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Retarded dispersion interaction energies between chiral molecules

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The dispersion interaction energy for a pair of chiral molecules in their ground states is calculated using the multipolar form of quantum electrodynamics. The calculations go beyond the electric-dipole approximation, and the interaction Hamiltonian includes the electric-quadrupole, magnetic-dipole, and diamagnetic coupling terms. The energy is calculated using two methods: one with standard fourth-order perturbation theory and another with a response formalism. In the perturbation approach, the intermolecular coupling arises from two-photon exchange whereas in the response method, the energy shift is calculated from the response of one molecule to the Maxwell fields of the other. In both calculations retardation effects are taken into account. It is shown that the dispersion energy contains a contribution that depends on the relative handedness of the two molecules. An expression for this discriminatory energy shift, valid for all intermolecular separations beyond the electron overlap, is presented. In addition to the discriminatory energy shift, results are presented for the interaction energy shift between a molecule with electric-dipole polarizability and another with magnetic-dipole or electric-quadrupole polarizability. The limiting behavior of these shifts in the near and the far zone is examined.

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I. INTRODUCTION

Early quantum-mechanical investigations of the interactions between neutral molecules separated by distances beyond the electron overlap were made using second-order perturbation theory with electrostatic dipolar coupling. The intermolecular energy shift, called the dispersion energy, showed an R^{-6} dependence. In these studies no account was taken of the finite speed of propagation of electromagnetic influences. Casimir and Polder [1,2], in a pioneering study took account of the speed of propagation of light and showed that such an inclusion led to a replacement of the R^{-6}-dependent dispersion energy by an R^{-7} dependence at large distances. Their prediction was later confirmed experimentally [3,4]. Interactions between chiral (optically active) molecules show an additional interesting behavior. The dispersion energy between two chiral molecules contains a contribution that depends on the relative handedness of the two molecules. The interaction energy between a right-handed molecule of one species A with a right-handed one of another species B is different from that of the right-left pair. Such a discriminatory interaction is known as chiral discrimination [5]. The origins of the discriminatory interaction lie in the low symmetry of chiral molecules and the transitions in these molecules are in general *both* electric-dipole and magnetic-dipole allowed.

Previous studies [6,7] of this discriminatory interaction have been confined to either small intermolecular separations (near zone) or large separations (far zone). In the near zone the discriminatory dispersion energy may be calculated using standard second-order perturbation theory with electric-dipole–electric-dipole and magnetic-dipole–magnetic-dipole potentials as perturbation. It has an inverse sixth power dependence on the intermolecular distance and is given by [6,7]

$$\Delta E_{\mathrm{NZ}}=\frac{-1}{12\pi^2\varepsilon_0^2c^2R^6}\times\frac{|\boldsymbol{\mu}^{0m}(A)\cdot\mathbf{m}^{m0}(A)||\boldsymbol{\mu}^{0n}(B)\cdot\mathbf{m}^{n0}(B)|}{E_{m0}+E_{n0}}\,, \tag{1.1}$$

where $\boldsymbol{\mu}^{rs}$ and $\mathbf{m}^{rs}$ are the electric- and magnetic-dipole moments of the transition $r\leftarrow s$ with transition energy E_{rs}. Since an electric dipole is a polar vector and a magnetic dipole is an axial vector, it is evident that the replacement of one of the molecules by its enantiomer leads to a change of sign.

In the far zone, where retardation effects are important, quantum electrodynamical calculations [6,8] showed an inverse ninth power on the distance and the energy shift was found to be

$$\Delta E_{\mathrm{FZ}}=-\frac{\hbar^3c}{3\pi^3\varepsilon_0^2R^9}\times\sum_{m,n}\frac{|\boldsymbol{\mu}^{0m}(A)\cdot\mathbf{m}^{m0}(A)||\boldsymbol{\mu}^{0n}(B)\cdot\mathbf{m}^{n0}(B)|}{E_{m0}^2E_{n0}^2}\,. \tag{1.2}$$

Again the discriminatory nature of the interaction energy is self-evident.

In this paper we report a result for the complete discriminatory dispersion potential for a pair of chiral molecules in their ground electronic states valid for *all* separations outside the electron overlap region. The calculations have been performed using two methods within the framework of molecular quantum electrodynamics in the multipolar formalism. Both are extensions of earlier studies used to derive the Casimir-Polder potential. One is based on fourth-order perturbation theory together with the use of diagrammatic techniques [8]. The other uses a form of response theory [9,10] where the Maxwell fields in the neighborhood of one molecule are first calcu-

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lated [11] and from the response of the second molecule to these fields the discriminatory interaction energy is extracted.

An outline of the two methods is given in Sec. II and the methods are applied in the subsequent sections to calculate dispersion energies. In Sec. III the discriminatory interaction energy shift between two chiral molecules is presented. It is found that the interference between electric-dipole and magnetic-dipole couplings leads to the discriminatory shift. The shift is shown to survive random orientational averaging. Although the interference between electric-dipole and -quadrupole couplings also leads to discriminatory shift for an oriented molecular pair, the shift vanishes, as shown in Sec. IV, on averaging. Sections V and VI are devoted to nondiscriminatory dispersion potentials which are of the same order as the discriminatory potential. It is shown that diamagnetic coupling can give rise to contributions of the same order. The asymptotic behavior of the potentials in the small- and large-R limits is discussed.

II. OUTLINE OF METHODS

A. Perturbation method

The multipolar Hamiltonian for a two-molecule system is given by

$$H = H_A + H_B + H_{\text{rad}} + H_{\text{int}}^{A} + H_{\text{int}}^{B} \ . \tag{2.1}$$

H_A and H_B are the Hamiltonians of the molecules A and B located at $\mathbf{R}_A$ and $\mathbf{R}_B$; H_{rad} is the second quantized Hamiltonian of the radiation field; H_{int}^{A} and H_{int}^{B} are the operators coupling A and B to the radiation field. In the multipolar formalism the field-molecule coupling is expressed in terms of the coupling of molecular multipole moments to the electric displacement and magnetic fields [12–14]. The fields are represented by the mode expansions

$$\mathbf{d}(\mathbf{r}) = i\sum_{\mathbf{k},\lambda} \left[\frac{\hbar c k \varepsilon_0}{2V} \right]^{1/2} [\mathbf{e}^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} - \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) a^{\dagger(\lambda)}(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}}] \ , \tag{2.2}$$

$$\mathbf{b}(\mathbf{r}) = i\sum_{\mathbf{k},\lambda} \left[\frac{\hbar k}{2\varepsilon_0 c V} \right]^{1/2} [\mathbf{b}^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} - \bar{\mathbf{b}}^{(\lambda)}(\mathbf{k}) a^{\dagger(\lambda)}(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}}] \ . \tag{2.3}$$

$a^{(\lambda)}(\mathbf{k})$ and $a^{\dagger(\lambda)}(\mathbf{k})$ are the photon annihilation and creation operators of a $(\mathbf{k},\lambda)$ mode photon; V is the quantization volume. The electric and magnetic polarization vectors $\mathbf{e}^{(\lambda)}(\mathbf{k})$ and $\mathbf{b}^{(\lambda)}(\mathbf{k})$ and the wave vector $\mathbf{k}$ form a right-handed triad.

In the electric-dipole approximation, the displacement vector field is assumed to be constant over the molecules; this corresponds to the neglect of the spatial variations of the vector potential over the molecules. In this approximation the radiation-molecule interaction is solely via the coupling of the electric dipole to the displacement vector field evaluated at the molecular center. In a higher approximation, first-order spatial variations of the vector potential are taken into account; in the multipolar formalism this corresponds to the inclusion of the electric-quadrupole, magnetic-dipole, and diamagnetic coupling terms. Thus calculations including magnetic-dipole and electric-quadrupole interactions to second order must also include the diamagnetic interaction to first order [10]. The calculations of dispersion energy reported here include interactions to this order of approximation. Thus, for the field-molecule coupling we have

$$H_{\text{int}} = H_{\text{int}} + H_{\text{int}}^{(2)} \ , \tag{2.4}$$

where

$$\begin{aligned} H_{\text{int}}^{(1)} = & -\varepsilon_0^{-1}\boldsymbol{\mu}(A)\cdot\mathbf{d}(\mathbf{R}_A) - \varepsilon_0^{-1}(B)\cdot\mathbf{d}(\mathbf{R}_B) \\ & -\mathbf{m}(A)\cdot\mathbf{b}(\mathbf{R}_A) - \mathbf{m}(B)\cdot\mathbf{b}(\mathbf{R}_B) \\ & -\varepsilon_0^{-1}Q_{ij}(A)\nabla_j d_i(\mathbf{R}_A) - \varepsilon_0^{-1}Q_{ij}(B)\nabla_j d_i(\mathbf{R}_B) \end{aligned} \tag{2.5}$$

and

$$H_{\text{int}}^{(2)} = \frac{e^2}{8m} \sum_{\alpha} \{\mathbf{q}_\alpha(A) \times \mathbf{b}(\mathbf{R}_A)\}^2 + \frac{e^2}{8m} \sum_{\alpha} \{\mathbf{q}_\alpha(B) \times \mathbf{b}(\mathbf{R}_B)\}^2 \ , \tag{2.6}$$

where the α sums are over the electrons. It must be noted that in the multipolar formalism, in contrast to the minimal coupling formalism, there is no direct electrostatic coupling between the molecules. All intermolecular interactions between neutral molecules are mediated by an exchange of transverse photons and the interactions are fully retarded.

The leading contribution to the dispersion interaction is of fourth order in $H_{\text{int}}^{(1)}$, corresponding to two-photon exchange, and the interaction energy between two nonpolar molecules in their ground states is given by

$$\Delta E = -\sum_{\text{I,II,III}} \frac{\langle 0|H_{\text{int}}|\text{III}\rangle\langle \text{III}|H_{\text{int}}|\text{II}\rangle\langle \text{II}|H_{\text{int}}|I\rangle\langle I|H_{\text{int}}|0\rangle}{(E_{\text{III}}-E_0)(E_{\text{II}}-E_0)(E_{\text{I}}-E_0)} \ . \tag{2.7}$$

The ket vector $|0\rangle$ is the ground state of the unperturbed system with the molecules in their ground states and the field in the vacuum state. The intermediate states are of four types: (a) both molecules excited and field in the vacuum, (b) one excited and one virtual photon present, (c) both in the ground state with two virtual photons present, and (d) both molecules excited with two virtual photons present. Their contributions to the energy shift are found with the aid of diagrammatic techniques. A typical two-photon exchange graph is shown in Fig. 1. A

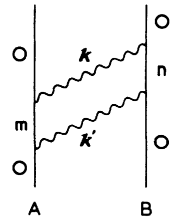

FIG. 1. Typical diagram with two-photon exchange for calculation of dispersion energy.

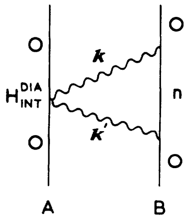

FIG. 2. Typical diagram involving diamagnetic coupling.

virtual-photon exchange is represented by a wavy line and is given the mode label $(\mathbf{k},\lambda)$. The intermediate states of molecule A are labeled m and those of B labeled n. The energy denominators are easily read off the graphs. For the graph in Fig. 1 the product of the energy denominators is $(E_{m0}+\hbar ck')(\hbar ck+\hbar ck')(E_{n0}+\hbar ck)$. The number of topologically different graphs involving two-photon exchange is 12. Each graph has a different set of denominators, independent of the nature of the interaction vertices. The nature of the vertices, however, depends on the type of energy shift. For example, in the graphs for the calculation of the Casimir-Polder potential, all four vertices are of the $-\varepsilon_0^{-1}\boldsymbol{\mu}\cdot\mathbf{d}$ type, whereas the discriminatory interaction energy calculation uses one $-\varepsilon_0^{-1}\boldsymbol{\mu}\cdot\mathbf{d}$ and one $-\mathbf{m}\cdot\mathbf{b}$ for each molecule. In the former, where all the vertices are of the same type, 12 graphs contribute. In the latter, the different time orderings of the two types of vertices must be taken into account and the number of graphs increases to 48. In the calculation of the energy shifts involving $H_{\rm int}^{(1)}$, three types of matrix elements (and their complex conjugates) are required. We list them here for future use:

$$\langle(\mathbf{k}',\lambda'),(\mathbf{k},\lambda);E_s|-\varepsilon_0^{-1}\boldsymbol{\mu}\cdot\mathbf{d}(\mathbf{R})|E_r;(\mathbf{k}',\lambda')\rangle = i\left[\frac{\hbar ck}{2\varepsilon_0 V}\right]^{1/2}\bar{e}_i^{(\lambda)}(\mathbf{k})\mu_i^{sr}e^{-i\mathbf{k}\cdot\mathbf{R}}\,, \tag{2.8}$$

$$\langle(\mathbf{k}',\lambda'),(\mathbf{k},\lambda);E_s|-\mathbf{m}\cdot\mathbf{b}(\mathbf{R})|E_r;(\mathbf{k}',\lambda')\rangle = i\left[\frac{\hbar k}{2\varepsilon_0 cV}\right]^{1/2}\bar{b}_i^{(\lambda)}(\mathbf{k})m_i^{sr}e^{-i\mathbf{k}\cdot\mathbf{R}}\,, \tag{2.9}$$

$$\langle(\mathbf{k}',\lambda'),(\mathbf{k},\lambda);E_s|-\varepsilon_0^{-1}Q_{ij}\nabla_j d_i(\mathbf{R})|E_r;(\mathbf{k}',\lambda')\rangle = -\left[\frac{\hbar ck}{2\varepsilon_0 V}\right]^{1/2}k_j\bar{e}_i^{(\lambda)}(\mathbf{k})Q_{ij}^{sr}e^{-i\mathbf{k}\cdot\mathbf{R}}\,, \tag{2.10}$$

where μ_i^{sr}, m_i^{sr} and Q_{ij}^{sr} are the electric-dipole, magnetic-dipole, and electric-quadrupole transition moments for the transition $s\leftarrow r$.

In the calculation of some energy shifts the diamagnetic coupling term of the Hamiltonian Eq. (2.6) must be included. The diamagnetic coupling is represented by a two-photon vertex and the two-photon exchange contributions are found from third-order perturbation theory with the aid of graphs of the type shown in Fig. 2. Typical matrix elements required for calculations involving diamagnetic coupling are

$$\left\langle(\mathbf{k}',\lambda'),(\mathbf{k},\lambda);E_s\left|\frac{e^2}{8m}\{\mathbf{q}\times\mathbf{b}(\mathbf{R})\}^2\right|E_s;0\right\rangle = -\frac{e^2}{8m}\varepsilon_{ijk}\varepsilon_{ilm}\left[\frac{\hbar k}{2\varepsilon_0 cV}\right]^{1/2}\left[\frac{\hbar k'}{2\varepsilon_0 cV}\right]^{1/2} \times\bar{b}_k^{(\lambda)}(\mathbf{k})b_m^{(\lambda')}(\mathbf{k}')\langle E_s|q_jq_l|E_s\rangle \times e^{-i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}}\,, \tag{2.11a}$$

$$\left\langle(\mathbf{k}',\lambda');E_s\left|\frac{e^2}{8m}\{\mathbf{q}\times\mathbf{b}(\mathbf{R})\}^2\right|E_s;(\mathbf{k},\lambda)\right\rangle = \frac{e^2}{8m}\varepsilon_{ijk}\varepsilon_{ilm}\left[\frac{\hbar k}{2\varepsilon_0 cV}\right]^{1/2}\left[\frac{\hbar k'}{2\varepsilon_0 cV}\right]^{1/2} \times b_k^{(\lambda)}(\mathbf{k})\bar{b}_m^{(\lambda')}(\mathbf{k}')\langle E_s|q_jq_l|E_s\rangle \times e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \tag{2.11b}$$

These are used in Sec. V.

B. Response method

The calculation of intermolecular energy shifts using a form of molecular response theory is made in two stages. The operators for the Maxwell fields in the proximity of a molecule are first calculated using the Heisenberg picture [11]. These fields are expanded in powers of the multipole moments. In our present studies we retain terms up to and including the magnetic-dipole and electric-quadrupole moments. As pointed out in Sec. II A, consistency demands the inclusion of the diamagnetic coupling term as well. The second stage involves the calculation of the response of the second molecule to the Maxwell fields of the first using the quantum-mechanical analog of the expression for the classical integration energy Eq. (2.12)

$$\Delta E = -\tfrac{1}{2}\alpha_{ij}d_id_j - G_{ij}d_ib_j - \tfrac{1}{2}\chi_{ij}b_ib_j - A_{ijk}d_i\nabla_j d_k - \tfrac{1}{2}\theta_{ijkl}\nabla_i d_j\nabla_k d_l + \cdots\,. \tag{2.12}$$

α_{ij}, G_{ij}, χ_{ij}, A_{ijk}, and θ_{ijkl} are the various multipole polarizabilities: their detailed forms are given in later sections. The leading term of the dispersion interaction energy Eq. (2.12) represents the response of a molecule with electric-dipole polarizability to the displacement field of an electric-dipole source. A quantum electrodynamical calculation using this term gives the Casimir-Polder potential [9]. Higher-order terms of Eq. (2.12) are used in the present work to calculate higher multipole contributions to the dispersion energy shift and in particular discriminatory interaction energies dependent upon the relative handedness of the molecules.

III. DISCRIMINATORY DISPERSION INTERACTIONS

A. Perturbation approach

The leading contribution to the discriminatory dispersion energy arises from mixed electric-dipole–magnetic-dipole interactions. The contributions are of fourth order where each molecule is associated with one $-\varepsilon_0^{-1}\boldsymbol{\mu}\cdot\mathbf{d}$ and one $-\mathbf{m}\cdot\mathbf{b}$ interaction terms. Forty-eight diagrams allowing for different time orderings of the two types of vertices contribute to the energy shift. They may be grouped into 12 sets of 4. The graphs within each set have the same energy denominators, but differ in the ordering of the vertices. For the four diagrams of the type shown in Fig. 1, with the common energy denominator $(E_{n0}+\hbar ck')(\hbar ck+\hbar ck')(E_{n0}+\hbar ck)$, but with different orderings of the vertices, the contribution to the interaction energy, using the matrix elements Eqs. (2.8) and (2.9) for the electric- and magnetic-dipole couplings, is

$$\Delta E=\sum_{\substack{m,n\\ \mathbf{k},\mathbf{k}'}}\left[\frac{\hbar k}{2\varepsilon_0 V}\right]\left[\frac{hk'}{2\varepsilon_0 V}\right]\mu_k^{0m}m_l^{m0}\mu_i^{0n}m_j^{n0}$$

$$\times[(\delta_{ik}-\hat{k}_i\hat{k}_k)(\delta_{jl}-\hat{k}'_j\hat{k}'_l)-\varepsilon_{ilm}\varepsilon_{kjn}(\hat{k}_m\hat{k}'_n+\hat{k}'_m\hat{k}_n)+(\delta_{ik}-\hat{k}'_i\hat{k}'_k)(\delta_{jl}-\hat{k}_j\hat{k}_l)]$$

$$\times\frac{e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}}{(E_{n0}+\hbar ck')(\hbar ck+\hbar ck')(E_{n0}+\hbar ck)}\ , \qquad (3.1)$$

where $\hat{\mathbf{k}}$ is the unit wave vector and the polarization sums have been performed using

$$\sum_\lambda e_i^{(\lambda)}(\mathbf{k})\bar{e}_j^{(\lambda)}(\mathbf{k})=(\delta_{ij}-\hat{k}_i\hat{k}_j)\ , \qquad (3.2)$$

$$\sum_\lambda e_i^{(\lambda)}(\mathbf{k})\bar{b}_j^{(\lambda)}(\mathbf{k})=\varepsilon_{ijk}\hat{k}_k\ , \qquad (3.3)$$

$$\sum_\lambda b_i^{(\lambda)}(\mathbf{k})\bar{b}_j^{(\lambda)}(\mathbf{k})=(\delta_{ij}-\hat{k}_i\hat{k}_j)\ . \qquad (3.4)$$

The angular integrations can be done with the aid of

$$\tau_{ij}(kR)=\frac{1}{4\pi}\int(\delta_{ij}-\hat{k}_i\hat{k}_j)e^{\pm\mathbf{k}\cdot\mathbf{R}}d\Omega \qquad (3.5)$$

$$=(\delta_{ij}-\hat{R}_i\hat{R}_j)\frac{\sin kR}{kR}+(\delta_{ij}-3\hat{R}_i\hat{R}_j)\left[\frac{\cos kR}{k^2R^2}-\frac{\sin kR}{k^3R^3}\right]\ , \qquad (3.6)$$

$$\mp i\eta_{ij}(kR)=\frac{1}{4\pi}\varepsilon_{ijk}\int\hat{k}_k e^{\pm i\mathbf{k}\cdot\mathbf{R}}d\Omega=\mp i\varepsilon_{ijk}\left[\frac{\cos kR}{kR}-\frac{\sin kR}{k^2R^2}\right]\hat{R}_k\ . \qquad (3.7)$$

The other 44 graphs may be grouped into 11 sets of 4, each set having a different energy denominator product. The contributions from these graphs are obtained in a similar manner and summed. In the summation step the energy denominators are decomposed into partial fractions in a manner similar to that used in the Casimir-Polder potential calculation [15]. The expression for the energy shift, which consists of two parts, one symmetric and one antisymmetric in k and k' is

$$\Delta E=-\frac{1}{4\pi^4\varepsilon_0^2\hbar c^3}\sum_{m,n}\frac{\mu_i^{0n}m_j^{n0}\mu_k^{0m}m_l^{m0}}{(k_{m0}+k_{n0})}$$

$$\times\int_0^\infty\int_0^\infty dk\,dk'k^3k'^3\left[\frac{1}{k+k'}-\frac{1}{k-k'}\right]$$

$$\times\left\{[\tau_{ik}(kR)\tau_{jl}(k'R)+\tau_{ik}(k'R)\tau_{jl}(kR)]\left[\frac{k}{(k_{m0}+k)(k_{n0}+k)}\right]\right.$$

$$\left.+[\eta_{il}(kR)\eta_{kj}(k'R)+\eta_{il}(k'R)\eta_{kj}(kR)]\left[\frac{k'}{(k_{m0}+k')(k_{kj}+k')}\right]\right\}\ . \qquad (3.8)$$

Integrating over k' and changing the k integral to one over an imaginary wave-vector u, we obtain

$$\Delta E = -\frac{1}{4\pi^3\varepsilon_0^2\hbar c^3}\sum_{m,n}\mu_i^{0n}m_j^{n0}\mu_k^{0m}m_l^{m0}\int_0^\infty du\frac{u^8 e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)}\left\{\frac{a_{ijkl}}{u^2R^2}+\frac{b_{ijkl}}{u^3R^3}+\frac{c_{ijkl}}{u^4R^4}+\frac{d_{ijkl}}{u^5R^5}+\frac{e_{ijkl}}{u^6R^6}\right\}, \tag{3.9}$$

where

$$\begin{aligned} a_{ijkl} &= \alpha_{ik}\alpha_{jl} - \varepsilon_{ils}\varepsilon_{jkt}\hat{R}_s\hat{R}_t , \\ b_{ijkl} &= \alpha_{ik}\beta_{jl} + \beta_{ik}\alpha_{jl} - 2\varepsilon_{ils}\varepsilon_{jkt}\hat{R}_s\hat{R}_t , \\ c_{ijkl} &= \alpha_{ik}\beta_{jl} + \beta_{ik}\alpha_{jl} + \beta_{ik}\beta_{jl} - \varepsilon_{ils}\varepsilon_{jkt}\hat{R}_s\hat{R}_t , \\ d_{ijkl} &= 2\beta_{ik}\beta_{jl} , \\ e_{ijkl} &= \beta_{ik}\beta_{jl} , \end{aligned} \tag{3.10}$$

with the dyadics α_{ij} and β_{ij} defined by

$$\alpha_{ij} = (\delta_{ij} - \hat{R}_i\hat{R}_j) , \quad \beta_{ij} = (\delta_{ij} - 3\hat{R}_i\hat{R}_j) . \tag{3.11}$$

Before proceeding to examine the asymptotic behavior of Eq. (3.9), we use the response method to derive the energy shift Eq. (3.9).

B. Response method

Transitions in chiral molecules are in general simultaneously electric- and magnetic-dipole allowed. A consequence of this is that a chiral molecule possesses a mixed dynamic polarizability tensor $G_{ij}(\omega)$, an electric-magnetic analog of the electric-dipole polarizability tensor, defined by

$$G_{ij}(\omega) = \sum_r \left\{ \frac{\mu_i^{0r}m_j^{r0}}{E_{r0}-\hbar\omega} + \frac{m_j^{0r}\mu_i^{r0}}{E_{r0}+\hbar\omega} \right\} . \tag{3.12}$$

In contrast to the electric-dipole polarizability tensor $\alpha_{ij}(\omega)$, the sign of the mixed tensor $G_{ij}(\omega)$ depends on the handedness of the enantiomer and it is this property that leads to dispersion interactions that depend on the relative handedness of the molecules. The discriminatory interaction energy, correct to second order in the moments, between two nonidentical chiral molecules is found from the response of one molecule to the fields of the other. It is given by

$$\begin{aligned} \Delta E = {} & \mathrm{Im}\left[\frac{i}{\varepsilon_0}\sum_m G_{ij}^B(\omega_{m0})[d_i^{(1)A}(\mu;\omega_{m0})b_j^{(1)A}(\mathrm{m};\omega_{m0}) + d_i^{(1)A}(\mathrm{m};\omega_{m0})b_j^{(1)A}(\mu;\omega_{m0})]\right] \\ & - \mathrm{Im}\left[\frac{i}{\varepsilon_0}\sum_{\mathbf{k},\lambda} G_{ij}^B(\omega)[b_j^{(0)}d_i^{(2)A}(\mu\mathrm{m}) + b_j^{(2)A}(\mu\mathrm{m})d_i^{(0)}]\right] . \end{aligned} \tag{3.13}$$

In Eq. (3.13) molecule A has been chosen to be the source and B the test body. The final expression for the energy is of course independent of this choice. We note that the term dependent on the zero-order field is a self-energy term and is not dependent on the source A. Also the term linear in the moments does not contribute to the energy shift as it involves an overall change in the photon number. The first term of Eq. (3.13) represents the response of molecule B through its mixed polarizability $G_{ij}^B(\omega_{m0})$ at frequency ω_{m0} to the first-order fields associated with the transition $m \leftarrow 0$ of A. The second term represents the response of B to the second-order field A and the vacuum field. Using the electric- and magnetic-dipole-dependent Maxwell fields linear in the moments, derived in Ref. [11], the first term of Eq. (3.13) is found to be

$$\frac{1}{16\pi^2\varepsilon_0^2c^2}\sum_m G_{ij}^B(k_{m0})\mu_k^{0m}m_l^{m0}k_{m0}^6\left[\frac{(\alpha_{ik}\alpha_{jl}+\varepsilon_{jls}\varepsilon_{ikt}\hat{R}_s\hat{R}_t)}{k_{m0}^2R^2} + \frac{(\beta_{ik}\beta_{jl}-\alpha_{ik}\beta_{jl}-\beta_{ik}\alpha_{jl}+\varepsilon_{ikt}\varepsilon_{jls}\hat{R}_s\hat{R}_t)}{k_{m0}^4R^4} + \frac{\beta_{ik}\beta_{jl}}{k_{m0}^6R^6}\right] . \tag{3.14}$$

An evaluation of the contribution dependent on the zeroth- and second-order fields of Eq. (3.13) with the aid of the expansions for the free field and the second-order fields gives

$$-\frac{1}{16\pi^2\varepsilon_0^2c^2}\sum_m G_{ij}^B(k_{m0})\mu_k^{0m}m_l^{m0}k_{m0}^6\left[\frac{(\alpha_{ik}\alpha_{jl}+\varepsilon_{jls}\varepsilon_{ikt}\hat{R}_s\hat{R}_t)}{k_{m0}^2R^2}+\frac{(\beta_{ik}\beta_{jl}-\alpha_{ik}\beta_{jl}-\beta_{ik}\alpha_{jl}+\varepsilon_{ikt}\varepsilon_{jls}\hat{R}_s\hat{R}_t)}{k_{m0}^4R^4}+\frac{\beta_{ik}\beta_{jl}}{k_{m0}^6R^6}\right]$$
$$-\frac{1}{4\pi^3\varepsilon_0^2\hbar c^3}\sum_{m,n}\mu_i^{0n}m_j^{n0}\mu_k^{0m}m_l^{m0}\int_0^\infty du\frac{u^8e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)}\left\{\frac{a_{ijkl}}{u^2R^2}+\frac{b_{ijkl}}{u^3R^3}+\frac{c_{ijkl}}{u^4R^4}+\frac{d_{ijkl}}{u^5R^5}+\frac{e_{ijkl}}{u^6R^6}\right\},\qquad(3.15)$$

where $a_{ijkl},\ldots,e_{ijkl}$ are given by Eqs. (3.10). It may be noted that the contribution Eq. (3.14), dependent on the first-order fields, exactly cancels the first term of Eq. (3.15). A similar cancellation has been noted in earlier calculations on the Casimir-Polder potential [16]. So the total interaction energy is simply the u-integral term of Eq. (3.15) and is identical to Eq. (3.9) obtained in Sec. III A by standard perturbation theory.

C. Complete potential for randomly oriented molecules

Expression (3.9) applies to a molecular pair with fixed relative orientations and may also be written in terms of the mixed-polarizability tensor G_{ij} over imaginary frequency as

$$\frac{\hbar}{16\pi^3\varepsilon_0^2c}\int_0^\infty du\,u^6e^{-2uR}G_{ij}^A(icu)G_{kl}^B(icu)$$
$$\times\left\{\frac{a_{ijkl}}{u^2R^2}+\frac{b_{ijkl}}{u^3R^3}+\frac{c_{ijkl}}{u^4R^4}+\frac{d_{ijkl}}{u^5R^5}+\frac{e_{ijkl}}{u^6R^6}\right\}\qquad(3.16)$$

or in terms of the rotary strength $R_{ij}^{s0}=\mathrm{Im}(\mu_i^{0s}m_j^{s0})$. To deal with molecules in the fluid phase, a rotational average of Eq. (3.16) is needed. By following the standard procedure [17], the discriminatory dispersion interaction energy for two freely rotating chiral molecules valid for all separation distances beyond the electron overlap is

$$-\frac{1}{18\pi^3\varepsilon_0^2\hbar c^3R^4}\sum_{m,n}|\boldsymbol{\mu}^{0m}\cdot\mathbf{m}^{m0}|\,|\boldsymbol{\mu}^{0n}\cdot\mathbf{m}^{n0}|$$
$$\times\int_0^\infty\frac{du\,u^4e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)}\left[4+\frac{6}{uR}+\frac{3}{u^2R^2}\right].\qquad(3.17)$$

D. Asymptotic behavior

We now examine the asymptotic behavior of Eq. (3.17) in the limits of large and small intermolecular separation. In the far-zone limit ($kR\gg1$) the molecular separation is much larger than the wavelengths of the molecular transitions. In the denominator of Eq. (3.17) u^2 may be ignored in relation to k_{m0} and k_{n0}. After performing the u integral, the discriminatory interaction energy in the far-zone limit is found to be

$$\Delta E_{\mathrm{FZ}}=\frac{-\hbar^3c}{3\pi^3\varepsilon_0^2R^9}\sum_{m,n}\frac{|\boldsymbol{\mu}^{0m}\cdot\mathbf{m}^{m0}|\,|\boldsymbol{\mu}^{0n}\cdot\mathbf{m}^{n0}|}{E_{m0}^2E_{n0}^2},\qquad(3.18)$$

in agreement with previous work [6]. In the near-zone limit ($kR\ll1$) it is sufficient to retain the leading term of Eq. (3.17), namely, the R^{-6}-dependent term, and the exponential factor can be set to unity. The near-zone shift is then found to be [7]

$$\Delta E_{\mathrm{NZ}}=\frac{-1}{12\pi^2\varepsilon_0^2c^2R^6}\sum_{m,n}\frac{|\boldsymbol{\mu}^{0m}\cdot\mathbf{m}^{m0}|\,|\boldsymbol{\mu}^{0n}\mathbf{m}^{n0}|}{E_{m0}+E_{n0}}.\qquad(3.19)$$

To obtain Eq. (3.19) from Eq. (3.17) we have used

$$\frac{1}{a+b}=\frac{2}{\pi}\int_0^\infty du\frac{u^2}{(a^2+u^2)(b^2+u^2)}.\qquad(3.20)$$

We mention in passing that the near-zone result Eq. (3.19) can also be obtained using second-order perturbation theory with static dipole-dipole coupling potentials

$$V_{ij}(\mu\mu)=\frac{\mu_i^A\mu_j^B}{4\pi\varepsilon_0R^3}(\delta_{ij}-3\hat{R}_i\hat{R}_j),\qquad(3.21)$$

$$V_{ij}(mm)=\frac{m_i^Am_j^B}{4\pi\varepsilon_0c^2R^3}(\delta_{ij}-3\hat{R}_i\hat{R}_j).\qquad(3.22)$$

The result for all R is given by Eq. (3.17) and those for large and small intermolecular separations are respectively given by Eqs. (3.18) and (3.19). This interaction potential is discriminatory, dependent upon the relative chirality of the molecules of the pair. The polarizability tensor $G_{ij}(\omega)$ changes sign with enantiomer since $\boldsymbol{\mu}$, a polar vector, is antisymmetric to inversion, in contrast to $\mathbf{m}$, which is symmetric. For molecules with absolute configurations R and S, the $A(R)$-$B(R)$ and $A(R)$-$B(S)$ interactions differ in sign. Since the rotary strength may be either greater or less than zero, it is not possible to determine the absolute sign of the interaction when the molecules are chemically distinct. For chemically identical molecules, however, the energy shift for opposite isomers is attractive, while that for like isomers is repulsive. The R^{-9} far-zone and R^{-6} near-zone results agree with those of Mavroyannis and Stephen [6] and Craig, Power, and Thirunamachandran [7].

IV. INTERACTION BETWEEN TWO MOLECULES WITH MIXED ELECTRIC-DIPOLE–ELECTRIC QUADRUPOLE POLARIZABILITIES

Electric-quadrupole interactions are of the same order as magnetic-dipole interactions. We now calculate the energy shifts dependent on the mixed electric-dipole–electric-quadrupole interactions and examine whether discriminatory energies analogous to those calculated in Sec. III exist. The calculations follow the same pattern and an outline of the calculations using the two methods is given.

A. The complete potential

As in Sec. III B, the energy shift is found from he response of one molecule to the fields of the other. The dispersion energy correct to second order is obtained from

$$\begin{aligned}\Delta E=&-\frac{1}{2\varepsilon_0^2}\sum_m A_{ijk}^B(\omega_{m0})[d_i^{(1)}(\mu;\omega_{m0})\nabla_k d_j^{(1)}(\mathrm{Q};\omega_{m0})+d_i^{(1)}(\mathrm{Q};\omega_{m0})\nabla_k d_j^{(1)}(\mu;\omega_{m0})\\&+\nabla_k d_j^{(1)}(\mu;\omega_{m0})d_i^{(1)}(\mathrm{Q};\omega_{m0})+\nabla_k d_j^{(1)}(\mathrm{Q};\omega_{m0})d_i^{(1)}(\mu;\omega_{m0})]\\&-\frac{1}{2\varepsilon_{b0}^2}\sum_{\mathbf{k},\lambda} A_{ijk}^B(\omega)[d_i^{(0)}\nabla_k d_j^{(2)}(\mu\mathrm{Q})+d_i^{(2)}(\mu\mathrm{Q})\nabla_k d_j^{(0)}+\nabla_k d_j^{(0)}d_i^{(2)}(\mu\mathrm{Q})+\nabla_k d_j^{(2)}(\mu\mathrm{Q})d_i^{(0)}]\ ,\end{aligned} \tag{4.1}$$

where the fields are those of A evaluated at the position of the test molecule B. Using the electric-dipole- and electric-quadrupole-dependent first-order and second-order displacement fields [11] in Eq. (4.1), we obtain

$$\begin{aligned}&-\frac{1}{8\pi^3\varepsilon_0^2\hbar c}\sum_{m,n}\mu_i^{0n}Q_{jk}^{n0}\mu_l^{0m}Q_{mn}^{m0}\\&\times\int_0^\infty du\frac{u^8e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)}k_{m0}k_{n0}\\&\times\left[\frac{P_{ijklmn}}{u^2R^2}+\frac{Q_{ijklmn}}{u^3R^3}+\frac{R_{ijklmn}}{u^4R^4}+\frac{S_{ijklmn}}{u^5R^5}\right.\\&\qquad\left.+\frac{T_{ijklmn}}{u^6R^6}+\frac{U_{ijklmn}}{u^7R^7}+\frac{V_{ijklmn}}{u^8R^8}\right]\ .\end{aligned} \tag{4.2}$$

Explicit expressions for the tensors $P_{ijklmn},\ldots,V_{ijklmn}$ are given in the Appendix.

The energy shift Eq. (4.2) has also been calculated using fourth-order perturbation theory. The calculation follows the same lines as in Sec. III A, after replacing the magnetic-dipole interaction by the electric-quadrupole interaction terms of Eq. (2.5). The number of graphs is again 48 and each diagram contains one electric dipole and one quadrupole vertex of each molecule. The relevant contributions from the diagrams are found with the aid of the electric-dipole and -quadrupole matrix elements Eqs. (2.8) and (2.10). Collecting terms from the 48 diagrams and integrating over k' leads to the shift Eq. (4.2).

B. Asymptotic limits

In the far zone, the energy shift shows an R^{-9} dependence and is given by

$$\begin{aligned}\Delta E_{\mathrm{FZ}}=&-\frac{\hbar c}{256\pi^3\varepsilon_0^2R^9}A_{ijk}^B(0)A_{lmn}^A(0)\\&\times[45P_{ijklmn}+15Q_{ijklmn}+6R_{ijklmn}\\&+3S_{ijklmn}+2T_{ijklmn}+2U_{ijklmn}+4V_{ijklmn}]\ ,\end{aligned} \tag{4.3}$$

where $A_{ijk}(0)$ is the static mixed polarizability tensor

$$A_{ijk}(0)=2\sum_r\frac{\mu_i^{0r}Q_{jk}^{r0}}{E_{r0}}\ . \tag{4.4}$$

In the near zone, the shift Eq. (4.2) shows an R^{-8} dependence, as expected, and is

$$\Delta E_{\mathrm{NZ}}=\frac{1}{16\pi^2\varepsilon_0^2R^8}\sum_{m,n}\frac{\mu_i^{0n}Q_{jk}^{n0}\mu_l^{0m}Q_{mn}^{m0}}{E_{m0}+E_{n0}}V_{ijklmn}\ . \tag{4.5}$$

The near-zone result Eq. (4.5) may also be obtained with second-order perturbation theory and the electrostatic potentials coupling two electric dipoles (3.21), an electric dipole and an electric quadrupole (4.6), and two electric quadrupoles (4.7):

$$\begin{aligned}V_{ijk}(\mu\mathrm{Q})=&\frac{\mu_i^AQ_{jk}^B}{4\pi\varepsilon_0R^4}[-3(\delta_{ij}\hat{R}_k+\delta_{jk}\hat{R}_i+\delta_{ik}\hat{R}_j)\\&+15\hat{R}_i\hat{R}_j\hat{R}_k]\ ,\end{aligned} \tag{4.6}$$

$$\begin{aligned}V_{ijkl}(\mathrm{QQ})=&\frac{Q_{ij}^AQ_{kl}^B}{4\pi\varepsilon_0R^5}[-3(\delta_{ij}\delta_{kl}+\delta_{jk}\delta_{il}+\delta_{ik}\delta_{jl})\\&+15(\delta_{ij}\hat{R}_k\hat{R}_l+\delta_{jk}\hat{R}_i\hat{R}_l+\delta_{ik}\hat{R}_j\hat{R}_l\\&+\delta_{jl}\hat{R}_i\hat{R}_k+\delta_{il}\hat{R}_j\hat{R}_k+\delta_{kl}\hat{R}_i\hat{R}_j)\\&-105\hat{R}_i\hat{R}_j\hat{R}_k\hat{R}_l]\ .\end{aligned} \tag{4.7}$$

Expressions (4.2), (4.3), and (4.5) hold for oriented molecules and are discriminatory since the tensor $\mu_i^{0r}Q_{jk}^{r0}$ depends on the handedness of the molecule. However, they vanish on random orientational averaging since the tensor $\mu_i^{0r}Q_{jk}^{r0}$ does. This behavior is in contrast to that found in Sec. III, where the discriminatory shifts dependent on mixed electric and magnetic interactions survive random averaging. Thus Eq. (3.9) is the sole contribution to the discriminatory energy shift to this order for a pair of randomly oriented molecules.

V. INTERACTION BETWEEN AN ELECTRIC-DIPOLE POLARIZABLE MOLECULE AND A MAGNETIC-DIPOLE POLARIZABLE MOLECULE

A. The complete potential

We now consider nondiscriminatory interactions which are of the same order as those calculated in the previous sections. In this section we obtain the interaction energy for a pair of molecules, one with electric-dipole polarizability α_{ij} and another with magnetic susceptibility χ_{ij}. This can be evaluated in two ways, depending on which molecule we choose as the source and which as the test. The result is of course independent of the choice. Taking A as the magnetic-dipole polarizable source and calculating the response of B to the Maxwell fields of A we calculate the interaction energy using

$$\Delta E = -\frac{1}{2\varepsilon_0^2}\alpha_{ij}^B d_i^A(\mathbf{R}_B) d_j^A(\mathbf{R}_B) \ , \tag{5.1}$$

where $\mathbf{d}^A(\mathbf{R}_B)$ is the displacement vector field of A at $\mathbf{R}_B$. Expanding the field of A in powers of magnetic moments and extracting the relevant terms we have

$$\begin{aligned}\Delta E = &-\frac{1}{2\varepsilon_0^2}\sum_m \alpha_{ij}^B(\omega_{m0}) d_i^{(1)}(\mathrm{m};\omega_{m0}) d_j^{(1)}(\mathrm{m};\omega_{m0}) \\ &-\frac{1}{2\varepsilon_0^2}\sum_{\mathbf{k},\lambda}\alpha_{ij}^B(\omega)[d_i^{(0)} d_j^{(2)}(\mathrm{mm}) + d_i^{(2)}(\mathrm{mm}) d_j^{(0)}] \ .\end{aligned} \tag{5.2}$$

As in the previous sections, the first term of Eq. (5.2), which depends on the first-order field, exactly cancels part of the second term, leaving behind only a u-integral contribution. It is given by

$$\begin{aligned}&\frac{1}{8\pi^3\varepsilon_0^2\hbar c^3}\varepsilon_{jlt}\varepsilon_{iks}\hat{R}_s\hat{R}_t\sum_{m,n}\mu_i^{0n}\mu_j^{n0} m_k^{0m} m_l^{m0} \\ &\quad\times\int_0^\infty du \frac{u^6 e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)} k_{m0}k_{n0} \\ &\quad\times\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\right] ,\end{aligned} \tag{5.3}$$

which after rotational averaging becomes

$$\begin{aligned}&\frac{1}{36\pi^3\varepsilon_0^2\hbar c^3}\sum_{m,n}|\boldsymbol{\mu}^{n0}|^2|\mathbf{m}^{m0}|^2 \\ &\quad\times\int_0^\infty du \frac{u^6 e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)} k_{m0}k_{n0} \\ &\quad\times\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\right] ,\end{aligned} \tag{5.4}$$

in agreement with previous work [10].

In the perturbation approach, 12 diagrams contribute to the energy shift. The interaction vertices of A are of the magnetic-dipole type and those of B are of the electric-dipole type. The matrix elements are calculated using Eqs. (2.8) and (2.9); the polarization sums performed with Eq. (3.3) and the angular integrations with the aid of Eq. (3.7). The total contribution from the 12 graphs may be written as

$$\begin{aligned}\Delta E = &\frac{1}{4\pi^4\varepsilon_0^2\hbar c^3}\sum_{m,n}\frac{\mu_i^{0n} m_j^{n0}\mu_k^{0m} m_l^{m0}}{(k_{m0}+k_{n0})} \\ &\times\int_0^\infty\int_0^\infty dk\, dk' k^3 k'^3 \eta_{ik}(k'R)\eta_{jl}(kR) \\ &\times\left[\frac{k_{m0}+k_{n0}+k'}{(k_{m0}+k)(k_{n0}+k)}\right] \\ &\times\left[\frac{1}{k+k'}-\frac{1}{k-k'}\right] .\end{aligned} \tag{5.5}$$

Integrating over k' and changing the k integral to one over imaginary frequency, we find the expression for the energy shift to be identical with Eq. (5.3).

B. Asymptotic behavior

For $kR \ll 1$, Eq. (5.4) becomes

$$\Delta E_{\mathrm{NZ}} = \frac{1}{72\pi^2\varepsilon_0^2\hbar^2 c^4 R^4}\sum_{m,n}\frac{|\mathbf{m}^{m0}|^2|\boldsymbol{\mu}^{n0}|^2}{E_{m0}+E_{n0}} E_{m0}E_{n0} \ . \tag{5.6}$$

It should be noted that Eq. (5.6) is not the static limit because there is no static coupling between an electric dipole and a magnetic dipole. Equation (5.6) is retarded and is the leading term in the small-R limit. In the far zone, Eq. (5.4) shows an R^{-7} dependence and is given by

$$\Delta E_{\mathrm{FZ}} = \frac{7\hbar}{64\pi^3\varepsilon_0^2 c R^7}\chi^A(0)\alpha^B(0) \ , \tag{5.7}$$

where $\chi(0)$ and $\alpha(0)$ respectively are the isotropic static magnetic-dipole susceptibility and the static electric-dipole polarizability of molecules A and B [6,10]. It should be noted that in contrast to the attractive nature of the Casimir-Polder potential, the dispersion energy Eq. (5.4) is repulsive.

C. Contribution from diamagnetic coupling

The energy shift Eq. (5.3) is incomplete in that no account has been taken of the diamagnetic coupling term. This coupling is quadratic in the charge and can therefore give an energy shift of the same order as that found above in Eq. (5.3). The response of B to the part of the field that is dependent on the diamagnetic source term of A is given by

$$\begin{aligned}\Delta E = &\frac{e^2}{8m}\varepsilon_{ikp}\varepsilon_{jlp} \\ &\times\sum_{\mathbf{k},\lambda}(q_i q_j)^A[b_k^{(0)} b_l^{(2)B}(\boldsymbol{\mu\mu}) + b_k^{(2)B}(\boldsymbol{\mu\mu}) b_l^{(0)}] \ .\end{aligned} \tag{5.8}$$

Using the expressions for the fields found earlier [11], we obtain

$$\begin{aligned}\Delta E = &-\frac{e^2}{64\pi^2\varepsilon_0^2 m c^2} \\ &\times\sum_n (q_i q_j)^A \mu_m^{0n}\mu_n^{n0}\varepsilon_{ikp}\varepsilon_{jlp}\varepsilon_{kms}\varepsilon_{lnt}\hat{R}_s\hat{R}_t \\ &\times\int_0^\infty du \frac{u^6 e^{-2uR}}{(k_{n0}^2+u^2)} \\ &\times k_{n0}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\right] ,\end{aligned} \tag{5.9}$$

which on averaging gives

$$-\frac{e^2}{144\pi^3\varepsilon_0^2c^2m}\sum_n|\mu^{n0}|^2\langle q^2\rangle^A\int_0^\infty du\frac{u^6e^{-2uR}}{(k_{n0}^2+u^2)}\times k_{n0}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\right] . \tag{5.10}$$

In the diagrammatic perturbation theory approach, the interaction vertex of A is a two-photon vertex representing the diamagnetic coupling. Three graphs of the type shown in Fig. 2 contribute to the energy shift. The sum is found to be

$$\Delta E=\frac{e^2}{64\pi^3m\varepsilon_0^2c^2}(\delta_{il}\delta_{ju}\delta_{fg}-\delta_{il}\delta_{jf}\delta_{ug}-\delta_{ig}\delta_{ju}\delta_{lf}+\delta_{ij}\delta_{lf}\delta_{ug})\times\sum_n\mu_i^{0n}\mu_j^{n0}(q_lq_u)^A\hat{R}_f\hat{R}_g\times\int_0^\infty\frac{1}{k_{n0}+k}\left[-\frac{\sin2kR}{k^2R^2}-2\frac{\cos2kR}{k^3R^3}+\frac{\sin2kR}{k^4R^4}\right]k^6dk . \tag{5.11}$$

Equation (5.11) is the same as Eq. (5.9) when expressed in imaginary frequencies.

D. Asymptotic behavior of the diamagnetic term

In the far zone, Eq. (5.10) reduces to

$$\Delta E_{\mathrm{FZ}}=\frac{3e^2\hbar}{128\pi^3\varepsilon_0^2mcR^7}\alpha^B(0)\langle q^2\rangle^A , \tag{5.12}$$

illustrating that at large intermolecular separations, the diamagnetic contribution to the dispersion interaction varies as R^{-7}. This result may be combined with Eq. (5.7), where the far-zone limit was also expressed in terms of the static electric-dipole polarizability of molecule B. From Eqs. (5.7) and (5.12),

$$\Delta E_{\mathrm{FZ}}^{\mathrm{tot}}=\frac{7\hbar}{64\pi^3\varepsilon_0^2cR^7}\alpha^B(0)\chi'^A(0) , \tag{5.13}$$

where the new, modified magnetic susceptibility tensor is defined by

$$\chi'^A(0)=\chi^A(0)-\frac{e^2}{6m}\langle q^2\rangle^A . \tag{5.14}$$

Although both $\alpha(0)$ and $\chi(0)$ are positive for molecules in the ground state, $\chi'(0)$ may be either positive or negative depending on the relative sizes of the two terms in Eq. (5.14). A molecule is termed diamagnetic if $\chi'(0) < 0$. Returning to Eq. (5.10) and examining the near-zone behavior, after the usual approximations, the leading term is found to be

$$\Delta E_{\mathrm{NZ}}=\frac{-e^2}{288\pi^3\varepsilon_0^2c^2mR^5}\sum_n|\mu^{n0}|^2\langle q^2\rangle^Ak_{n0} . \tag{5.15}$$

Comparing Eq. (5.15) with the corresponding limit Eq. (5.6) obtained between electric-dipole and magnetic-dipole polarizable molecules, the ratio of the two is given by

$$\frac{\Delta E_{\mathrm{NZ}}(\alpha\chi)}{\Delta E_{\mathrm{NZ}}(\mathrm{dia})}\simeq kR . \tag{5.16}$$

In the near zone, where $kR << 1$, the contribution from the diamagnetic coupling term dominates the interaction.

VI. INTERACTION BETWEEN AN ELECTRIC-DIPOLE POLARIZABLE MOLECULE AND AN ELECTRIC-QUADRUPOLE POLARIZABLE MOLECULE

A. The complete potential

Magnetic-dipole and electric-quadrupole couplings are of the same order, and contributions to energy shift from interactions between a molecule with electric-dipole polarizability and one with electric-quadrupole polarizability are therefore comparable to those found in the preceding section. In this section we calculate this shift by the two methods. For the response method we choose molecule A with quadrupole polarizability as the source and B with dipole polarizability as the test. The interaction energy arising from the response of B to the fields of A is found to be

$$\Delta E=-\frac{1}{2\varepsilon_0^2}\sum_m\alpha_{ij}^B(\omega_{m0})d_i^{(1)}(\mathrm{Q};\omega_{m0})d_j^{(1)}(\mathrm{Q};\omega_{m0})-\frac{1}{2\varepsilon_0^2}\sum_{\mathbf{k},\lambda}\alpha_{ij}^B(\omega)[d_i^{(0)}d_j^{(2)}(\mathrm{QQ})+d_i^{(2)}(\mathrm{QQ})d_j^{(0)}] . \tag{6.1}$$

Using the electric-quadrupole displacement fields, evaluated in Ref. [11], and the free field in Eq. (6.1), we obtain

$$-\frac{1}{8\pi^3\varepsilon_0^2\hbar c}\sum_{m,n}\mu_i^{0n}\mu_j^{n0}Q_{kl}^{0m}Q_{mn}^{m0}\times\int_0^\infty du\frac{u^8e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)}k_{m0}k_{n0}\times\left[\frac{A_{ijklmn}}{u^2R^2}+\frac{B_{ijklmn}}{u^3R^3}+\frac{C_{ijklmn}}{u^4R^4}+\frac{D_{ijklmn}}{u^5R^5}+\frac{E_{ijklmn}}{u^6R^6}+\frac{F_{ijklmn}}{u^7R^7}+\frac{G_{ijklmn}}{u^8R^8}\right] . \tag{6.2}$$

Explicit expressions for the geometric tensors $A_{ijklmn},\ldots,G_{ijklmn}$ are given in the Appendix. As in previous cases, the contribution from the first-order fields is exactly canceled by a contribution from the free-field–second-order field term, namely, the second term of Eq. (6.1). It should be emphasized that for a pair of molecules with one or both in excited states, this cancellation does not occur; the two contributions in fact reinforce each other resulting in an additional contribution to the energy shift. Expression (6.2) is applicable at all separations outside electron overlap for an oriented pair. To obtain the interaction for a randomly oriented pair, an orientational average is performed and Eq. (6.2) becomes

$$-\frac{1}{720\pi^3\varepsilon_0^2\hbar c}\sum_{m,n}|\mu^{0n}|^2 Q^{0m}_{\lambda\mu}Q^{m0}_{\lambda\mu}$$

$$\times\int_0^\infty du\frac{u^8 e^{-2uR}}{(k_{m0}^2+u^2)(k_{n0}^2+u^2)}k_{m0}k_{n0}$$

$$\times\left[\frac{6}{u^2R^2}+\frac{36}{u^3R^3}+\frac{162}{u^4R^4}+\frac{504}{u^5R^5}\right.$$

$$\left.+\frac{972}{u^6R^6}+\frac{1080}{u^7R^7}+\frac{540}{u^8R^8}\right] . \qquad (6.3)$$

The calculation of the dispersion energy using diagrammatic perturbation theory involves steps similar to those in the previous sections and details may be found in Ref. [17]. Suffice it to remark that 12 graphs with electric-quadrupole vertices for A and electric-dipole ones for B are used together with the matrix elements Eqs. (2.8) and (2.10).

B. Asymptotic behavior

We now examine the asymptotic behavior of Eq. (6.3). In the far zone, u is small compared with k_{m0} and k_{n0} and may be neglected. The integral is then easily evaluated and the shift in the far zone can be expressed in terms of static polarizabilities as

$$\Delta E_{\mathrm{FZ}}=-\frac{1593\hbar c}{1280\pi^3\varepsilon_0^2R^9}\alpha^B(0)\theta^A_{\lambda\mu\lambda\mu}(0) , \qquad (6.4)$$

where the static electric-quadrupole polarizability $\theta^A_{\lambda\mu\lambda\mu}(0)$ is defined by

$$\theta^A_{\lambda\mu\lambda\mu}(0)=2\sum_m\frac{Q^{0m}_{\lambda\mu}Q^{m0}_{\lambda\mu}}{E_{m0}} . \qquad (6.5)$$

This asymptotic result agrees with a previous derivation [10] where the roles of the two molecules had been reversed.

In the near zone, the shift shows and R^{-8} dependence and is given by

$$\Delta E_{\mathrm{NZ}}=-\frac{3}{8\pi^2\varepsilon_0^2R^8}\sum_{m,n}\frac{|\mu^{n0}|^2 Q^{0m}_{\lambda\mu}Q^{m0}_{\lambda\mu}}{E_{m0}+E_{n0}} , \qquad (6.6)$$

which may also be written as an integral over imaginary frequencies

$$\Delta E_{\mathrm{NZ}}=-\frac{9\hbar c}{16\pi^3\varepsilon_0^2R^8}\int_0^\infty du\,\alpha^B(icu)\theta^A_{\lambda\mu\lambda\mu}(icu) . \qquad (6.7)$$

In Eq. (6.7), $\alpha(icu)$ is the electric-dipole polarizability at imaginary frequency; the electric-quadrupole polarizability $\theta_{\lambda\mu\lambda\mu}(icu)$ is defined by

$$\theta_{\lambda\mu\lambda\mu}(icu)=\frac{2}{\hbar c}\sum_m\frac{Q^{0m}_{\lambda\mu}Q^{m0}_{\lambda\mu}}{k_{m0}^2+u^2}k_{m0} . \qquad (6.8)$$

We remark that the near-zone result can also be derived using second-order perturbation theory using the dipole-quadrupole coupling potential as the perturbation.

Although the magnetic-dipole and electric-quadrupole couplings are comparable, the asymptotic behavior of the dispersion energy shifts is different in the two cases. In the near zone, it is the electric-dipole–electric-quadrupole coupling that gives the dominant contribution with an R^{-8} dependence. In the far zone, the electric-dipole–magnetic-dipole and diamagnetic couplings give the dominant contribution with an R^{-7} dependence [Eqs. (5.7) and (5.13)].

VII. SUMMARY

Retarded dispersion energies for a pair of chiral molecules have been calculated using the conventional fourth-order perturbation theory as well as a response theory. In both cases the interaction Hamiltonian includes electric-dipole, electric-quadrupole, and magnetic-dipole couplings. Diamagnetic coupling has also been included as its contributions can be comparable to those from multipole interactions. A part of the dispersion energy is discriminatory in that it depends on the relative handedness of the molecules. This contribution is expressed in two equivalent forms: one in terms of mixed electric-magnetic polarizability tensors at imaginary frequencies and the other in terms of rotatory strengths. Nondiscriminatory dispersion energies of comparable magnitude have also been calculated. They depend on electric-dipole and -quadrupole polarizabilities and magnetic susceptibilities. The contributions calculated in this paper are valid for all separations beyond the electron overlap region. Their asymptotic behavior is analyzed and compared with previous work. A possible manifestation of discriminatory interactions is the difference in the enthalpy of solution. Though previous measurements of differential enthalpy of solution have been inconclusive, more accurate experimental studies may confirm the existence of interactions that depend on the relative handedness of the molecules.

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APPENDIX: TENSOR EXPRESSIONS

In this appendix the expressions for the products of the geometric tensors that appear in Eqs. (4.2) and (6.2) are given. We first define

$$\alpha_{kl}=(\delta_{kl}-\hat{R}_k\hat{R}_l) , \qquad (\mathrm{A1})$$

$$\beta_{kl}=(\delta_{kl}-3\hat{R}_k\hat{R}_l) , \qquad (\mathrm{A2})$$

$$X_{lmn}=(\delta_{lm}\hat{R}_n+\delta_{ln}\hat{R}_m+\delta_{mn}\hat{R}_l-5\hat{R}_l\hat{R}_m\hat{R}_n) , \qquad (\mathrm{A3})$$

$$Y_{klmn}=\delta_{kl}\beta_{mn}+(\delta_{kl}\hat{R}_m\hat{R}_n-\delta_{mn}\hat{R}_k\hat{R}_l)$$
$$-(X_{klm}\hat{R}_n+X_{kln}\hat{R}_m) , \qquad (\mathrm{A4})$$

$$Z_{klmn}=(\delta_{kl}\delta_{mn}+\delta_{km}\delta_{ln}+\delta_{lm}\delta_{kn}) \qquad (\mathrm{A5})$$
$$-5(\delta_{kl}\hat{R}_m\hat{R}_n+\delta_{km}\hat{R}_l\hat{R}_n+\delta_{kn}\hat{R}_l\hat{R}_m$$
$$+\delta_{lm}\hat{R}_k\hat{R}_n+\delta_{ln}\hat{R}_k\hat{R}_m+\delta_{mn}\hat{R}_k\hat{R}_l)$$
$$+35\hat{R}_k\hat{R}_l\hat{R}_m\hat{R}_n . \qquad (\mathrm{A6})$$

We note that β_{kl} and X_{klm} appear in the expressions for the electric-dipole and electric-quadrupole fields and Z_{klmn} appears in the gradient of the electric-quadrupole field.

The tensors $A_{ijklmn}, \dots, G_{ijklmn}$ that appear in Eqs. (4.2) and (6.2) are given by

$$A_{ijklmn}=\alpha_{il}\alpha_{jm}\hat{R}_k\hat{R}_n\ , \tag{A7}$$

$$B_{ijklmn}=2\alpha_{il}\alpha_{jm}\hat{R}_k\hat{R}_n+\alpha_{il}\hat{R}_kX_{jmn}+\alpha_{jm}\hat{R}_nX_{ilk}\ , \tag{A8}$$

$$\begin{aligned}C_{ijklmn}=&\alpha_{il}\alpha_{jm}\hat{R}_k\hat{R}_n+4\alpha_{il}\hat{R}_kX_{jmn}\\&+4\alpha_{jm}\hat{R}_nX_{ilk}+X_{ilk}X_{jmn}\ ,\end{aligned} \tag{A9}$$

$$D_{ijklmn}=6(\alpha_{il}\hat{R}_kX_{jmn}+\alpha_{jm}\hat{R}_nX_{ilk}+X_{ilk}X_{jmn})\ , \tag{A10}$$

$$E_{ijklmn}=(3\alpha_{il}\hat{R}_kX_{jmn}+3\alpha_{jm}\hat{R}_nX_{ilk}+15X_{ilk}X_{jmn})\ , \tag{A11}$$

$$F_{ijklmn}=18X_{ilk}X_{jmn}\ , \tag{A12}$$

$$G_{ijklmn}=9X_{ilk}X_{jmn}\ , \tag{A13}$$

$$H_{ijklmn}=-\alpha_{il}\alpha_{kj}\hat{R}_m\hat{R}_n\ , \tag{A14}$$

$$I_{ijklmn}=-\beta_{il}\alpha_{kj}\hat{R}_m\hat{R}_n+\alpha_{il}Y_{kjmn}\ , \tag{A15}$$

$$J_{ijklmn}=-\beta_{il}\alpha_{kj}\hat{R}_m\hat{R}_n+(\alpha_{il}+\beta_{il})Y_{kjmn}+\alpha_{il}Z_{kjmn}\ , \tag{A16}$$

$$K_{ijklmn}=2\beta_{il}Y_{kjmn}+(3\alpha_{il}+\beta_{il})Z_{kjmn}\ , \tag{A17}$$

$$L_{ijklmn}=\beta_{il}Y_{kjmn}+(3\alpha_{il}+4\beta_{il})Z_{kjmn}\ , \tag{A18}$$

$$M_{ijklmn}=6\beta_{il}Z_{kjmn}\ , \tag{A19}$$

$$N_{ijklmn}=3\beta_{il}Z_{kjmn}\ , \tag{A20}$$

$$P_{ijklmn}=A_{ijklmn}+H_{ijklmn}\ , \tag{A21}$$

$$Q_{ijklmn}=B_{ijklmn}+I_{ijklmn}\ , \tag{A22}$$

$$R_{ijklmn}=C_{ijklmn}+J_{ijklmn}\ , \tag{A23}$$

$$S_{ijklmn}=D_{ijklmn}+K_{ijklmn}\ , \tag{A24}$$

$$T_{ijklmn}=E_{ijklmn}+L_{ijklmn}\ , \tag{A25}$$

$$U_{ijklmn}=F_{ijklmn}+M_{ijklmn}\ , \tag{A26}$$

$$V_{ijklmn}=G_{ijklmn}+N_{ijklmn}\ , \tag{A27}$$

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