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New approaches to chiral discrimination in coupling between molecules*

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Abstract. Results in the coupling of chiral molecules are reviewed from elementary points of view and some new results are given. We show that interactions between chiral molecules can be treated by using molecular quantum electrodynamics in electric and magnetic dipole approximation in ways different from standard diagrammatic perturbation theory. The interactions are the dispersive coupling of ground-state chiral molecules and excitation transfer, with emphasis on chiral discrimination. For ground-state molecules the coupling is dealt with first by calculating the coupling, at all separation distances, of electric and magnetic dipoles induced in the two molecules by fluctuations in the vacuum radiation field. The second method is the response by one chiral molecule to the field generated by the other. Excitation transfer is treated as the response by the accepting ground-state molecule to the dipole field of the donor. A novel variant in finding the rate of excitation transfer is by using Poynting's theorem.

Key words: Chiral discrimination – Excitation exchange – Dispersive coupling

1 Introduction

There is a long history of experimental demonstration of chiral discrimination, beginning with Pasteur [1] showing in 1858 that in attacking ammonium tartrate the mould penicillium discriminates in its rate of attack on dextro and laevo forms of the salt. He also showed that the two enantiomers of asparagine excite different physiological responses, having different flavours. However, then and for many years after, the systems that were studied were too complex to treat theoretically. Dwyer and Gyarfas [2] worked with smaller chiral systems, showing, for example, that the thermodynamic activities of the dextro and laevo forms of the ruthenium ion of tris-orthophenanthroline were different from one another in the presence of potassium D-tartrate. This work stimulated studies of model systems to represent the effects between real molecules and ions, both achiral and chiral. The experimental results and some theoretical discussions are summarized by Craig and Mellor [3].

For close approach it has been realized for a long time that the packing of molecules and ions in crystals is dominated by surface form, and can be understood in an approximate way by supposing the molecules to be bounded by hard surfaces. The energetics were modelled in calculations of intramolecular discriminations in optically active and meso forms of 2,3-cyanobutane [4]. Beyond contact distances it was generally supposed that electrostatic forces and dispersion forces become important, each with characteristic dependences on distance and orientation. At intermediate and longer distances, the main topic of this paper, there is a transition from electrostatic to electromagnetic interactions, with the central feature being that at long range the influences between molecules are mediated by the radiation field, propagated at the speed of light.

The motivation for what follows is to describe elementary physical pictures of interactions. We shall then extend recent results, particularly for the interaction of chiral systems beyond contact distance, both in dispersion interactions and excitation transfer, in which an electronically excited molecule transfers energy to another by photon exchange.

Early theories of coupling between molecules applied to separation distances R up to a few tens of molecular diameters. The idea was that charge fluctuations in one molecule acted on the other through the dipolar field: dipole moments were induced in the second molecule. The induced and inducing dipoles gave the characteristic R^{-6} interaction energy dependence, and the dipole-dipole angle dependence. In London's 1930 quantum

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mechanical version the coupling of virtual dipole transition moments replaced charge fluctuations in the classical sense, but the essential physics was the same. The extension to large R was first made by Casimir, and will be described in Sect. 1.1. He showed that at long distances the fluctuating dipoles had their effect through their radiation fields, with a characteristic R^{-7} energy law. The quantum electrodynamical theory that has since developed, applicable to all distances, includes the radiation field in the dynamics. It is interesting that the notion of fluctuations, but now of the electromagnetic field, has reappeared (Sect. 1.2) in a viewpoint that gives a clear physical picture.

As is well known [5] the discussion of interactions in terms of quantum electrodynamics depends on the treatment of molecules coupled to the quantized radiation field, with the Hamiltonian,

$$H = H_{\mathrm{mol}} + H_{\mathrm{rad}} + H_{\mathrm{int}} \ , \tag{1.1}$$

where the terms on the right refer to Hamiltonians for the free molecules, the free radiation field, and the molecule-field coupling. An essential feature of quantum electrodynamics is the quantization of the electromagnetic field. The field is subject to quantum conditions within a box. The allowed field modes are quantized according to the rules for the harmonic oscillator. The associated particles are photons, which play a key role in molecule-molecule coupling. In the multipolar form of quantum electrodynamics the leading terms that describe the coupling of the molecules to the electromagnetic field are

$$\begin{aligned} H_{\mathrm{int}} = & -\varepsilon_0^{-1}\boldsymbol{\mu}(\mathrm{A})\cdot\boldsymbol{d}(\boldsymbol{R}_{\mathrm{A}}) - \varepsilon_0^{-1}\boldsymbol{\mu}(\mathrm{B})\cdot\boldsymbol{d}(\boldsymbol{R}_{\mathrm{B}}) \\ & - \boldsymbol{m}(\mathrm{A})\cdot\boldsymbol{b}(\boldsymbol{R}_{\mathrm{A}}) - \boldsymbol{m}(\mathrm{B})\cdot\boldsymbol{b}(\boldsymbol{R}_{\mathrm{B}}) \ , \end{aligned} \tag{1.2}$$

where $\boldsymbol{\mu}$ and $\boldsymbol{m}$ are the electric and magnetic dipole moments, $\boldsymbol{d}$ and $\boldsymbol{b}$ the electric displacement field and the magnetic field, and ε_0 the vacuum permittivity. With this form of H_{int}, interactions at all distances are solely mediated by the radiation field by exchange of photons. A useful distinction is between instantaneous and retarded interactions, with a progressive change as the distance increases through and beyond the reduced wavelength for a characteristic molecular transition.

Rates of energy transfer and energy shifts are usually calculated with standard perturbation theory together with diagrammatic techniques. For example, excitation transfer between molecules may be viewed as one-photon exchange, the amplitude being found using second-order perturbation theory. Dispersion interactions arise from two-photon exchange, and standard fourth-order perturbation theory gives the dispersion energies. The aim of the present paper is to deal with these problems by methods that have familiar classical analogues.

We first sketch two physical pictures that give good physical insight. They depend on the quantum properties of the vacuum state of the radiation field. The vacuum state is the state with all modes in their ground states. It has the important property that the average value of the field is zero though the square of the field is not; that is, the field fluctuates about a mean value of zero and has a zero-point energy $(1/2)\sum \hbar\omega$, summed over the allowed frequencies ω. Though this is infinite the changes in the presence of molecules are finite and can be related to intermolecular interactions.

1.1 Molecular interaction energy as a perturbation of the electromagnetic vacuum

The physical pictures to be described are both connected to aspects of the quantized field. In the first, Casimir [6] developed the idea that a polarizable atom or molecule placed in a box would change the electromagnetic zero-point energy. The energy change caused by two such bodies separated by distance R could be visualized as the source of the intermolecular potential.

Following Casimir, the fractional change in frequency ω by a body at (x_1, y_1, z_1) of polarizability α_1 in a mode with electric field $E_0(x,y,z)\sin\omega t$ is given by

$$\frac{\delta\omega}{\omega} = -\frac{2\pi\alpha_1 E_0^2(x_1,y_1,z_1)}{\int\int\int E_0^2\,dx\,dy\,dz} \ , \tag{1.3}$$

with integration over the volume of the box. A second body, polarizability α_2, further modifies the mode frequencies through the action of the electric field $(E_0 + E_1)\sin\omega t$, where E_1 is the field of the first body assumed to be propagated to the position of the second as if the first were a classical radiating Hertzian dipole. Casimir extracted the expression (Eq. 1.4) for the long-range energy of attraction, for limiting large values of R,

$$\Delta E = -\frac{23\hbar c}{64\pi^3\varepsilon_0^2}\frac{\alpha_1\alpha_2}{R^7} \tag{1.4}$$

in terms of the static polarizabilities. The expression is the limiting case of the complete results found before by Casimir and Polder [7].

Power [8] made the calculation by treating the energy shift as a perturbation on the vacuum state by the coupling $-(1/2)\alpha\boldsymbol{E}^2$, without explicit reference to the mode structure of the electromagnetic field. He extended Casimir's result to systems with axial symmetry. In a later paper Power and Thirunamachandran [9], again using the difference in the zero-point energy sums over the modes of the cavity caused by introducing polarizable bodies, broadened the results to N bodies at any distance beyond contact in any relative orientation, thus generalizing to include all cases of interacting neutral bodies in their ground states.

This picture connecting intermolecular interaction energy with energy change in the electromagnetic vacuum is thus of general application and is found to be valuable for visualizing physical situations.

1.2 Molecular interactions connected to fluctuations of the vacuum electromagnetic field

The second viewpoint is based on another property of the vacuum state of the electromagnetic field. In a stationary energy state exact values cannot be assigned to variables which do not commute with the Hamiltonian. The electric and magnetic field variables $\boldsymbol{e}$ and $\boldsymbol{b}$ do not commute with each other or with the energy. In the vacuum state we have [5] for a mode of frequency ck the expectation values for $\boldsymbol{e}$ and $\boldsymbol{e}^2$,

$$\langle 0|\boldsymbol{e}|0\rangle = 0; \quad \langle 0|\boldsymbol{e}^2|0\rangle = \frac{\hbar ck}{2\varepsilon_0 V} \ , \tag{1.5}$$

where V is the quantization volume. Thus, in every mode in the vacuum state the expectation value of the electric field, and likewise the magnetic field, is zero, but according to the second expression in Eq. (1.5) there are fluctuations and the fields are not identically zero. In one version of this model [10] the electric field fluctuations induce a dipole moment $\boldsymbol{\mu} = \alpha\boldsymbol{e}$ in a polarizable body. The instantaneous moment induces a moment in the other; the coupling between the two is attractive. At short range we get the van der Waals attraction going as R^{-6}, corresponding to the R^{-3} dipole-dipole coupling in second order. At longer distances the finite propagation time of the fields gives a retardation in the response of the second molecule to the field of the first and in the limit the attraction becomes the Casimir–Polder energy (Eq. 1.4).

A second route along these lines to the Casimir–Polder potential [11] is to suppose that dipole moments are induced in both of the coupled systems by fluctuations in the displacement field in the same mode. The interaction is then between systems in resonance treated according to the potential [12] given in Eq. (1.6), at separation R,

$$V_{ij}(k,\boldsymbol{R}) = \frac{1}{4\pi\varepsilon_0 R^3}\left[\left(\delta_{ij} - 3\hat{R}_i\hat{R}_j\right)(\cos kR + kR\sin kR) - \left(\delta_{ij} - \hat{R}_i\hat{R}_j\right)k^2R^2\cos kR\right] \ , \tag{1.6}$$

where $k = \omega/c$ is the wave number. The method is closely related to Casimir's described following Eq. (1.3).

The plan of the rest of the paper is as follows. In Sect. 2, the induced electric-dipole method is reviewed for the cases where the inducing field is (1) a static electric field, (2) an incident radiation field, and (3) the vacuum radiation field, recovering the familiar results. In Sect. 3, the method is extended to chiral systems, in which both electric and magnetic dipole moments can be induced by the electromagnetic vacuum, and in which a discrimination exists between left-handed/right-handed and left-handed/left-handed interactions between them. The calculation of the dispersion energy by the response method is described in Sect. 4. The method is applied in Sect. 5 to calculate the discriminatory rate of excitation transfer between an excited chiral molecule and a chiral molecule in its ground state. In Sect. 6, the rate is calculated in a novel manner using the Poynting vector.

In later sections we extend this method to chiral systems, in which both electric and magnetic dipole moments can be induced by the electromagnetic vacuum field, and in which a discrimination exists between left-handed/right-handed and left-handed/left-handed interactions.

2 The induced-dipole method in simple cases

2.1 For static and incident radiation fields

Two identical polarizable bodies A and B, atoms or molecules, in a static external electric field $\boldsymbol{E}$, each possess induced electric moments given by Eq. (2.1),

$$\mu_i^{\text{ind}} = \alpha_{ij}(0)E_j \ , \tag{2.1}$$

where $\alpha_{ij}(0)$ is the static electric dipole polarizability. The coupling energy of the moments for all separations R is the dipole-dipole energy found from the potential energy tensor Eq. (2.2),

$$V_{ij}(\boldsymbol{R}) = \frac{1}{4\pi\varepsilon_0 R^3}\left(\delta_{ij} - 3\hat{R}_i\hat{R}_j\right) \tag{2.2}$$

and is given by

$$\Delta E = \mu_i^{\text{ind}}(\text{A})\mu_j^{\text{ind}}(\text{B})V_{ij}(\boldsymbol{R}) = \frac{1}{4\pi\varepsilon_0 R^3}\alpha_{ik}(0;\text{A})\alpha_{jl}(0;\text{B})\left(\delta_{ij} - 3\hat{R}_i\hat{R}_j\right)E_kE_l \ . \tag{2.3}$$

A novel extension of this method is to calculate the interaction in the presence of a radiation field. A further extension leads to the calculation of the discriminating dispersion energy for coupled chiral molecules. The application is straightforward. For a monochromatic field of frequency ω the induced moment is

$$\mu_i^{\text{ind}} = \varepsilon_0^{-1}\alpha_{ij}(\omega)d_j(\omega) \ , \tag{2.4}$$

where, for later applications, we have introduced the electric displacement field $\boldsymbol{d}$. The frequency-dependent polarizability is given in Eq. (2.5),

$$\alpha_{ij}(\omega) = \sum_m\left(\frac{\mu_i^{0m}\mu_j^{m0}}{E_{m0} - \hbar\omega} + \frac{\mu_j^{0m}\mu_i^{m0}}{E_{m0} + \hbar\omega}\right) \ . \tag{2.5}$$

The interaction between A and B now depends on the retarded potential tensor Eq. (1.6); it is given in Eq. (2.6),

$$\Delta E = \mu_i^{\text{ind}}(\text{A})\mu_j^{\text{ind}}(\text{B})V_{ij}(k,\text{R}) = \varepsilon_0^{-2}\alpha_{ik}(k,\text{A})\alpha_{je}(k,\text{B}) \times \langle d_k(\boldsymbol{k},\boldsymbol{R}_\text{A})d_l(\boldsymbol{k},\boldsymbol{R}_\text{B})\rangle\, V_{ij}(k,\boldsymbol{R}_\text{B} - \boldsymbol{R}_\text{A}) \ . \tag{2.6}$$

The factor inside the angle brackets in Eq. (2.6) is the correlation factor between displacement fields at $\boldsymbol{R}_\text{A}$ and $\boldsymbol{R}_\text{B}$ in mode $\boldsymbol{k}$. It is easily found for the n photon state of the incident field and is related to the incident field intensity. Using the mode expansion of $\boldsymbol{d}$ in Eq. (2.7),

$$\boldsymbol{d}(\boldsymbol{r}) = i\sum_{k,\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\left[\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k})\exp(i\boldsymbol{k}.\boldsymbol{r}) - \bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k})a^{*(\lambda)}(\boldsymbol{k})\exp(-i\boldsymbol{k}.\boldsymbol{r})\right] \tag{2.7}$$

we have

$$\begin{aligned}&\left\langle n\left|\sum_\lambda d_i(\boldsymbol{k},\lambda;\boldsymbol{R}_\mathrm{A})d_j(\boldsymbol{k},\lambda;\boldsymbol{R}_\mathrm{B})\right|n\right\rangle\\&\quad=(2n+1)\,\frac{\hbar ck\varepsilon_0}{2V}\\&\qquad\times\sum_\lambda e_i(\lambda)\bar{e}_j(\lambda)\exp[-i\boldsymbol{k}.(\boldsymbol{R}_\mathrm{B}-\boldsymbol{R}_\mathrm{A})]\ ,\end{aligned}\tag{2.8}$$

in which $\boldsymbol{k}$ is the wave vector and λ is the polarization index. For an external field of n quanta in this mode acting on a pair of molecules in a fixed orientation, we find after summing over polarizations,

$$\begin{aligned}\Delta E(\boldsymbol{k})&=(2n+1)\left(\frac{\hbar ck}{2\varepsilon_0V}\right)\alpha_{ik}(k;\mathrm{A})\alpha_{jl}\\&\quad\times(k;\mathrm{B})V_{ij}(k,\boldsymbol{R}_\mathrm{B}-\boldsymbol{R}_\mathrm{A})\\&\quad\times\left(\delta_{ij}-\hat{k}_i\hat{k}_j\right)\exp[-i\boldsymbol{k}.(\boldsymbol{R}_\mathrm{B}-\boldsymbol{R}_\mathrm{A})]\ .\end{aligned}\tag{2.9}$$

After calculating the effect of tumbling of the molecule pair, and expressing the energy shift in terms of the irradiance I of the incident field, we find

$$\begin{aligned}\Delta E=\frac{I}{8\pi\varepsilon_0^2c}\frac{\alpha(k,\mathrm{A})\alpha(k,\mathrm{B})}{R^3}&\Big(kR\sin 2kR+2\cos 2kR\\&-\frac{5\sin 2kR}{kR}-\frac{6\cos 2kR}{k^2R^2}+\frac{3\sin 2kR}{k^3R^3}\Big)\end{aligned}\tag{2.10}$$

in agreement with the result [13] from conventional fourth-order perturbation theory with the first two terms of the interaction Hamiltonian Eq. (1.2) as perturbation.

2.2 Energy shift for the vacuum field

To introduce the method given in later sections for chiral molecules we illustrate the use of the result Eq. (2.8) to obtain the Casimir–Polder potential. The field correlation factor does not vanish for the vacuum field. For $n=0$ Eq. (2.8) gives the result,

$$\begin{aligned}&\left\langle 0\left|d_i(\boldsymbol{k},\boldsymbol{R}_\mathrm{A})\,d_j(\boldsymbol{k},\boldsymbol{R}_\mathrm{B})\right|0\right\rangle\\&\quad=\frac{\hbar ck\varepsilon_0}{2V}\exp\left(i\boldsymbol{k}.\boldsymbol{R}\right)\left(\delta_{ij}-\hat{k}_i\hat{k}_j\right)\ .\end{aligned}\tag{2.11}$$

The total energy shift is the sum of Eq. (2.9) over all modes, $\Delta E=\sum_k\Delta E(k)$. Converting the $\boldsymbol{k}$ sum to an integral,

$$\sum_k(\ldots)=\int(\ldots)\frac{k^2dk\,d\Omega\,V}{(2\pi)^3}\tag{2.12}$$

and using

$$\begin{aligned}&\frac{1}{4\pi}\int\left(\delta_{ij}-\hat{k}_i\hat{k}_j\right)\exp\left(i\boldsymbol{k}.\boldsymbol{R}\right)d\Omega\\&\quad=\left(\delta_{ij}-\hat{R}_i\hat{R}_j\right)\frac{\sin kR}{kR}\\&\qquad+\left(\delta_{ij}-3\hat{R}_i\hat{R}_j\right)\left(\frac{\cos kR}{k^2R^2}-\frac{\sin kR}{k^3R^3}\right)\end{aligned}\tag{2.13}$$

the shift may be shown [11] to be

$$\begin{aligned}\Delta E=-\frac{\hbar c}{16\pi^3\varepsilon_0^2R^2}&\int_0^\infty\alpha(k,\mathrm{A})\,\alpha(k,\mathrm{B})\\&\times\left(1+\frac{2i}{kR}-\frac{5}{k^2R^2}-\frac{6i}{k^3R^3}+\frac{3}{k^4R^4}\right)\\&\times\exp(2ikR)\,k^4dk\ .\end{aligned}\tag{2.14}$$

This is usually expressed as the integral over imaginary frequencies,

$$\begin{aligned}\Delta E=-\frac{\hbar c}{16\pi^3\varepsilon_0^2R^2}&\int_0^\infty\alpha(icu,\mathrm{A})\alpha(icu,\mathrm{B})\\&\times\left(1+\frac{2}{uR}+\frac{5}{u^2R^2}+\frac{6}{u^3R^3}+\frac{3}{u^4R^4}\right)\\&\times\exp(2uR)u^4du\ ,\end{aligned}\tag{2.15}$$

which is the Casimir–Polder potential.

3 The induced-dipole method for chiral systems

3.1 Discrimination in the dispersion energy

In chiral molecules electronic transitions may be allowed to both electric and magnetic dipole fields. Corresponding to Eq. (2.4), we have in each molecule an induced magnetic dipole moment,

$$m_i^\mathrm{ind}=\chi_{ij}(\omega)b_j(\omega)\ ,\tag{3.1}$$

where χ_{ij} is the magnetic dipole susceptibility at frequency ω and $\boldsymbol{b}$ is the magnetic field. The coupling of the induced magnetic dipole moments in molecules A and B is not discriminatory and is not considered further: it is a small contribution to the total dispersive binding.

For chiral molecules, with transitions allowed to both magnetic and electric dipole radiation, in the radiation-molecule coupling in Eq. (1.2), there is a correction to the electric polarizability given by the mixed electric-magnetic polarizability,

$$G_{ij}=\sum_r\left(\frac{\mu_i^{0r}m_j^{r0}}{E_{r0}-\hbar\omega}+\frac{m_j^{0r}\mu_i^{r0}}{E_{r0}+\hbar\omega}\right)\ .\tag{3.2}$$

The $\boldsymbol{G}$ tensor is bilinear in the electric and magnetic moments, and has opposite sign for a chiral molecule and its enantiomer. It thus discriminates between them, whereas the electric dipole polarizability and its magnetic analogue, being quadratic in the respective moments, are not discriminatory.

To find the discrimination energy in the induced dipole-model, namely the energy difference between a right-handed molecule interacting with another right-handed molecule, and a left-handed molecule, we find the moments induced through the tensor Eq. (3.2). These are, for molecule A,

$$\begin{aligned}\mu_i^\mathrm{ind}(\mathrm{A})&=G_{ij}(\omega,\mathrm{A})b_j(\boldsymbol{k};\boldsymbol{R}_\mathrm{A})\\m_j^\mathrm{ind}(\mathrm{A})&=\varepsilon_0^{-1}G_{ij}(\omega,\mathrm{A})d_i(\boldsymbol{k};\boldsymbol{R}_\mathrm{A})\ .\end{aligned}\tag{3.3}$$

The discrimination comes in two ways. For the first, we note that the interaction of electric moments induced in A and B, and that of magnetic moments, depends on the retarded interaction potential (Eq. 1.6),

$$\Delta E^{\mathrm{disc1a}} = \varepsilon_0^{-2} c^{-2} V \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} G_{ki}(k,\mathrm{A}) G_{lj}(k,\mathrm{B}) \times \langle d_k(\boldsymbol{k},\boldsymbol{R}_\mathrm{A}) d_l(\boldsymbol{k},\boldsymbol{R}_\mathrm{B})\rangle V_{ij}(k,\boldsymbol{R}) \tag{3.4}$$

$$\Delta E^{\mathrm{disc1b}} = V \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} G_{ki}(k,\mathrm{A}) G_{lj}(k,\mathrm{B}) \times \langle b_k(\boldsymbol{k},\boldsymbol{R}_\mathrm{A}) b_l(\boldsymbol{k},\boldsymbol{R}_\mathrm{B})\rangle V_{ij}(k,\boldsymbol{R}) \ . \tag{3.5}$$

The magnetic field correlation factor in Eq. (3.5), analogous to Eq. (2.11) for the displacement field is

$$\langle 0|b_k(\boldsymbol{k},\boldsymbol{R}_\mathrm{A}) b_l(\boldsymbol{k},\boldsymbol{R}_\mathrm{B})|0\rangle = \frac{\hbar k}{2\varepsilon_0 c V} \exp[-i\boldsymbol{k}.(\boldsymbol{R}_\mathrm{B}-\boldsymbol{R}_\mathrm{A})]\left(\delta_{kl} - \hat{k}_k \hat{k}_l\right) \ . \tag{3.6}$$

Equations (3.4) and (3.5) together, after angular integration and rotational averaging, give a contribution to the energy shift,

$$\Delta E^{\mathrm{disc1}} = -\frac{\hbar}{8\pi^3 \varepsilon_0^2 c R^6} \int_0^\infty dk\, G(k,\mathrm{A}) G(k,\mathrm{B}) \times \left(3\sin 2kR - 6kR\cos 2kR - 5k^2R^2 \sin 2kR + 2k^3R^3\cos 2kR + k^4R^4 \sin 2kR\right) \ , \tag{3.7}$$

where $\boldsymbol{R} = \boldsymbol{R}_\mathrm{B} - \boldsymbol{R}_\mathrm{A}$, and $G(k) = G_{\lambda\lambda}(k)/3$.

Expressed in imaginary frequencies icu Eq. (3.7) becomes

$$\Delta E^{\mathrm{disc1}} = \frac{\hbar}{8\pi^3 \varepsilon_0^2 c R^6} \int_0^\infty du\, G(iu,\mathrm{A}) G(iu,\mathrm{B}) \times \left(3 + 6uR + 5u^2R^2 + 2u^3R^3 + u^4R^4\right) \times \exp(-2uR) \ . \tag{3.8}$$

The second source of discrimination is the interaction between the induced electric moment in one molecule and the magnetic moment in the other. This gives terms that depend on the potential function [5],

$$U_{ij}(k,\boldsymbol{R}) = \frac{1}{4\pi\varepsilon_0 c R^3} \varepsilon_{ijk} \hat{R}_k \left(kR\cos kR + k^2R^2 \sin kR\right) \ . \tag{3.9}$$

The corresponding terms in the energy shift are

$$\Delta E^{\mathrm{disc2}} = \varepsilon_0^{-1} c^{-1} V \int_0^\infty \frac{d^3k}{(2\pi)^3} G_{ki}(k,\mathrm{A}) G_{jl}(k,\mathrm{B}) \times \langle d_k(\boldsymbol{k},\boldsymbol{R}_\mathrm{A}) b_l(\boldsymbol{k},\boldsymbol{R}_\mathrm{B})\rangle\, U_{ij}(k,\boldsymbol{R}) \ , \tag{3.10}$$

and a second with $\boldsymbol{d}$ and $\boldsymbol{b}$ interchanged in the correlation factor. With use of the correlation factor Eq. (3.11),

$$\langle 0|d_k(\boldsymbol{k},\boldsymbol{R}_\mathrm{A}) b_l(\boldsymbol{k},\boldsymbol{R}_\mathrm{B})|0\rangle = \frac{\hbar k}{2V} \varepsilon_{klm} \hat{k}_m \exp(-i\boldsymbol{k}.\boldsymbol{R}) \tag{3.11}$$

and the relation

$$\int \hat{k}_m \exp(-i\boldsymbol{k}.\boldsymbol{R}) d\Omega = 4\pi i \left(\frac{\cos kR}{kR} - \frac{\sin kR}{k^2R^2}\right) \hat{R}_m \tag{3.12}$$

the contribution Eq. (3.10) after rotational averaging becomes

$$\Delta E^{\mathrm{disc2}} = -\frac{\hbar}{8\pi^3 \varepsilon_0^2 c R^6} \int_0^\infty dk\, G(k,\mathrm{A}) G(k,\mathrm{B}) \times \left(k^2R^2 \sin 2kR - 2k^3R^3 \cos 2kR - k^4R^4 \sin 2kR\right) \ . \tag{3.13}$$

In terms of imaginary frequencies Eq. (3.13) is

$$\Delta E^{\mathrm{disc2}} = -\frac{\hbar}{8\pi^3 \varepsilon_0^2 c R^6} \int_0^\infty du\, G(iu,\mathrm{A}) G(iu,\mathrm{B}) \times \left(u^2R^2 + 2u^3R^3 + u^4R^4\right) \exp(-2uR) \ , \tag{3.14}$$

so the total discriminatory interaction energy, the sum of Eqs. (3.8) and (3.14), is

$$\Delta E^{\mathrm{disc}} = -\frac{\hbar}{8\pi^3 \varepsilon_0^2 c R^6} \int_0^\infty du\, G(iu,\mathrm{A})\, G(iu,\mathrm{B}) \times \left(3 + 6uR + 4u^2R^2\right) \exp(-2uR) \tag{3.15}$$

or, in terms of the transition electric and magnetic moments in Eq. (3.3),

$$\Delta E^{\mathrm{disc}} = -\frac{1}{18\pi^3 \varepsilon_0^2 \hbar c^3 R^6} \sum_{m,n} \left[\boldsymbol{\mu}^{0m}(\mathrm{A}) \cdot \boldsymbol{m}^{m0}(\mathrm{A})\right] \times \left[\mu^{0n}(\mathrm{B}) \cdot \boldsymbol{m}^{n0}(\mathrm{B})\right] \int_0^\infty \frac{u^2}{\left(k_{m0}^2 + u^2\right)\left(k_{n0}^2 + u^2\right)} \times \left(3 + 6uR + 4u^2R^2\right) \exp(-2uR) du \ . \tag{3.16}$$

Equation (3.16) was earlier found by an entirely different method from conventional fourth-order perturbation theory [14].

In the limiting (far zone) case of the intermolecular separation greater than the reduced wavelength of a typical molecular transition, u^2 can be neglected relative to the wave numbers k_{m0}^2, k_{n0}^2. The u integral in Eq. (3.15) is straightforward, giving for the far-zone energy shift,

$$\Delta E^{\mathrm{disc}}_{\text{far zone}} = -\frac{\hbar^3 c}{3\pi^3 \varepsilon_0^2 R^9} \times \sum_{m,n} \frac{\left[\boldsymbol{\mu}^{0m}(\mathrm{A}) \cdot m^{m0}(\mathrm{A})\right]\left[\boldsymbol{\mu}^{0n}(\mathrm{B}) \cdot m^{n0}(\mathrm{B})\right]}{E_{m0}^2 E_{n0}^2} \ . \tag{3.17}$$

In the near zone it is enough to keep the R^{-6} term from Eq. (3.16), and the exponential factor can be set to unity, giving the near-zone shift first found by Mavroyannis and Stephen [15],

$$\Delta E_{\text{near zone}} = -\frac{1}{12\pi^2\varepsilon_0^2 c^2 R^6} \times \sum_{m,n} \frac{\left[\boldsymbol{\mu}^{0m}(\mathrm{A}) \cdot m^{m0}(\mathrm{A})\right]\left[\boldsymbol{\mu}^{0n}(\mathrm{B}) \cdot m^{n0}(\mathrm{B})\right]}{E_{m0} + E_{n0}} \ . \tag{3.18}$$

4 The response method for dispersive chiral discrimination

4.1 The driving field and the response method

We discuss this method both for discrimination in dispersive interactions and in energy transfer from an electronically excited to a ground-state molecule. For achiral systems the method was described by Power and Thirunamachandran [16] and for dispersive interactions in chiral systems by Jenkins et al. [14]. The essential feature is that one molecule is treated as passive, responding through its dynamic polarizability to the Maxwell field of the other (source) molecule.

The dispersive energy shift is calculated using the quantum mechanical analogue of the classical expression

$$\Delta E = -\frac{1}{2\varepsilon_0^2}\, \alpha(\omega, \mathrm{B})\, d^2(\boldsymbol{R}_\mathrm{B}) \ , \tag{4.1}$$

where $\alpha(\omega, \mathrm{B})$ is the electric dipole isotropic frequency-dependent polarizability and $\boldsymbol{d}$ is the Maxwell displacement field at the molecular centre of B. It is made up of the free field and the field of the source molecule A. The total field is expanded in powers of the electric dipole moment,

$$\boldsymbol{d}(\boldsymbol{r}) = \boldsymbol{d}^{(0)}(\boldsymbol{r}) + \boldsymbol{d}^{(1)\mathrm{A}}(\boldsymbol{r}) + \boldsymbol{d}^{(2)\mathrm{A}}(\boldsymbol{r}) + \cdots \ . \tag{4.2}$$

The first term is the free field given in Eq. (2.7). The second term is linearly dependent on the transition moments of A, and enters as a real dipole field in the energy transfer process to be discussed later. The third term depends on the square of the transition moments through the electric dipole polarizability. It is given [16] by,

$$d_i^{(2)\mathrm{A}}(\boldsymbol{r}) = \frac{i}{4\pi} \sum_k \alpha(k, \mathrm{A}) \left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2} \left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) \times \frac{1}{r}\left[e_i(\boldsymbol{k})a(\boldsymbol{k})\exp(ikr) - \bar{e}_j(\boldsymbol{k})a^*(\boldsymbol{k})\exp(-ikr)\right] \ . \tag{4.3}$$

The leading contribution to the dispersion energy Eq. (4.1) is, from the $\boldsymbol{d}^{(0)} \cdot \boldsymbol{d}^{(2)}$ cross-term in Eq. (4.4),

$$\Delta E = -\frac{1}{2\varepsilon_0^2} \sum_k \alpha(k, \mathrm{B}) \times \left[\boldsymbol{d}^{(0)}(\boldsymbol{R}_\mathrm{B}) \cdot \boldsymbol{d}^{(2)\mathrm{A}}(\boldsymbol{R}_\mathrm{B}) + \boldsymbol{d}^{(2)\mathrm{A}}(\boldsymbol{R}_\mathrm{B}) \cdot \boldsymbol{d}^{(0)}(\boldsymbol{R}_\mathrm{B})\right] \ . \tag{4.4}$$

With use of Eqs. (2.7) and (4.1), the result after summing over polarizations is

$$\Delta E = -\frac{1}{8\pi\varepsilon_0} \sum_k \alpha(k, \mathrm{A})\, \alpha(k, \mathrm{B})\, \frac{\hbar ck}{2\varepsilon_0 V} \left(\delta_{ij} - \hat{k}_i\hat{k}_j\right) \times \exp(-ikR)\left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) \frac{\exp(ikR)}{R} + c.c. \tag{4.5}$$

from which the Casimir–Polder potential Eq. (2.14) is obtained.

4.2 A higher approximation and chiral discrimination

A simple extension of this method allows us to find the discriminatory part of the dispersion energy for a pair of chiral molecules. It is necessary to go beyond electric dipole coupling and to take account of the mixed electric-magnetic polarizability $\boldsymbol{G}$ in Eq. (3.2). In contrast to the electric dipole polarizability α in Eq. (2.5) the sign of $\boldsymbol{G}$ changes according to the handedness of the enantiomer, and it is this property that leads to discriminatory interactions. The discriminatory interaction energy, correct to second order in the moments for a pair of chiral molecules [14], is given by

$$\Delta E^{\text{disc}} = -\frac{1}{2\varepsilon_0}\, G^\mathrm{B}[\boldsymbol{d}(\boldsymbol{R}_\mathrm{B}) \cdot \boldsymbol{b}(\boldsymbol{R}_\mathrm{B}) + \boldsymbol{b}(\boldsymbol{R}_\mathrm{B}) \cdot \boldsymbol{d}(\boldsymbol{R}_\mathrm{B})] \ , \tag{4.6}$$

where molecule B is passive and the $\boldsymbol{d}$ and $\boldsymbol{b}$ fields are sums of the free fields and the source fields of A.

The second-order fields have additional contributions dependent on $\boldsymbol{G}$ [17]. They are

$$d_i^{(2)\mathrm{A}}(G; r) = \frac{i}{4\pi\varepsilon_0} \sum_{\text{modes}} G(k, \mathrm{A}) \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} \times \left\{ \begin{array}{l} \left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right)\frac{1}{r} \\ \quad \times\left[b_j(k)a(k)\exp(ikr) - \bar{b}_j(k)a^+(k)\exp(-ikr)\right] \\ \quad + ik\varepsilon_{ijk}\nabla_k\frac{1}{r}\left[e_j(k)a(k)\exp(ikr)\right. \\ \quad \left.-\bar{e}_j(k)a^+(k)\exp(-ikr)\right] \end{array} \right\} \tag{4.7}$$

$$b_i^{(2)\mathrm{A}}(G; r) = \frac{i}{4\pi c} \sum_{\text{modes}} G(k, \mathrm{A}) \left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2} \times \left\{ \begin{array}{l} \left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right)\frac{1}{r} \\ \quad \times\left[b_j(k)a(k)\exp(ikr) - \bar{b}_j(k)a^+(k)\exp(-ikr)\right] \\ \quad + ik\varepsilon_{ijk}\nabla_k\frac{1}{r}\left[e_j(k)a(k)\exp(ikr)\right. \\ \quad \left.-\bar{e}_j(k)a^+(k)\exp(-ikr)\right] \end{array} \right\} . \tag{4.8}$$

The discriminatory terms in the energy shift are those from Eqs. (4.7) and (4.8). We have

$$\Delta E^{\mathrm{disc}} = -\frac{1}{2\varepsilon_0} G^{\mathrm{B}} \times \begin{pmatrix} \boldsymbol{d}^{(0)}(\boldsymbol{R}_{\mathrm{B}}) \cdot \boldsymbol{b}^{(2)\mathrm{A}}(\boldsymbol{R}_{\mathrm{B}}) + \boldsymbol{b}^{(2)\mathrm{A}}(\boldsymbol{R}_{\mathrm{B}}) \cdot \boldsymbol{d}^{(0)}(\boldsymbol{R}_{\mathrm{B}}) \\ + \boldsymbol{d}^{(2)\mathrm{A}}(\boldsymbol{R}_{\mathrm{B}}) \cdot \boldsymbol{b}^{(0)}(\boldsymbol{R}_{\mathrm{B}}) + \boldsymbol{b}^{(0)}(\boldsymbol{R}_{\mathrm{B}}) \cdot \boldsymbol{d}^{(2)\mathrm{A}}(\boldsymbol{R}_{\mathrm{B}}) \end{pmatrix} . \tag{4.9}$$

Now with use of the mode expansions of the free fields and the second-order fields in Eqs. (4.7) and (4.8) we recover the discriminatory shift given in Eq. (3.16).

5 The response method for excitation transfer

5.1 Achiral systems

Excitation transfer is the simplest of the radiation-mediated processes between pairs of atoms or molecules. It is of wide importance in physical processes. For molecules close together as in crystals an initially excited molecule transfers excitation to neighbours, and the transfer leads to exciton phenomena in absorption and emission. In solution there is the process first explained by Förster in which absorption by one molecular species is followed by emission from another species at a different frequency, after excitation transfer between molecules that can be separated by distances of up to 100 nm. Transfer between systems at very long distances by purely radiative interaction are also known. For achiral systems it is a well-studied problem in molecular quantum electrodynamics [16, 18, 19] with use of perturbation theory, and later by the response method [20]. The latter has the attractive feature that the causal nature of energy transfer is transparent, since the source field is causal. Wider aspects of causality have been discussed [21].

In the case of an achiral molecule A transferring excitation to an identical molecule B with an electric dipole allowed transition 0–m the interaction potential at all distances is given in Eq. (1.6). According to time-dependent perturbation theory the rate of transfer of excitation energy [19] by the Fermi rule is

$$\Gamma(\mathrm{A} \to \mathrm{B}) = \frac{\rho}{36\pi\varepsilon_0^2\hbar R^6} \left|\boldsymbol{\mu}^{0m}(\mathrm{A})\right|^2 \left|\boldsymbol{\mu}^{0m}(\mathrm{B})\right|^2 \left(3 + k_0^2R^2 + k_0^4R^4\right) , \tag{5.1}$$

where k_0 is the wave number of the electronic transition, and ρ is the density of final states. Where B is identical with A the density of states is that of the collision-broadened pure electronic excited electronic state m. In the case that B is a nonidentical molecule, as in the Förster transfer, the density is that of its vibrational manifold at the frequency ck_0.

Now from the point of view of the response method the driving field is the first-order displacement field of the transition in A,

$$\langle 0; E_0 | \boldsymbol{d}(\boldsymbol{r}, t) | E_m; 0 \rangle = \frac{1}{4\pi} \mu_j^{0m}(\mathrm{A}) \left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) \frac{\exp[ik_{m0}(r - ct)]}{r} , \tag{5.2}$$

and with the response function for molecule B,

$$-\varepsilon_0^{-1}\mu^{m0}(\mathrm{B}) \exp(ik_{m0}t) \boldsymbol{d}^{(\mathrm{A})}(\boldsymbol{R}, t) \tag{5.3}$$

we get the energy-transfer matrix element

$$M^{(\mu\mu)} = -(4\pi\varepsilon_0)^{-1} \mu_i^{0m}(\mathrm{A}) \times \mu_j^{m0}(\mathrm{B}) \left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) \frac{\exp(ik_0R)}{R} , \tag{5.4}$$

from which the Fermi rate Eq. (5.1) follows.

5.2 Excitation transfer between chiral molecules

For a chiral molecule A in which the electronic transition 0–m is allowed to both electric and magnetic dipole radiation the displacement field corresponding to Eq. (5.2) has contributions from both transition moments [17, 22],

$$d_i(\boldsymbol{r}, t) = \frac{1}{4\pi} \left\{ \mu_j^{0m}(\mathrm{A}) \left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) - \frac{1}{c} m_j^{0m}(\mathrm{A}) \left(ik_{m0}\varepsilon_{ijk}\nabla_k\right) \right\} \times \frac{\exp(ik_{m0})(r - ct)}{r} \tag{5.5}$$

and the magnetic field likewise,

$$b_i(\boldsymbol{r}, t) = \frac{1}{4\pi\varepsilon_0 c} \left\{ \mu_j^{0m}(\mathrm{A}) \left(ik_{m0}\varepsilon_{ijk}\nabla_k\right) + \frac{1}{c} m_j^{0m}(\mathrm{A}) \left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) \right\} \times \frac{\exp(ik_{m0})(r - ct)}{r} . \tag{5.6}$$

The fields represented by Eqs. (5.5) and (5.6) have the same form as the classical electric and magnetic dipole fields radiating from oscillating current distributions of frequency ck_0 with moments $\boldsymbol{\mu}$ and $\boldsymbol{m}$. The fields show the familiar symmetry between the functional forms. The electric field of an oscillating electric dipole and the magnetic field of a magnetic dipole are the same in form; the electric field of an oscillating magnetic dipole and the magnetic field of an electric dipole have opposite signs. Further the latter pair vanish for $km_0 = 0$; the former give the static limit expressions.

The response of B to the fields descriped by Eqs. (5.5) and (5.6) is found with Eq. (5.3) for the electric field, and the analogous Eq. (5.7) for the magnetic field,

$$-\boldsymbol{m}^{m0}(\mathrm{B}) \exp(-ik_{m0}t) \boldsymbol{b}^{(\mathrm{A})}(\boldsymbol{R}, t) . \tag{5.7}$$

The total gives the matrix element leading to the transfer rate by the Fermi Rule. We get two contributions to the rate discrimination. The electric field part of Eq. (5.5) and the magnetic part of Eq. (5.6) together give

$$\Gamma^{\text{disc1}} = \frac{\rho}{36\pi\varepsilon_0^2\hbar c^2} R^{0m}(\mathrm{A})R^{m0}(\mathrm{B}) \times \left|\left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right)\frac{\exp(ik_0R)}{R}\right|^2 = \frac{\rho}{18\pi\varepsilon_0^2\hbar c^2R^6} R^{0m}(\mathrm{A})R^{m0}(\mathrm{B})\left(3 + k_0^2R^2 + k_0^4R^4\right) , \tag{5.8}$$

where $R^{0m} = -i\boldsymbol{\mu}^{0m} \cdot \boldsymbol{m}^{0m}$ is the optical rotatory strength.

The magnetic field in Eq. (5.5), and the electric field of Eq. (5.6) with the corresponding response functions Eqs. (5.3) and (5.7) give a contribution

$$\Gamma^{\text{disc2}} = \frac{\rho}{18\pi\varepsilon_0^2\hbar c^2R^6} R^{0m}(\mathrm{A})R^{0m}(\mathrm{B})\left(k_0^2R^2 + k_0^4R^4\right) . \tag{5.9}$$

At $k_0R = 0$ the fields go to zero and Eq. (5.9) likewise.

The total discriminating rate, the sum of Eqs. (5.8) and (5.9), is

$$\Gamma^{\text{disc}} = \frac{\rho}{18\pi\varepsilon_0^2\hbar c^2R^6} R^{0m}(\mathrm{A})R^{0m}(\mathrm{B}) \times \left(3 + 2k_0^2R^2 + 2k_0^4R^4\right) . \tag{5.10}$$

This is the rate found previously [23] by an independent method in which A and B are coupled by the interaction Hamiltonian (Eq. 1.2) and calculated by second-order perturbation theory.

6 Chiral interactions by Poynting's theorem

There is a conceptually attractive approach to excitation transfer. It is in two steps. The first is to find the rate of flow of radiation energy emitted by the excited molecule. The second is the calculation of the absorption of the energy by the ground-state molecule. According to Poynting's theorem the rate of energy flow per unit surface area of a sphere of radius r is equal to $\boldsymbol{S}(\boldsymbol{r}) \cdot \hat{\boldsymbol{r}}$ where $\boldsymbol{S}(\boldsymbol{r})$ is the Poynting vector

$$\boldsymbol{S}(\boldsymbol{r}) = \frac{c^2}{4}\left[\boldsymbol{d}(\boldsymbol{r}) \times \boldsymbol{b}(\boldsymbol{r}) - \boldsymbol{b}(\boldsymbol{r}) \times \boldsymbol{d}(\boldsymbol{r})\right] \tag{6.1}$$

and $\hat{\boldsymbol{r}}$ is the unit radius vector.

It is known [23] that the total net flow is equal to the emission rate times $\hbar\omega$ found from the Einstein A coefficient. In order to find the discriminatory contributions to excitation transfer we need to find separately the rate of flow of left- and right-handed circularly polarized radiation emitted by the excited molecule. For this we need the Poynting vector separately for each of the two circularly polarized components. This is conveniently found with the use of chiral fields,

$$\boldsymbol{f}(\boldsymbol{r}) = 2^{-1/2}\left[\varepsilon_0^{-1}\boldsymbol{d}(\boldsymbol{r}) + ic\boldsymbol{b}(\boldsymbol{r})\right]$$

$$\boldsymbol{f}^+(\boldsymbol{r}) = 2^{-1/2}\left[\varepsilon_0^{-1}\boldsymbol{d}(\boldsymbol{r}) - ic\boldsymbol{b}(\boldsymbol{r})\right] , \tag{6.2}$$

so the Poynting vector Eq. (6.1) can be written

$$\boldsymbol{S}(\boldsymbol{r}) = \frac{i\varepsilon_0 c}{4}\left[\boldsymbol{f}(\boldsymbol{r}) \times \boldsymbol{f}^+(\boldsymbol{r}) - \boldsymbol{f}^+(\boldsymbol{r}) \times \boldsymbol{f}(\boldsymbol{r})\right] . \tag{6.3}$$

Choosing the polarization vectors to refer to right and left circular polarization, we have for the mode expansions of the fields in Eq. (6.2),

$$\boldsymbol{f}(\boldsymbol{r}) = i\sum_k\left(\frac{\hbar ck}{\varepsilon_0V}\right)^{1/2}\Big[e^{(L)}(\boldsymbol{k})a^{(L)}(\boldsymbol{k})\exp(ikr) - \bar{e}^{(R)}(\boldsymbol{k})a^{+(R)}(\boldsymbol{k})\exp(-ikr)\Big]$$

$$\boldsymbol{f}^+(\boldsymbol{r}) = i\sum_k\left(\frac{\hbar ck}{\varepsilon_0V}\right)^{1/2}\Big[e^{(R)}(\boldsymbol{k})a^{(R)}(\boldsymbol{k})\exp(ikr) - \bar{e}^{(L)}(\boldsymbol{k})a^{+(L)}(\boldsymbol{k})\exp(-ikr)\Big] . \tag{6.4}$$

$\boldsymbol{f}$ annihilates left-handed photons and creates right-handed photons. $\boldsymbol{f}^+$ has the opposite property.

The calculation of the Poynting vector for an emitting dipole depends on the displacement and magnetic fields up to terms quadratic in the dipole moment sources. The terms in second-order fields are precisely equal to those from first-order fields, so we need only find the latter and double the result.

In terms of linear combinations of transition moments

$$\boldsymbol{\zeta} = 2^{-1/2}\left(\boldsymbol{\mu} + \frac{i}{c}\boldsymbol{m}\right); \quad \boldsymbol{\zeta}^+ = 2^{-1/2}\left(\boldsymbol{\mu} - \frac{i}{c}\boldsymbol{m}\right) \tag{6.5}$$

we construct the chiral fields from the first-order fields Eqs. (6.6) and (6.7) for the 0–m transition,

$$f_i(\boldsymbol{r}, t) = \frac{1}{4\pi\varepsilon_0}\zeta_j^{0m}\left[\left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) - k_{m0}\varepsilon_{ijk}\nabla_k\right] \times \frac{\exp[ik_{m0}(r - ct)]}{r} , \tag{6.6}$$

$$f_i^+(r, t) = \frac{1}{4\pi\varepsilon_0}\zeta_j^{+0m}\left[\left(-\nabla^2\delta_{ij} + \nabla_i\nabla_j\right) + k_{m0}\varepsilon_{ijk}\nabla_k\right] \times \frac{\exp[ik_{m0}(r - ct)]}{r} . \tag{6.7}$$

To get the Poynting vector for left circularly polarized light we use Eqs. (6.6) and (6.7) in Eq. (6.3). Since $\boldsymbol{f}$ annihilates and $\boldsymbol{f}^+$ creates the left-polarized part of the field we need only the first term of Eq. (6.3). The expectation value for the state $|E_m{,}0\rangle$, referring to the molecular state $|E_m\rangle$ and the vacuum field state $|0\rangle$, is given in Eq. (6.8),

$$= \frac{c}{64\pi^2\varepsilon_0}\varepsilon_{ijk}i\zeta_l^{m0}\left\{\left[\left(-\nabla^2\delta_{jl} + \nabla_j\nabla_l\right) + k_{m0}\varepsilon_{jlm}\nabla_m\right] \times \frac{\exp(ik_{m0})(\rho - ct)}{r}\right\}\zeta_n^{0m}\left\{\left[\left(-\nabla^2\delta_{kn} + \nabla_k\nabla_n\right) + k_{m0}\varepsilon_{knp}\nabla_p\right]\frac{\exp(ik_{m0})(\rho - ct)}{r}\right\} , \tag{6.8}$$

where $\rho = \boldsymbol{r} - \boldsymbol{R}$. After evaluation and random averaging there are terms in ρ^{-2}, ρ^{-4} and ρ^6. The latter two appear only in oscillatory charge movements across the bounding spherical surface, and make no contribution to the net flow. Extracting the inverse square terms we find the Poynting vector $\boldsymbol{S}^{(L)}(\boldsymbol{r})$ for net left-handed flow. A similar calculation gives $\boldsymbol{S}^{(R)}(\boldsymbol{r})$. For the net rate of energy flux per unit area of a sphere of radius R the result is

$$\hat{\boldsymbol{r}} \cdot \boldsymbol{S}^{(L/R)}(\boldsymbol{r}) = \frac{ck_{m0}^4}{48\pi^2\varepsilon_0 R^2}\left|\boldsymbol{\mu}^{0m} \pm \frac{i}{c}\boldsymbol{m}^{0m}\right|^2 , \tag{6.9}$$

with the upper and lower signs for left- and right-polarized emission. There is an identical contribution from the cross term between zero- and second-order fields, so that the total is twice Eq. (6.9). Treating this energy flux from the emission of the excited molecule as incident radiation it is straightforward to calculate the absorption rate by molecule B. We have

$$\Gamma^{\text{abs}} = \frac{\rho k_{m0}^4}{72\pi\varepsilon_0^2\hbar R^2}\left|\boldsymbol{\mu}^{0m}(\mathrm{A}) \pm \frac{i}{c}\boldsymbol{m}^{0m}(\mathrm{A})\right|^2 \times \left|\boldsymbol{\mu}^{0m}(\mathrm{B}) \pm \frac{i}{c}\boldsymbol{m}^{0m}(\mathrm{B})\right|^2 , \tag{6.10}$$

where ρ is the density of states introduced earlier.

The discrimination in the transfer rate is found by summing the electric-magnetic terms in Eq. (6.10) for left- and right-handed circularly polarized photons. The result is the same as found in the response method, given in Eq. (5.10).

7 Conclusion

Molecular quantum electrodynamics provides a conceptually attractive framework for a deep understanding of intermolecular interactions. The essential feature of the theory is the quantization of the eletromagnetic field. Intermolecular interactions are viewed as arising from exchange of photons between molecules. In this paper we have described two approaches based on quantum electrodynamics which carry simple physical pictures. The induced moment viewpoint is that the vacuum field induces moments in the two molecules, the induced moments interacting with each other via retarded potentials. These potentials are known from earlier calculations for moments coupled through the quantized radiation field.

The Casimir approach to intermolecular forces and its description as related to fluctuations in the vacuum radiation field has in both cases the merit of a simple physical picture. In the extension of the second method to chiral systems there is the same objective. At first sight it may appear that the calculation is simpler than by conventional diagrammatic perturbation theory, but this is partly because the retarded interaction potentials Eqs. (1.6) and (3.9) for electric-electric and electric-magnetic dipole moments are already known. Although these are of the same form as the classical expressions for macroscopic systems they have to be found ab initio for atom or molecule moments coupled through the quantized radiation field, usually by perturbation theory. In Casimir's early work the classical electric dipole coupling potential was taken to apply to microscopic systems.

For chiral systems, fluctuations in the electromagnetic field induce virtual electric and magnetic dipole moments in molecules. The discrimination in the pairwise coupling between dextro-dextro and dextro-laevo appears as the interference between the contributions by electric-electric and magnetic-magnetic terms, and in the electric-magnetic term. Discrimination at short distances is from the former and shows an inverse sixth-power dependence on the separation. At longer distances the discrimination is from both and shows an inverse ninth-power dependence.

The application of the response method to energy transfer between chiral molecules depends on the idea that energy passes via the radiation field in left- and right-circularly polarized photons, and that the dextro-dextro, dextro-laevo, discrimination in the transfer rate depends on the different rates of absorption by the acceptor of the two circular polarizations, as in circular dichroism. The broader consideration of energy flow from spontaneous emission by a chiral molecule is discussed for the first time through the quantum electrodynamical form of the Poynting vector and the transfer rate calculated.

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