^{(1)}(\xi;\vec{r};\vec{\mu})$ is the electric displacement field linear in the electric dipole moment, while the third term of Eq. (1.10) is the $d^{\perp}$-field dependent quadratically on $\vec{\mu}$, etc. Explicit functional forms for these three operators, as well as their magnetic field counterparts may be found in Refs. [11,14]. As expected, the Casimir-Polder potential Eq. (1.3) results on taking the expectation value of formula (1.9) over molecular ground electronic states and the vacuum state of the radiation field. Interestingly, terms due to the interference of the zeroth order field with the quadratic field contribute to the dispersion potential. Effects due to retardation are once again automatically included since the displacement field in the neighbourhood of a source is strictly causal [14].

In addition to the alternative approaches briefly reviewed above, several other methods have been developed, mostly within the context of multipolar coupling, in order to shed further insight into the manifestation and computation of the retarded dispersion potential. These include examination of differences in zero-point energy [15], radiation reaction [16], source theory [17,18], covariant scattering theory [19], and changes in the electromagnetic energy density in the vicinity of polarizable molecules [20].
One last method, which explicitly retains the salient features associated with Casimir effects, and which offers a number of calculational advantages, as well as having intuitive physical appeal, is the induced multipole moment approach [21-24]. This computational method is the focus of the present contribution. A brief introduction and outline of the approach is given in the next Section. This is followed by briefly recapitulating its application to the calculation of the Casimir-Polder potential in Section 3. It is then shown in Section 4 how the method can be used in a facile way to calculate the dispersion energy shift when one or both of the molecular pair are in excited states. This is followed in Section 5 by a presentation of the calculation of the change in mutual interaction energy when an external radiation field is applied to a pair of coupled molecules [25] in a straightforward extension of the induced moment method. This application is of current high interest in the context of light-induced optical forces and their subsequent control and manipulation [26].

2. Method of Induced Multipole Moments
The induced multipole moment method has recently proved to be extremely efficient and successful in describing a number of intermolecular interactions [21-24, 27-29]. It is closely related to the idea originally used to calculate London dispersion forces, namely the induction of dipoles by quantum fluctuations, but differs from the picture adopted by Spruch and Kelsey in which the effect of one dipole due to the electromagnetic field of another was evaluated [30]. Underlying the present approach are a few simple concepts and principles. Firstly, that application of an electric displacement field to an electrically polarizable molecule induces an electric dipole moment in leading order. Secondly, the dipoles induced at each molecular centre couple via an interaction potential. Thirdly, taking the expectation value of this product of induced moments and coupling factor over specific molecule and field states gives the energy shift for the particular intermolecular process under study. These steps are first applied to recalculate the Casimir-Polder interaction energy in order to illustrate the applicability of the approach. It should be remarked that the induced multipole moment method to be outlined and applied in the present contribution may be considered complementary to the approach adopted by Compagno, Passante and Persico and co-workers, in which the virtual photon cloud perpetually surrounding an atom is viewed as dressing the source. This field-dressed atom induces a change in the radiation field from which interatomic energy shifts may then be calculated by evaluating correlations of the vacuum electromagnetic field. Details of this technique may be found in Ref. [31].

3. Ground State Dispersion Interaction
Consider an isotropic polarizable molecule $\xi$ positioned at $\vec{R}_s$ subject to the action of a transverse displacement field $\vec{d}^\perp(\vec{r})$ of mode $(\vec{k}, \lambda)$ as given by Eq. (1.8). The $i$-th component of the induced moment is

$$\mu_i^{ind}(\vec{\xi}, \vec{k}) = e_0^{-1} \alpha(\vec{\xi}, k) \mu_i^\perp(\vec{R}_s; \vec{k}, \lambda),$$

(3.1)

where $\alpha(\vec{\xi}, k)$ is the isotropic dynamic polarizability of $\vec{\xi}$. The induced dipole moments associated with the two molecules $A$ and $B$ interact through the dipolar coupling potential, resulting in an energy shift

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

(3.2)

where $V_{ij}(k, \vec{R})$ is the single frequency, retarded resonant interaction tensor [32].
$$V_0(k, \vec{R}) = \frac{1}{4\pi\epsilon_0 R^3} \left[ (\delta_{ij} - 3\hat{R}_i\hat{R}_j)(1 - ikR) - (\delta_{ij} - \hat{R}_i\hat{R}_j)k^2R^2 \right] e^{ikR}, \quad (3.3)$$

and $|\vec{R}_B - \vec{R}_A| = R$ as before.

An expression for the energy shift written explicitly in terms of the dynamic electric dipole polarizability of each species is easily obtained on substituting Eq. (3.1) into (3.2). The result is

$$\Delta E = \sum_{k, \lambda} \varepsilon_0^{-2} \alpha(A; k)\alpha(B; k)d_j^+ (\vec{R}_A; \vec{k}, \lambda)d_j^+ (\vec{R}_B; \vec{k}, \lambda) \text{Re} V_0(k, \vec{R}). \quad (3.4)$$

It is worth pointing out that appearing in formula (3.4) is the product of displacement fields at two different positions, which is immediately recognizable as the field-field spatial correlation function. In order to obtain the dispersion potential, the expectation value is taken of relation (3.4) over the ground state of each molecule and the vacuum state of the radiation field. The first of these is rudimentary and yields the molecular ground state polarizability of species $\xi = A, B$, whose form equivalent to the polarizability Eq. (1.4) at real frequency $\omega = ck$ is

$$\alpha(\xi; k) = \frac{2}{3} \sum_k \frac{\mathcal{B}_0(\xi)^2 E_{\xi \xi}}{E_{\xi \xi} - (ck)^2}. \quad (3.5)$$

For the factor involving the radiation field, the required quantity is

$$<0| (\vec{k}, \lambda) | d_j^+ (\vec{R}_A; \vec{k}, \lambda) d_j^+ (\vec{R}_B; \vec{k}, \lambda) | 0(\vec{k}, \lambda) = \frac{\hbar c e_{\lambda \lambda}}{\omega} j_{\lambda}^{(\lambda)}(\vec{k}) e_{\lambda}^{(\lambda)}(\vec{k}) e^{-ik\vec{k}}, \quad (3.6)$$

on employing the operator for the mode specific transverse displacement field Eq. (1.8). The energy shift Eq. (3.4) now becomes

$$\Delta E = \sum_{k, \lambda} \left( \frac{\hbar c e_{\lambda \lambda}}{\omega} \right) \alpha(A; k)\alpha(B; k)\varepsilon_j^{(\lambda)}(\vec{k})\varepsilon_j^{(\lambda)}(\vec{k}) e^{-ik\vec{k}} \text{Re} V_0(k, \vec{R}). \quad (3.7)$$

To proceed further, the mode sum has to be carried out. The standard way is to evaluate the polarization index sum using the identity

$$\sum_{\lambda} \varepsilon_j^{(\lambda)}(\vec{k})\varepsilon_j^{(\lambda)}(\vec{k}) = \delta_{ij} - \hat{k}_i \hat{k}_j, \quad (3.8)$$

convert the wavevector sum to an integral via the prescription $\frac{1}{V} \sum_k \Rightarrow \frac{1}{(2\pi)^3} \int d^3 \vec{k}$, followed by integration over angular variables and integration over wavevector since in spherical polar coordinates the volume element is $d^3 \vec{k} = k^2 dk d\Omega$, with $d\Omega$ an element of solid angle. For the angular integral, relation (3.9) is used,

$$\frac{1}{4\pi} \left[ (\delta_{ij} - \hat{k}_i \hat{k}_j) e^{-ik\vec{k}} \right] d\Omega = \left[ (\delta_{ij} - \hat{R}_i\hat{R}_j) \frac{\sin kR}{kR} + (\delta_{ij} - 3\hat{R}_i\hat{R}_j) \left( \frac{\cos kR}{k^2R^2} - \frac{\sin kR}{k^3R^3} \right) \right], \quad (3.9)$$

giving for $\Delta E$, the expression
\[ \Delta E = -\frac{\hbar c}{16\pi^2\varepsilon_0\varepsilon_0'} \int_0^\infty dk \alpha(A;k)\alpha(B;k)k^4 \times \left[ 2\sin kR\cos kR + \frac{2}{R^2} (\cos^2 kR - \sin^2 kR) - \frac{10}{R^4}\sin kR\cos kR \right] \]  
\hfill (3.10)

after inserting the coupling tensor Eq. (3.3). Simplifying the trigonometric terms and transforming the integral to one over imaginary wavevector \( k = iu \) results in the Casimir-Polder potential Eq. (1.3).

### 4. Coupling Between Excited Molecules

When both molecules are in ground electronic states, only upward transitions to intermediate states are possible. If either one or both of \( A \) and \( B \) are in excited electronic states, however, downward transitions as well as excitation to higher lying levels can now occur, giving contributions additional to the \( u \)-integral term of the Casimir-Polder potential. Let \( A \) and \( B \) now both be in excited electronic states \( |m> \) and \( |n> \), respectively making electric dipole allowed transitions to higher or lower lying intermediate states \( |r> \) and \( |s> \). The \( u \)-integral contribution to the total intermolecular interaction energy is similar to Eq. (1.3), having the functional form

\[ \Delta E = -\frac{1}{36\pi^2}\sum_{r,s} |\tilde{\mu}^{mr}(A)|^2 |\tilde{\mu}^{ns}(B)|^2 \times \int_0^\infty du R e^{-2uR} \frac{k_{r,m}k_{s,n}}{k_{r,m}^2 + u^2k_{s,n}^2} \left[ \frac{1}{u^2R^2} + \frac{2}{u^4R^4} + \frac{5}{u^6R^6} + \frac{6}{u^8R^8} \right] \]  
\hfill (4.1)

which can be expressed in terms of the excited state polarizability at imaginary frequency of each molecule using Eq. (1.4) with replacement of appropriate state labels. Note that Eq. (4.1) contains contributions from both upward and downward transitions from the initial state of each molecule as exemplified by the unrestricted nature of the summation over intermediate states.

For the contribution to the energy shift due solely to downward transitions, in which a real photon is emitted from the excited state, the expression analogous to Eq. (3.4) is

\[ \Delta E^{RES} = \sum_{k,A} \epsilon_0^2 \alpha(A;k)\alpha(B;k)k^4 (\tilde{R}_r;\tilde{\nu},\tilde{\lambda})d_j^{(\tilde{R}_r;\tilde{\nu},\tilde{\lambda})} (\tilde{R}_r;\tilde{\nu},\tilde{\lambda})d_j^{(\tilde{R}_r;\tilde{\nu},\tilde{\lambda})} \left[ V^{RES}_{ij}(k_{r,m},\tilde{R}) + V^{RES}_{ij}(k_{m,r},\tilde{R}) \right] \]  
\hfill (4.2)

where \( V^{RES}_{ij}(k_{pq},\tilde{R}) \) is the retarded interaction tensor Eq. (3.3) evaluated at the resonant frequency \( \omega_{pq} = c k_{pq} \) corresponding to a downward transition \(|q> \leftrightarrow |p>\). The evaluation of Eq. (4.2) is carried out in a manner similar to that used in the calculation of the ground state potential. Now the expectation value is taken over the molecular states \( |m^A,n^B> \), with the radiation field in the vacuum state as before, with the expectation value of the field-field spatial correlation function given by Eq. (3.6). Converting the mode sum to an integral produces

\[ \Delta E^{RES} = \frac{\hbar c}{16\pi^2\varepsilon_0} \int d^3\tilde{k} (\delta_{ij} - \tilde{k}_i\tilde{k}_j) e^{-i\tilde{k}\tilde{R}} \alpha(A;k)\alpha(B;k) \left[ V^{RES}_{ij}(k_{r,m},\tilde{R}) + V^{RES}_{ij}(k_{m,r},\tilde{R}) \right] \]  
\hfill (4.3)

In carrying out the angular average it is convenient to apply a formula alternate to Eq. (3.9)
\[
\frac{1}{4\pi} \left( \delta_{ij} - \hat{k}_i \hat{k}_j \right) e^{-ik \cdot \vec{R}} d\Omega = \frac{1}{2\pi^2} \left( -\nabla^2 \delta_{ij} + \nabla_i \nabla_j \right) \frac{1}{R} \left( e^{ik \cdot \vec{R}} - e^{-ik \cdot \vec{R}} \right),
\]

(4.4)
giving,

\[
\Delta E^{\text{RES}} = \frac{1}{12\pi^2 \varepsilon_0} \left( -\nabla^2 \delta_{ij} + \nabla_i \nabla_j \right) \frac{1}{R} \delta_{ij} \delta_{mk} \sum_{s} \frac{k_m}{k_m^2 - s^2} \left| \tilde{\mu}^{sn}(B) \right|^2 \gamma_{ij}^{\text{RES}}(k_{rs}, \vec{R}) \\
\times \left[ \sum_{s} \alpha(A; k_{sn}) \left| \tilde{\mu}^{sm}(B) \right|^2 e^{ik \cdot \vec{R} \cdot k_{sn}} \gamma_{ij}^{\text{RES}}(k_{rs}, \vec{R}) \right] e^{ik \cdot \vec{R}} - e^{-ik \cdot \vec{R}}. \]

(4.5)

On performing the \( k \)-integral, Eq. (4.5) becomes

\[
\Delta E^{\text{RES}} = \frac{1}{12 \pi^2 \varepsilon_0} \left( -\nabla^2 \delta_{ij} + \nabla_i \nabla_j \right) \frac{1}{R} \left[ \sum_{s} \alpha(A; k_{sn}) \left| \tilde{\mu}^{sm}(B) \right|^2 e^{ik \cdot \vec{R} \cdot k_{sn}} \gamma_{ij}^{\text{RES}}(k_{rs}, \vec{R}) \right] e^{ik \cdot \vec{R}} - e^{-ik \cdot \vec{R}}. \]

(4.6)

Inserting the alternate form for the resonant coupling tensor,

\[
V_{ij}^{(k)}(k, \vec{R}) = \frac{1}{4\pi \varepsilon_0} \left( -\nabla^2 \delta_{ij} + \nabla_i \nabla_j \right) \frac{e^{ik \cdot \vec{R}}}{R}, \]

(4.7)
at the appropriate resonant frequency into Eq. (4.6), yields for the additional contribution to the interaction energy the result

\[
\Delta E^{\text{RES}} = -\frac{1}{4\pi \varepsilon_0} \left( -\nabla^2 \delta_{ij} + \nabla_i \nabla_j \right) \frac{e^{ik \cdot \vec{R}}}{R} \left[ \sum_{s} \alpha(A; k_{sn}) \left| \tilde{\mu}^{sm}(B) \right|^2 e^{ik \cdot \vec{R} \cdot k_{sn}} \gamma_{ij}^{\text{RES}}(k_{rs}, \vec{R}) \right] e^{ik \cdot \vec{R}} - e^{-ik \cdot \vec{R}}. \]

(4.8)

which after evaluating the gradients and simplifying produces

\[
\Delta E^{\text{RES}} = -\frac{1}{24 \pi^2 \varepsilon_0} \sum_{s} \alpha(A; k_{sn}) \left| \tilde{\mu}^{sm}(B) \right|^2 k_m^6 \left[ \frac{1}{k_{sn} R^2} + \frac{1}{k_{sn} R^4} + \frac{3}{k_{sn} R^6} \right] \gamma_{ij}^{\text{RES}}(k_{rs}, \vec{R}) \]

(4.9)

with the total energy shift given by the sum of Eqs. (4.1) and (4.9), and is in agreement with previous perturbation [33] and response [34] theory calculations.

Only the first term of Eq. (4.9) and the \( \nu \)-integral term Eq. (4.1) survive if only \( B \) is excited, while if only \( A \) is excited the first term of Eq. (4.9) vanishes, with the appropriate ground state polarizability appearing in both situations.
At separation distances $R$ large relative to characteristic molecular transition wavelengths, the dominant contribution to the energy shift when both $A$ and $B$ are excited arises from expression Eq. (4.9), exhibiting inverse square dependence, as to be expected for emission of a real photon from the excited electronic state,

$$
\Delta E^\text{FZ} = -\frac{1}{36\pi^2 \varepsilon_0^2 (hc)^3 R^2} \sum_{r,s} \frac{|\vec{\mu}^m(A)|^2|\vec{\mu}^m(B)|^2}{(E_{mr} + E_{ms})} E_{mr} E_{rs} (E_{mr}^2 + E_{ms} E_{rs} + E_{rs}^2),
$$

(4.10)

while the far-zone limit of the $\nu$-integral term Eq. (4.1) has an $R^{-7}$ dependence as given by Eq. (1.6), with excited state polarizabilities replacing their ground state counterparts. In the near-zone, on the other hand, the asymptotic behaviour is $R^{-6}$ and arises from both Eqs. (4.1) and (4.9), their sum yielding

$$
\Delta E^\text{NZ} = -\frac{1}{24\pi^2 \varepsilon_0^2 R^6} \sum_{r,s} \frac{|\vec{\mu}^m(A)|^2|\vec{\mu}^m(B)|^2}{(E_{mr} + E_{ms})}.
$$

(4.11)

Dispersion potentials involving one or two excited molecules are harder to obtain using diagrammatic perturbation theory due to the presence of resonant energy denominators which arise when a real photon is emitted or absorbed. In the response theory calculation, this aspect is dealt with more easily as the total Maxwell field operators in the proximity of a molecule already include contributions from photons on the energy shell. The induced moment approach, however, proves to be the most facile.

5. Modification of Dispersion Force by External Radiation

It is remarkable that the method of induced moments may be used to calculate the change in dispersion potential between a pair of polarizable molecules when subject to an applied electromagnetic field. In the leading electric dipole approximation, the change in mutual interaction energy is again given by formula (3.2) on omitting the mode sum since the external electric displacement field is mode specific.

If one or both molecules is polar, the induced moment given by expression Eq. (3.1) contains terms additional to that proportional to the electric dipole polarizability when the inducing field is of the electric displacement variety. For the present application these extra contributions include the permanent electric dipole moment of the molecule, $\mu^i(\vec{r})$, and a contribution dependent on the first hyperpolarizability, $\beta_{ijk}(\vec{r};k)$. The extension of Eq. (3.1) is now given by

$$
\mu^{\text{ind}}_i(\vec{r};k) = \mu^i(\vec{r}) + \varepsilon_0^{-1} \alpha_{ij}(\vec{r};k) d^j(\vec{R}_i;\vec{k},\vec{\lambda}) + \varepsilon_0^{-2} \beta_{ijk}(\vec{r};k) d^j(\vec{R}_i;\vec{k},\vec{\lambda}) d^k(\vec{R}_j;\vec{\lambda},\vec{\lambda}).
$$

(5.1)

Inserting Eq. (5.1) into Eq. (3.2) and retaining terms correct up to the fourth power in the electronic charge yields for the energy shift the formula

$$
\Delta E = \varepsilon_0^{-2} \left[ \alpha_{ij}(A;k) \alpha_{ij}(B;k) d^i(\vec{R}_i;\vec{k},\vec{\lambda}) d^j(\vec{R}_i;\vec{k},\vec{\lambda}) \Re V_{ij}(k,\vec{R}) + \frac{1}{2} \mu^{\text{ind}}_i(A) \beta_{ijk}(B;k) d^j(\vec{R}_j;\vec{k},\vec{\lambda}) d^k(\vec{R}_i;\vec{k},\vec{\lambda}) + \beta_{ijk}(A;k) \mu^{\text{ind}}_j(B) d^j(\vec{R}_j;\vec{k},\vec{\lambda}) d^k(\vec{R}_i;\vec{k},\vec{\lambda}) V_{ij}(0,\vec{R}) \right].
$$

(5.2)
where $V_{ij}(k, \vec{R})$ is the retarded coupling tensor given by Eq. (3.3), $V_{ij}(0, \vec{R})$ is its zero frequency form,

$$V_{ij}(0, \vec{R}) = \frac{1}{4\pi\epsilon_0 \vec{R}} (\delta_{ij} - 3\hat{R}_i \hat{R}_j),$$

(5.3)

and represents static ($k$ independent) coupling. As in the computation of the dispersion potential between systems in the ground electronic state, the expectation value of the operator for the energy shift involving matter is taken over the state $|0^A, 0^B\rangle$. Instead of taking the expectation value over the vacuum state of the radiation field, as was done for the calculation of the Casimir-Polder potential in Section 3, now the expectation value of the factor involving the product of the electric displacement fields is taken over a state of the field which contains $N$ photons of mode $(\vec{k}, \lambda)$, $|N(\vec{k}, \lambda)\rangle$. The extension of Eq. (3.6) is easily seen to be

$$<N(\vec{k}, \lambda)|d^{\dagger}_i(\vec{R}_A; \vec{k}, \lambda)d^{\dagger}_j(\vec{R}_B; \vec{k}, \lambda)|N(\vec{k}, \lambda)>\]

$$= \left(\frac{\hbar c}{2\pi}\right)(N + 1)\epsilon_k^{(\lambda)}(\vec{k})\sigma_k^{(\lambda)}(\vec{k})e^{-i\vec{k} \cdot \vec{R}} + NC_k^{(\lambda)}(\vec{k})\epsilon_k^{(\lambda)}(\vec{k})e^{i\vec{k} \cdot \vec{R}},$$

(5.4)

with $\vec{R}$ as defined earlier to be the separation distance vector of $B$ relative to $A$. The quantity Eq. (5.4) is used in the first term of Eq. (5.2). Interestingly, Eq. (5.4) reduces to Eq. (3.6) on letting $N = 0$. For the radiation field factor occurring in the second part of Eq. (5.2), where the product of the fields is evaluated at the same point in space, the relevant expectation value is

$$<N(\vec{k}, \lambda)|d^{\dagger}_i(\vec{R}; \vec{k}, \lambda)d^{\dagger}_j(\vec{R}; \vec{k}, \lambda)|N(\vec{k}, \lambda)>\]

$$= \left(\frac{\hbar c}{2\pi}\right)(N + 1)\epsilon_k^{(\lambda)}(\vec{k})\sigma_k^{(\lambda)}(\vec{k}) + NC_k^{(\lambda)}(\vec{k})\epsilon_k^{(\lambda)}(\vec{k}),$$

(5.5)

which is a special case of Eq. (5.4) in which $\vec{R}_B = \vec{R}_A$, giving $\vec{R} = 0$. Thus evaluating Eq. (5.2) over the state $|0^A, 0^B; N(\vec{k}, \lambda)\rangle$ and using the last two relations produces for the radiation-induced intermolecular energy shift the expression

$$\Delta E = \frac{\hbar c}{2\pi}\epsilon_k^{(\lambda)}(\vec{k})\sigma_k^{(\lambda)}(\vec{k}) \left\{ \alpha_{ik}(A; k)\alpha_{jk}(B; k)e^{i\vec{k} \cdot \vec{R}} + e^{-i\vec{k} \cdot \vec{R}} \right\} \Re V_{ij}(k, \vec{R})$$

$$+ \left\{ \mu^{(0)}(A)\beta_{ikl}(B; k) + \beta_{ikl}(A; k)\mu^{(0)}(B) \right\} V_{ij}(0, \vec{R}),$$

(5.6)

which can be decomposed as

$$\Delta E = \Delta E_{dyn} + \Delta E_{stat},$$

(5.7)

where the so-called “dynamic” contribution to the interaction energy – for reasons which will become clear later on, is given by

$$\Delta E_{dyn} = \frac{\hbar c}{2\pi}\epsilon_k^{(\lambda)}(\vec{k})\sigma_k^{(\lambda)}(\vec{k})\alpha_{ik}(A; k)\alpha_{jk}(B; k)e^{i\vec{k} \cdot \vec{R}} \Re V_{ij}(k, \vec{R}),$$

(5.8)

and similarly the “static” term is
\[ \Delta E_{\text{stat}} = \frac{f}{4\pi\varepsilon_0 (k) (k) (k)} \left[ \mu_i^{00} (A) \beta_{ijk} (B; k) + \beta_{ijk} (A; k) \mu_i^{00} (B) \right] V_{ij} (0, \vec{R}). \] (5.9)

In these results, the irradiance of the incident laser beam is defined by \( I = Nh\varepsilon^2 k / V \). The frequency dependent polarizability tensor appearing in the dynamic contribution is given by
\[
\alpha_g (\xi; k) = \sum_r \left\{ \frac{\mu_i^0 (\xi) \mu_i^{00} (\xi)}{E_{\gamma \omega} - \hbar \omega} + \frac{\mu_i^0 (\xi) \mu_i^{00} (\xi)}{E_{\gamma \omega} + \hbar \omega} \right\},
\] (5.10)

and the molecular first hyperpolarizability tensor that contributes to the static term is
\[
\beta_{ijk} (\xi; k) = \sum_{r,s} \left\{ \frac{\mu_i^0 (\xi) \mu_i^{00} (\xi) \mu_i^{00} (\xi)}{E_{\gamma \omega} + \hbar \omega} \right\} + \frac{\mu_i^0 (\xi) \mu_i^{00} (\xi) \mu_i^{00} (\xi)}{E_{\gamma \omega} + \hbar \omega} + \frac{\mu_i^0 (\xi) \mu_i^{00} (\xi) \mu_i^{00} (\xi)}{E_{\gamma \omega} + \hbar \omega} \right\},
\] (5.11)

with \( \mu_i^{00} (\xi) \) the i-th component of the ground state static dipole moment. Note that the form of Eq. (5.6) allows the cases in which \( A \) and \( B \) are the same or different species to be treated. Moreover, \( \Delta E_{\text{stat}} \) is zero if either \( A \) or \( B \) are centrosymmetric since \( \mu_i^{00} \) and \( \beta_{ijk} \) are then both vanishing quantities.

The result (5.6) has been obtained straightforwardly using the induced moment approach, and with considerably less arduousness than if carried out using diagrammatic perturbation theory techniques. In the latter method, each of the contributions to Eq. (5.6) are obtained by summing over forty-eight time-ordered diagrams [25,27,29] or state sequence pathways [35], with the initial and final states being equal to each other, and which are also the same for both mechanisms, namely \( | i \rangle \neq \langle f | = 0^0, 0^0; N (\vec{k}, \lambda) \). In one mechanism, termed the dynamic one, scattering of a real photon takes place at different centres, with a virtual photon propagating between the pair, carrying electronic excitation energy with it. Hence two (real and virtual photon) emission events, or two absorption events, or one of each kind occur at both \( A \) and \( B \), and the overall contribution requires fourth order perturbation theory for its evaluation, giving rise to term (5.8) which is proportional to the electric dipole polarizability of each molecule. For the second term contributing to the energy shift in Eq. (5.7), the fourth order formula of perturbation theory may again be employed. This time absorption and emission of a real photon from the incident laser field occurs at the same site, with a virtual photon again migrating between \( A \) and \( B \). Because no energy is relayed in this transfer process, the mechanism is called the static one, and \( V_{ij} (0, \vec{R}) \) appears. In the language of time-dependent perturbation theory, since there are three electric dipole interaction vertices at one centre, and one at the other, and vice versa, \( \Delta E_{\text{stat}} \) is proportional to the product of the first hyperpolarizability tensor and the permanent moment, as given explicitly by Eq. (5.9).

The energy shift result Eq. (5.6) holds for all separation distances \( R \) beyond overlap of molecular charge distributions for anisotropic \( A \) and \( B \), and with the molecular pair having a fixed orientation relative to the direction of motion of the applied electric displacement field. For \( A \) and \( B \) randomly oriented with respect to each other, a molecular average can be carried out using standard tensor averaging techniques [36]. \( \Delta E_{\text{stat}} \) is found to vanish after such a procedure. Further, for freely tumbling pairs, as occurs in the fluid phase, an average over all directions of \( \vec{R} \) for a fixed \( \vec{k} \), or vice
versa must be performed. Carrying out both of the averages in the order stated on the remaining
dynamic contribution to the energy shift Eq. (5.8) results in

\[ \Delta E_{\text{dy}} = -\frac{k}{8\pi\varepsilon_0 c^3} \alpha(A;k)\alpha(B;k)[2kR\sin kR\cos kR + 2(\cos^2 kR - \sin^2 kR) - \frac{10}{kR}\sin kR\cos kR - \frac{6}{k^2 R^2}(\cos^2 kR - \sin^2 kR) + \frac{6}{k^3 R^3}\sin kR\cos kR], \]

(5.12)

which is independent of polarization, is linearly proportional to the intensity of the incident beam, and
agrees with the result obtained using perturbation theory [25,35]. From Eq. (5.12) it is seen that the
force induced by the laser is an attractive one, and constitutes an optical binding force. The asymptotic
limits are readily derived from Eq. (5.12). In the near-zone the energy shift has an inverse dependence
on \( R \), which can be appreciable for a molecular assembly. At large separations, the interaction energy
varies by a modulated inverse square behaviour.

6. Summary
In conclusion it has been shown how the method of induced multipole moments provides an
alternative physical viewpoint and an efficient calculational scheme for the evaluation of a number of
intermolecular interactions which exhibit all of the key features associated with Casimir effects. In this
method, an electric dipole moment induced in a polarizable molecule by the application of an external
electric displacement field interacts with a similarly induced electric dipole in a second molecule. The
coupling takes place via the retarded resonant interaction tensor. An expression for the interaction
energy shift can then be written in terms of the electric dipole polarizability of each species, the spatial
field-field correlation function and the coupling tensor. On evaluating the expectation value of this
quantity over the ground electronic state of each molecule and the state of the field containing no
photons, remarkably the Casimir-Polder potential results. A particular advantage of the approach is
that the energy shift when one or both molecules are electronically excited is obtained in a
straightforward manner. Now the expectation value is taken over the appropriate molecular excited
state, with the radiation field in the vacuum state as before. In addition to a Casimir-Polder like \( u \)-
integral term which contains excited state polarizabilities, a contribution due to real photon emission
from the excited state is present, with the coupling tensor now evaluated at the resonant frequency of
the downward transition from the higher lying energy state to a lower one. In a further facile extension
of the method, the change in the dispersion energy shift caused by the application of an intense
external radiation field is also readily calculable. Once again the underlying equation for the energy
shift is the same as for the dispersion force. But now the expectation value is taken over a state of the
field containing \( N \) photons instead of zero, with both molecules in the ground state. For this process,
two terms are found to contribute to the interaction energy for molecules that are polar. One
contribution is proportional to the product of electric dipole polarizability of each species, while the
second depends on the product of the permanent moment of one body and the first hyperpolarizability
of the other. All of the results presented agree with previous diagrammatic perturbation theory
calculations, but have been obtained with far greater ease. Perturbation theory evaluation of the
ground state dispersion potential requires summation over twelve time ordered graphs, its modification
by a radiation field involves addition of contributions from ninety-six diagrams, while when one or
both entities is excited, intermediate state resonances have to be identified and tacked properly to yield
the correct dispersion energy, and in all three computations, virtual photon summation has to be
performed. While the induced moment approach has been shown to reproduce in a facile way leading
order contributions to the dispersion potential and its modification by external radiation, calculational
advantages offered by the method show up most clearly when higher order processes are tackled such
as those involving terms arising from the inclusion of multipole moments in addition to the leading
electric dipole interaction term, such as magnetic dipole and electric quadrupole couplings, which are crucial when evaluating interactions between chiral molecules, as well as when three-body energy shifts are computed [37]. By including fields that are explicitly time-dependent, which thereby induce moments that are a function of $t$, it is anticipated that time-dependent energy shifts may be computed in future using this approach. Hence the induced multipole method offers a viable and practical alternative to conventional techniques for the computation of various intermolecular processes.

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