Intermolecular energy transfer in the presence of dispersing and absorbing media

Ho Trung Dung, Ludwig Knöll, and Dirk-Gunnar Welsch
Theoretisch-Physikalisches Institut, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany
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I. INTRODUCTION

Intermolecular energy transfer as a fundamental process in many biochemical and solid-state systems has been of increasing interest. It is often distinguished between two cases, namely (radiationless) short-range transfer (also called Förster transfer) and (radiative) long-range transfer. In the former the distance \( R \) between donor and acceptor is small compared with the electronic energy transfer wavelength \( \lambda_A \), \( R/\lambda_A \ll 1 \). The free-space transfer rate behaves as \( R^{-6} \), which can be explained by the instantaneous (longitudinal) Coulomb interaction between the two molecules. In the latter the intermolecular distance substantially exceeds the transition wavelength, \( R/\lambda_A \gg 1 \). The observed \( R^{-2} \) dependence of the transfer rate can be regarded as being the result of emission and reabsorption of real (transverse) photons. It is worth noting that in a rigorous approach to the problem (e.g., within the framework of the multipolar formalism of QED) the \( R^{-6} \) and \( R^{-2} \) distance dependences are limiting cases of a unified theory.

When the two molecules are near material bodies, then the electromagnetic field felt by them can be quite different from that in free space and the intermolecular energy transfer can change accordingly. The effect has attracted attention, because it offers the possibility of controlling the energy transfer, with regard to potential applications, e.g., in high-efficiency light-harvesting systems, optical networks, and quantum computing. Enhanced energy transfer between molecules randomly distributed within a single glycerol droplet (of about 10 \( \mu \)m diameter) and within a polymer Fabry–Pérot microcavity has been observed. Using monomolecular layers of donor and acceptor molecules (separated by distances of 10...20 nm) in planar microstructures, the dependence of short-range energy transfer on the local photon mode density has been demonstrated.

Calculations of the energy transfer rate have been performed in order to include the effect of bulk material, microspheres, and planar microcavities. The quantum theory given in Ref. becomes based on a microscopic model that allows for both dispersing and absorbing bulk material. In Refs. the classical field generated by a donor dipole and felt by an acceptor dipole in the presence of a microsphere is substituted into the free-space Fermi’s golden rule expression. A strictly quantum mechanical treatment that starts from a mode decomposition of the electromagnetic field according to the Helmholtz equation of the macroscopic Maxwell equations is given in Refs. Unfortunately, the microscopic theory developed for bulk material becomes quite cumbersome when boundaries are present, and studies based on the standard mode expansion cannot incorporate material absorption.

In the present paper we give a rigorous derivation of the rate of intermolecular energy transfer in the presence of arbitrarily shaped, dispersing, and absorbing material bodies, starting from the quantized version of the macroscopic electromagnetic field. The quantization is based on the introduction of Langevin noise current and charge densities into the classical Maxwell equations, which can then be transferred to quantum theory, with the electromagnetic-field operators being expressed in terms of a continuous set of fundamental bosonic fields via the classical Green tensor (see and references therein). In particular, we show that the minimal-coupling scheme and the multipolar-coupling scheme yield exactly the same form of the rate formula. It is worth noting that the formalism includes material absorption and dispersion in a consistent way, without restriction to a particular frequency domain, and applies to an arbitrary (inhomogeneous) medium configuration.

Here, we apply the theory to bulk material, multi-slab planar structures, and microspheres, with special emphasis on media of Drude–Lorentz type. In particular, we show that the energy transfer can be strongly modified, if the two molecules are sufficiently near an interface and surface-guided waves at the energy transfer wavelength...
exist. Four- and five-layered planar structures are studied, and the results are compared with recent measurements. Finally, the effect of surface-guided waves and whispering-gallery waves in the case of the molecules being near a microsphere is briefly discussed.

The paper is organized as follows. In Section II the basic-theoretical concept of electromagnetic-field quantization is outlined and the energy transfer rate is derived. Section II is devoted to applications, with special emphasis on multi-slab planar structures, and concluding remarks are made in Section IV. Some deepening calculations are given in the Appendix.

II. BASIC EQUATIONS

A. The Hamiltonian

Let us consider an ensemble of point charges, interacting with the quantized electromagnetic field in the presence of absorbing media. The minimal-coupling Hamiltonian in Coulomb gauge reads

\[ \hat{H} = \int \! d^3 \mathbf{r} \int_0^\infty \! d\omega \, \hbar \omega \hat{f}_\omega^\dagger (\mathbf{r}, \omega) \hat{f}(\mathbf{r}, \omega) + \sum_\alpha \frac{1}{2m_\alpha} \left[ \hat{p}_\alpha - q_\alpha \hat{A}(\mathbf{r}_\alpha) \right]^2 + \frac{1}{2} \int \! d^3 \mathbf{r} \, \hat{\rho}(\mathbf{r}) \hat{\phi}(\mathbf{r}) + \int \! d^3 \mathbf{r} \, \hat{\rho}(\mathbf{r}) \hat{\phi}(\mathbf{r}), \]  

(1)

where \( \hat{\mathbf{r}}_\alpha \) is the position operator and \( \hat{\mathbf{p}}_\alpha \) is the canonical momentum operator of the \( \alpha \)-th (nonrelativistic) particle of charge \( q_\alpha \) and mass \( m_\alpha \). The first term of the Hamiltonian is the energy of the medium-assisted electromagnetic field, expressed in terms of bosonic vector fields \( \hat{f}_\omega(\mathbf{r}, \omega) \) with commutation relations

\[ [\hat{f}_\omega(\mathbf{r}, \omega), \hat{f}^{\dagger}_\omega'(\mathbf{r}', \omega')] = \delta_{\omega\omega'} \delta(\mathbf{r} - \mathbf{r}') \delta(\omega - \omega'), \]

(2)

\[ [\hat{f}_\omega(\mathbf{r}, \omega), \hat{f}_\omega'(\mathbf{r}', \omega')] = 0. \]

(3)

The second term is the kinetic energy of the charged particles, and the third term is their Coulomb energy, where the corresponding scalar potential \( \hat{\phi}(\mathbf{r}) \) is given by

\[ \hat{\phi}(\mathbf{r}) = \int \! d^3 \mathbf{r}' \frac{\hat{\rho}(\mathbf{r}')}{4\pi \varepsilon_0 |\mathbf{r} - \mathbf{r}'|}, \]

(4)

with

\[ \hat{\rho}(\mathbf{r}) = \sum_\alpha q_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha) \]

(5)

being the charge density of the particles, and \( \varepsilon_0 \) the vacuum dielectric permittivity. The last term is the Coulomb energy of interaction of the particles with the medium.

The scalar potential \( \hat{\phi}(\mathbf{r}) \) and the vector potential \( \hat{\mathbf{A}}(\mathbf{r}) \) of the medium-assisted electromagnetic field are given by

\[ - \nabla \hat{\phi}(\mathbf{r}) = \int_0^\infty \! d\omega \, \hat{E}^\parallel(\mathbf{r}, \omega) + \text{H.c.,} \]

(6)

\[ \hat{\mathbf{A}}(\mathbf{r}) = \int_0^\infty \! d\omega \, (i\omega)^{-1} \hat{E}^\perp(\mathbf{r}, \omega) + \text{H.c.,} \]

(7)

where

\[ \hat{E}^{\parallel(\parallel)}(\mathbf{r}, \omega) = \int \! d^3 \mathbf{r}' \delta^{\parallel(\parallel)}(\mathbf{r} - \mathbf{r}') \hat{E}(\mathbf{r}', \omega), \]

(8)

with \( \delta^{\parallel}(\mathbf{r}) \) and \( \delta^{\perp}(\mathbf{r}) \) being the transverse and longitudinal dyadic \( \delta \)-functions, respectively, and

\[ \hat{E}(\mathbf{r}, \omega) = i \sqrt{\frac{\hbar}{\pi \varepsilon_0 c^2}} \int \! d^3 \mathbf{r}' \sqrt{\varepsilon_1(\mathbf{r}', \omega)} G(\mathbf{r}, \mathbf{r}', \omega) \hat{f}(\mathbf{r}', \omega). \]

(9)

Here, \( G(\mathbf{r}, \mathbf{r}', \omega) \) is the classical Green tensor, which obeys the inhomogeneous, partial differential equation

\[ \left[ \frac{\omega^2}{c^2} \varepsilon(\mathbf{r}, \omega) - \nabla \times \nabla \times \right] G(\mathbf{r}, \mathbf{r}', \omega) = - \delta(\mathbf{r} - \mathbf{r}') \]

(10)

together with the boundary condition at infinity \( [\delta(\mathbf{r}) \text{ is the dyadic } \delta \text{-function}] \), with \( \varepsilon(\mathbf{r}, \omega) = \varepsilon_1(\mathbf{r}, \omega) + i \varepsilon_2(\mathbf{r}, \omega) \) being the complex, space- and frequency-dependent permittivity.

Let us consider the case where the particles are constituents of neutral molecules (at positions \( \mathbf{r}_M \)) that are well separated from each other. The Hamiltonian \( \hat{H} \) can then be decomposed into an unperturbed part \( \hat{H}_0 \) and an interaction part \( \hat{H}_{\text{int}} \) as follows

\[ \hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \]

(11)

\[ \hat{H}_0 = \int \! d^3 \mathbf{r} \int_0^\infty \! d\omega \, \hbar \omega \hat{f}^\dagger(\mathbf{r}, \omega) \hat{f}(\mathbf{r}, \omega) + \sum_M \hat{H}_M, \]

(12)

\[ \hat{H}_{\text{int}} = \frac{1}{2} \sum_{M \neq M'} \hat{V}_{MM'} + \sum_M \hat{H}_{M \text{ int}}. \]

(13)

Here,

\[ \hat{H}_M = \sum_{\alpha_M} \frac{1}{2m_{\alpha_M}} \hat{p}^2_{\alpha_M} + \frac{1}{2} \hat{V}_{MM} \]

(14)

is the Hamiltonian of the \( M \)-th molecule,

\[ \hat{V}_{MM'} = \sum_{\alpha_M, \alpha_M'} \frac{q_{\alpha_M} q_{\alpha_M'}}{4\pi \varepsilon_0 |\mathbf{r}_{\alpha_M} - \mathbf{r}_{\alpha_M'}|} \]

(15)

is the Coulomb interaction energy between the \( M \)-th and the \( M' \)-th molecule, and
\[ \hat{H}_{\text{int}} = \sum_{\alpha_M} \left( -\frac{q_{\alpha_M}}{m_{\alpha_M}} \hat{p}_{\alpha_M} \cdot \hat{A}(\hat{r}_{\alpha_M}) \right) + \sum_{\alpha_M} \left( \frac{q_{\alpha_M}^2}{2m_{\alpha_M}} \right) \hat{A}^2(\hat{r}_{\alpha_M}) + \int d^3r \hat{\rho}_M(r) \hat{\varphi}(r) \] (16)

is the interaction energy between the \( M \)-th molecule [charge density \( \hat{\rho}_M(r) \)] and the medium-assisted electromagnetic field.

In what follows we shall restrict our attention to the (electric-)dipole approximation, so that Eq. (13) simplifies to

\[ \hat{V}_{MM'} = \varepsilon_0^{-1} \hat{d}_M \cdot \hat{\delta}_{\parallel}(\mathbf{r}_{M'} - \mathbf{r}_M) \hat{d}_M, \] (17)

where

\[ \hat{d}_M = \sum_{\alpha_M} q_{\alpha_M} (\hat{r}_{\alpha_M} - \mathbf{r}_M) \] (18)

is the dipole operator of the \( M \)-th molecule. Disregarding the \( \hat{A}^2 \) term in Eq. (13), which does not give rise to off-diagonal molecular matrix elements, making use of Eqs. (17)-(18), and applying the dipole approximation, \( \hat{H}_{\text{int}} \) takes the form of

\[ \hat{H}_{\text{int}} = -\int_0^\infty d\omega \int d^3r \hat{\mu}_M(\mathbf{r}, \omega) \hat{E}(\mathbf{r}, \omega) + \text{H.c.}, \] (19)

where

\[ \hat{\mu}_M(\mathbf{r}, \omega) = -\frac{1}{\hbar \omega} \left[ \hat{d}_M, \hat{H}_\omega \right] \delta^\parallel(\mathbf{r} - \mathbf{r}_M) + \hat{d}_M \delta^\parallel(\mathbf{r} - \mathbf{r}_M). \] (20)

### B. The transfer rate

Let us consider the resonant energy transfer between two molecules \( A \) and \( B \) at positions \( \mathbf{r}_A \) and \( \mathbf{r}_B \). The initial (final) state \( |i\rangle \) (\( |f\rangle \)) describes the excited molecule \( A \) (\( B \)), the molecule \( B \) (\( A \)) being in the ground state, and the medium-assisted field in vacuum, such that

\[ |i\rangle = |a', b\rangle \otimes |\{0\}\rangle, \quad E_i = E_{a'} + E_b, \] (21)

\[ |f\rangle = |a, b\rangle \otimes |\{0\}\rangle, \quad E_f = E_a + E_{b'} \] (22)

(cf. 12). Note that imposing this initial condition requires that the time of state preparation is sufficiently short compared with the time of energy transfer. Using the Born expansion 13 up to the second order perturbation theory, the (total) rate of energy transfer can be given by

\[ w = \sum_{f,i} p_i w_{fi}, \] (23)

where \( p_i \) is the occupation probability of the state \( |i\rangle \), and

\[ w_{fi} = \frac{2\pi}{\hbar} \langle f|\hat{T}|i\rangle^2 \delta(E_f - E_i) \] (24)

with

\[ \hat{T} = \hat{H}_{\text{int}} + \hat{H}_{\text{int}} \frac{1}{E_i - E_0 + is} \hat{H}_{\text{int}}, \quad s \to +0. \] (25)

Applying the decomposition (13), we may write

\[ \langle f|\hat{T}|i\rangle = \langle a, b'|\hat{T}|a', b \rangle = \langle a, b'|\hat{V}_{AB}|a', b \rangle + \langle a, b'|\hat{T}|a', b \rangle, \] (26)

where

\[ \langle a, b'|\hat{V}_{AB}|a', b \rangle = \varepsilon_0^{-1} \left[ \hat{d}_{b'\parallel} \delta^\parallel(\mathbf{r}_B - \mathbf{r}_A) \hat{d}_{a\parallel} \right], \] (28)

where

\[ \hat{d}_{a\alpha'}(\mathbf{r}) = \langle a(b)|\hat{d}_{A(B)}|\alpha'(\alpha')\rangle. \] (29)

In order to calculate \( \langle a, b'|\hat{T}|a', b \rangle \), we make use of Eqs. (19) and (24), perform the summation and integrations over the possible intermediate states \( |a', b\rangle \int f(s, \omega)|\{0\}\rangle \) and \( |a, b\rangle \int f(s, \omega)|\{0\}\rangle \). After some calculation we derive, on applying Eq. (15) and the relationship 14, 17,

\[ \text{Im} G_{kl}(\mathbf{r}, \mathbf{r}', \omega) \]

\[ = \int d^3s \frac{\omega^2}{c^2} \varepsilon_1(s, \omega) G_{km}(r, s, \omega) G^*_{lm}(r', s, \omega), \] (30)

\[ \langle a, b'|\hat{V}_{AB}|a', b \rangle = \frac{\hbar \omega^2_{ab}}{\pi \varepsilon_0 c^2} \int d^3r' \int d^3r \int_0^\infty d\omega \times \left\{ \frac{[d_{a'b} \Delta_B(r', -\omega)] \text{Im} G(r', r, \omega) \Delta_A(r, -\omega) d_{a\alpha'}]}{\hbar \omega_{a\alpha'} - \hbar \omega + is} \right. \]

\[ + \frac{[d_{a'b} \Delta_B(r', \omega)] \text{Im} G(r', r, \omega) \Delta_A(r, \omega) d_{a\alpha'}]}{\hbar \omega_{a\alpha'} - \hbar \omega + is} \right\}, \] (31)

where

\[ \omega_{a\alpha'} = (E_{a'} - E_a)/\hbar = (E_{b'} - E_b)/\hbar = \omega_{b'b} \] (32)

and

\[ \Delta_A(B)(\mathbf{r}, \omega) = \delta^\parallel(\mathbf{r} - \mathbf{r}_A(B)) + \frac{\omega}{\omega_{a\alpha'}(\alpha')} \delta^\parallel(\mathbf{r} - \mathbf{r}_A(B)) \] (33)
[note that \( \Delta_{A(B)}(r, \omega_{a'a'b'}) = \delta(r - r_{A(B)}) \)]. Recalling that \( \text{Im} \ G(r', r, -\omega) = -\text{Im} \ G(r', r, \omega) \), we may rewrite Eq. (31) as
\[
\langle a, b' | \bar{T} | a', b \rangle = \frac{\hbar \omega^2_{a'a'}}{\pi \varepsilon_0 c^2} \int d^3 r' \int d^3 r \int_{-\infty}^{\infty} d\omega \nonumber \times \left\{ \frac{[d_{\bar{b}b} \Delta_B(r', \omega) G(r', r, \omega) \Delta_A(r, \omega)d_{a'a'}]}{\hbar \omega_{a'a'} - \hbar \omega + i\varepsilon \text{sign} (\omega)} \right\} \text{ (34)}
\]
or, equivalently,
\[
\langle a, b' | \bar{T} | a', b \rangle = \frac{\hbar \omega^2_{a'a'}}{\pi \varepsilon_0 c^2} \int d^3 r' \int d^3 r \int_{-\infty}^{\infty} d\omega \times \frac{1}{2i} \left\{ \left[ \frac{[d_{\bar{b}b} \Delta_B(r', \omega) G(r', r, \omega) \Delta_A(r, \omega)d_{a'a'}]}{\hbar \omega_{a'a'} - \hbar \omega + i\varepsilon \text{sign} (\omega)} \right] - \left[ \frac{[d_{\bar{b}b} \Delta_B(r', \omega) G(r', r, \omega) \Delta_A(r, \omega)d_{a'a'}]}{\hbar \omega_{a'a'} - \hbar \omega - i\varepsilon \text{sign} (\omega)} \right] \right\} \text{ (35)}
\]

The \( \omega \)-integral in Eq. (33) may now be evaluated by means of contour-integral techniques, by taking into account that the Green tensor is a holomorphic function of \( \omega \) in the upper complex half-plane, which asymptotically behaves as \[17\]
\[
\lim_{|\omega| \rightarrow \infty} \frac{\omega^2}{\varepsilon^2} G(r, r', \omega) = -\delta(r - r'). \text{ (36)}
\]
We therefore close the path of integration by an infinitely large semicircle in the upper complex half-plane, \( |\omega| \rightarrow \infty \), and subsequently subtract the semicircle integral. It is easily seen that only the terms in \( \Delta_A(r, \omega) \) and \( \Delta_B(r, \omega) [\text{Eq. (13)] which are proportional to \( \omega \) contribute to the integral over the semicircle,

\[
\langle a, b' | \bar{T} | a', b \rangle \big|_{\text{semicircle}} = \varepsilon_0^{-1} \left[ d_{\bar{b}b} \delta(r_B - r_A) d_{a'a'} \right]. \text{ (37)}
\]

It is further seen that only the first term in the curly bracket contributes to the integral over the closed path. We thus arrive at
\[
\langle a, b' | \bar{T} | a', b \rangle = -\varepsilon_0^{-1} \left[ d_{\bar{b}b} \delta(r_B - r_A) d_{a'a'} \right] - \frac{\omega^2_{a'a'}}{\varepsilon_0 c^2} \left[ d_{\bar{b}b} G(r_B, r_A, \omega_{a'a'}) d_{a'a'} \right]. \text{ (38)}
\]
Substitution of the expressions (23) and (28) into Eq. (26) yields the transition amplitude
\[
\langle a, b' | \bar{T} | a', b \rangle = \frac{\omega^2_{a'a'}}{\varepsilon_0 c^2} \left[ d_{\bar{b}b} G(r_B, r_A, \omega_{a'a'}) d_{a'a'} \right]. \text{ (39)}
\]
Note that the first term in Eq. (38) and the Coulomb term (28) exactly cancel out. We eventually combine Eqs. (24) and (33) and find that the rate of energy transfer between the chosen states \( |a', b \rangle \) and \( |a, b' \rangle \) reads as \( w_{fi} = w_{ab}^{a'b'} \)
\[
w_{ab}^{a'b'} = \frac{2\pi}{\hbar^2} \left( \frac{\omega^2_{a'a'}}{\varepsilon_0 c^2} \right)^2 \times |d_{\bar{b}b} G(r_B, r_A, \omega_{a'a'}) d_{a'a'}|^2 \delta(\omega_{a'a'} - \omega_{b'b}). \text{ (40)}
\]
It can be proved (Appendix A) that the use of the multipolar Hamiltonian \[17\] instead of the minimal-coupling Hamiltonian \[11\] exactly leads to the same expression of the energy transfer rate.

Let us now consider the total energy transfer rate according to Eq. (23), by taking into account the vibronic structure of the molecular energy levels. Restricting our attention to the Born–Oppenheimer approximation and neglecting the weak dependence of the electronic transition-dipole matrix element on the nuclear coordinates (see, e.g., [20]), we may factorize the dipole transition matrix elements according to
\[
d_{a'a'}(b'b) = d_{A(B)}(v_{aa'}(b'b)), \text{ (41)}
\]
where \( d_{A(B)} \) is the purely electronic transition-dipole matrix element of the transition between the lower and the upper electronic state of the molecule \( A(B) \), and \( v_{aa'}(b'b) \) are the overlaps integrals between the vibrational quantum states in the two electronic states of the respective molecule. Note that the vibrational overlap integrals take account of both displaced and distorted energy surfaces. Combining Eqs. (23) and (10) yields
\[
w = \frac{2\pi}{\hbar^2} \sum_{a, a'} \sum_{b, b'} p_a p_b \left( \frac{\omega^2_{a'a'}}{\varepsilon_0 c^2} \right)^2 \left| v_{a'b'} \right|^2 \times \left| d_{\bar{b}b} G(r_B, r_A, \omega_{a'a'}) d_{a'a'} \right|^2 \delta(\omega_{a'a'} - \omega_{b'b}), \text{ (42)}
\]
which can be rewritten as
\[
w = \int d\omega \tilde{w}(\omega) \sigma^m_A(\omega) \sigma^b_B(\omega), \text{ (43)}
\]
where
\[
\tilde{w}(\omega) = \frac{2\pi}{\hbar^2} \left( \frac{\omega^2_{a'a'}}{\varepsilon_0 c^2} \right)^2 \left| d_{\bar{b}b} G(r_B, r_A, \omega) d_{a'a'} \right|^2, \text{ (44)}
\]
and
\[
\sigma^m_A(\omega) = \sum_{a, a'} \left| p_{a'} \right|^2 \left| v_{a'a} \right|^2 \delta(\omega_{a'a'} - \omega), \text{ (45)}
\]
and
\[
\sigma^b_B(\omega) = \sum_{b, b'} \left| p_{b'} \right|^2 \left| v_{b'b} \right|^2 \delta(\omega_{b'b} - \omega), \text{ (46)}
\]
respectively, are proportional to the (single-photon) emission spectrum of molecule \( A \) and the (single-photon) absorption spectrum of molecule \( B \) in free space each [20]. Thus, the rate of energy transfer is proportional to the overlap of the two spectra weighted by the square of the absolute value of the actual Green tensor. It is worth
mentioning that Eqs. (40)–(46) apply to the resonant energy transfer between two molecules in the presence of an arbitrary configuration of dispersing and absorbing macroscopic bodies. All the relevant parameters of the bodies are contained in the Green tensor. Note that the emission (absorption) spectrum observed in this case is not proportional to $\sigma_{A}^{em}(\omega)|\sigma_{B}^{abs}(\omega)|$ in general, as it can be seen from a comparison of Eq. (13) with Eq. (14).

In particular when the Green tensor slowly varies with frequency on a scale given by the (relevant) vibrational frequencies of the molecules, then $\check{w}(\omega)$ is also a slowly varying function of frequency and can (approximately) be taken at the electronic energy transfer frequency $\omega_{A} (\approx \omega_{B})$ and put in front of the integral in Eq. (13), thus

$$w \simeq \check{w}(\omega_{A}) \sigma,$$  \hspace{1cm} (47)

where

$$\sigma = \int d\omega \sigma_{A}^{em}(\omega) \sigma_{B}^{abs}(\omega).$$  \hspace{1cm} (48)

In this case, the influence of matter environment on the (total) energy transfer rate is fully contained in $\check{w}(\omega_{A})$. Clearly, when the two molecules are near a resonator-like environment, so that the molecule can “feel” sharply-peaked field resonances, then $\check{w}(\omega)$ cannot be assumed to be a slowly varying function of frequency in general (see Section II C).

It may be interesting to compare the rate of energy transfer with the donor decay rate. Straightforward generalization of the well-known formula for a two-level transition yields, on applying the Born–Oppenheimer approximation,

$$\Gamma_{A} = \int d\omega \tilde{\Gamma}_{A}(\omega) \sigma_{A}^{em}(\omega),$$  \hspace{1cm} (49)

where

$$\tilde{\Gamma}_{A}(\omega) = \frac{2\omega^{2}}{\hbar\varepsilon_{0} c^{2}} [d_{A}^{\dagger} \text{Im} G(r_{A}, r_{A}, \omega) d_{A}],$$  \hspace{1cm} (50)

and $\sigma_{A}^{em}(\omega)$ is given by Eq. (15). Whereas the decay rate is determined by the imaginary part of the Green tensor (taken at equal positions), the transfer rate is determined by the full Green tensor (taken at different positions). Thus, decay rate and transfer rate can quite differently respond to a change of the environment.

III. APPLICATIONS

A. Bulk material

Let us first consider the case when the two molecules are embedded in bulk material of arbitrary complex permittivity $\varepsilon(\omega)$. Using the well-known expression of the bulk-material Green tensor $G^{\text{bulk}}(r, r', \omega)$ (see, e.g., [7]), application of Eq. (14) yields

$$\check{w}(\omega) = \frac{2\pi}{\hbar} \left( \frac{\omega^{2}}{\varepsilon(\omega)} \right)^{2} |d_{B}^{\dagger} G^{\text{bulk}}(r_{B}, r_{A}, \omega) d_{A}|^{2},$$  \hspace{1cm} (51)

where

$$d_{B}^{\dagger} G^{\text{bulk}}(r_{B}, r_{A}, \omega) d_{A} = \frac{q(\omega)}{4\pi} \exp[iq(\omega)R]$$

$$\times \left[ -\left( d_{B}^{\dagger} d_{A} - 3\frac{d_{B}^{\dagger} R}{R} \frac{d_{A} R}{R} \right) \frac{1}{q^{2}(\omega)R^{3}} - \frac{i}{q^{2}(\omega)R^{2}} \right] + \left( d_{B}^{\dagger} d_{A} - \frac{d_{B}^{\dagger} R}{R} \frac{d_{A} R}{R} \right) \frac{1}{q(\omega)R} \right]$$  \hspace{1cm} (52)

with $q(\omega) = \sqrt{\varepsilon(\omega)} \frac{\omega}{c}$. $R = r_{B} - r_{A}$. (53)

The energy transfer rate is then obtained according to Eq. (13). Obviously, the Green tensor of bulk material can be regarded as being a slowly varying function of frequency, so that the approximation (14) applies.

From Eqs. (51) and (52) it is seen that the energy transfer rate includes both the small-distance case ( Förster transfer), with the rate being proportional to $R^{-6}$, and the large-distance (radiative) case, where the rate becomes proportional to $R^{-2}$. Note that the exponential $|\exp[iq(\omega)R]|^{2} = |\exp[-2\eta_{n}(\omega)R/c]|$, which typically arises from material absorption, drastically diminishes the large-distance energy transfer [\sqrt{\varepsilon(\omega)} = n(\omega) = n_{R}(\omega) + i\eta_{n}(\omega)]. In Eq. (51) local-field corrections are ignored. They may be taken into account by applying, e.g., the scheme used in Ref. [18] for correcting the rate of spontaneous decay.

It is worth noting that the above given result, which is based on the quantization of the macroscopic Maxwell field for given complex permittivity, exactly corresponds to the result obtained in Ref. [6] within the framework of a fully microscopic approach on the basis of some model medium coupled to the radiation field and a heat bath. Already from the study of the spontaneous decay of an excited atom near an interface [21] it is clear that in the case of inhomogeneous media (of complicated atomic structure) a microscopic approach would be rather involved and closed solutions would hardly be found.

B. Multi-slab planar structures

Let us consider a planar multi-slab structure and assume that the two molecules are in the same slab. The relevant Green tensor (for the energy transfer between the two molecules relevant) of an inhomogeneous system of this type can always be written in the form of

$$G(r_{B}, r_{A}, \omega) = G^{\text{bulk}}(r_{B}, r_{A}, \omega) + G^{\text{refl}}(r_{B}, r_{A}, \omega),$$  \hspace{1cm} (54)
where $G^{\text{bulk}}(r_B, r_A, \omega)$ is the Green tensor according to Eq. (52), with $\varepsilon(\omega)$ being the permittivity of the slab in which the two molecules are located, and the reflection term $G^{\text{refl}}(r_B, r_A, \omega)$ insures the correct boundary conditions at the surfaces of discontinuity. Clearly, a decomposition of the type of Eq. (54) is also valid for other than planar systems, provided that the two molecules are located in a region of space-independent permittivity.

To be more specific, let the $z$-direction be the direction of variation of the permittivity of the multi-slab system and assume that $r_A$ and $r_B$ are in the $j$th slab of thickness $d_j$ (Fig. 1). The reflection term in Eq. (54) can then be given by $\refl$ (see also Ref. 23)

$$G^{\text{refl}}(r_B, r_A, \omega) = \frac{i}{4\pi} \int_0^\infty \frac{dk_j k_{||}}{2\beta_j} e^{i \beta_j d_j} G^{\text{refl}}(r_B, r_A, \omega, k_{||})(55)$$

where $[k_j = \sqrt{\varepsilon_j(\omega)}/c; \beta_j = (k_j^2 - k_{||}^2)^{1/2}]$. Choosing the coordinate system such that $R_y = 0$, the nonvanishing components of $G^{\text{refl}}$ read

$$\tilde{G}^{\text{refl}}_{xx(\gamma\gamma)} = -\frac{\beta_j^2}{k_j^2} C_p^{-} \left[ J_0(k_j R_x) - (+) J_2(k_j R_x) \right]$$

$$+ C_p^{+} \left[ J_0(k_j R_x) + (-) J_2(k_j R_x) \right], \quad (56)$$

$$\tilde{G}^{\text{refl}}_{xz(zx)} = -(+2i) \frac{\beta_j k_{||}}{k_j^2} S^{p}_{(+)} J_1(k_j R_x), \quad (57)$$

$$\tilde{G}^{\text{refl}}_{zz} = 2 \frac{k_j^2}{k_{||}^2} C_p^{+} J_0(k_j R_x) \quad (58)$$

$[J_n(x) - Bessel function], where

$$C_p^q(\pm) = \left[ p_q e^{i\beta_j(z_A + z_B - d_j)} + p_q e^{-i\beta_j(z_A + z_B - d_j)} \right]$$

$$+ (-) 2p_q r_q^p \cos(\beta_j R_x) e^{i\beta_j d_j} \right] D_q^{-1}, \quad (59)$$

$$\begin{align*}
S^q_{(+)} &= \left[ p_q e^{i\beta_j(z_A + z_B - d_j)} - p_q e^{-i\beta_j(z_A + z_B - d_j)} \\
&+ (-) 2ir_q^p r_q^\parallel \sin(\beta_j R_x) e^{i\beta_j d_j} \right] D_q^{-1}, \quad (60)
\end{align*}$$

$$D_q = 1 - p_q^2 e^{2i\beta_j d_j}. \quad (61)$$

Here, $q = p(s)$ means TM(TE) polarized waves, and $r_q^q(\pm)$ are the total reflection coefficients at the upper (lower) stack of slabs $[y' < j (j' > j)]$ of the waves in the $j$th slab (for details, see Ref. 24). Note that when $r_A$ and $r_B$ are in the top (bottom) slab, then Eqs. (55)-(61) (formally) apply provided that $r_+^{q(\pm)} = 0$ and $d_j = 0$ are set.

If the frequencies of the vibronic transitions that are involved in the energy transfer are sufficiently far from a medium resonance, so that material absorption (in the $j$th slab) may be disregarded, then the permittivity may be considered as being real and positive. In this case, it may be useful to decompose the integral in Eq. (55) into two parts,

$$G^{\text{refl}}(r_B, r_A, \omega) = G_1^{\text{refl}}(r_B, r_A, \omega) + G_2^{\text{refl}}(r_B, r_A, \omega), \quad (62)$$

$$G_1^{\text{refl}}(r_B, r_A, \omega) = \frac{i}{4\pi} \int_0^\infty \frac{dk_j k_{||}}{2\beta_j} e^{i \beta_j d_j} G^{\text{refl}}(r_B, r_A, \omega, k_{||}), \quad (63)$$

$$G_2^{\text{refl}}(r_B, r_A, \omega) = \frac{i}{4\pi} \int_0^\infty \frac{dk_j k_{||}}{2\beta_j} e^{-|\beta_j|d_j} \tilde{G}^{\text{refl}}(r_B, r_A, \omega, k_{||}). \quad (64)$$

Obviously, $G_1^{\text{refl}}$ results from waves that have a propagating component in the $z$-direction, whereas the waves that contribute to $G_2^{\text{refl}}$ are purely evanescent in the $z$-direction.

1. Interface

Let the two molecules be embedded in a half-space medium (medium 1) and assume that in the relevant frequency interval the permittivity of the medium $\varepsilon_1(\omega)$ can be regarded as being real and positive. When the molecules are near the interface between the two half-space media such that $k_1(z_A + z_B) \ll 1$, it can be proved that Eqs. (55)-(58) reduce to ($k_1 R_x \ll 1$)
the electronic part of the corresponding donor decay rate allows influence the resonant energy transfer. In particular, decaying waves play an important role and can notice-
sibly influence the resonant energy transfer. In particular, decaying waves play an important role and can noticeably influence the resonant energy transfer.

\[ G^\text{refl}(\mathbf{r}_B, \mathbf{r}_A, \omega) \approx \frac{1}{4\pi k^2} \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \left( \frac{z_A + z_B}{2} \right)^2 - \left( + \right) 2R_x^2, \]  

(65)

\[ G^\text{refl}(\mathbf{r}_B, \mathbf{r}_A, \omega) \approx \frac{1}{4\pi k^2} \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \left( \frac{z_A + z_B}{2} \right)^2 - \left( + \right) 2R_x^2, \]  

(66)

\[ G^\text{refl}(\mathbf{r}_B, \mathbf{r}_A, \omega) \approx \frac{1}{4\pi k^2} \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \left( \frac{z_A + z_B}{2} \right)^2 - \frac{1}{2R_x^2} \left( \frac{z_A + z_B}{2} \right)^2 + 1 \]  

(67)

\[ \varepsilon_2(\omega), \text{complex permittivity of medium 2}. \]

Note that for \( \mathbf{r}_A = \mathbf{r}_B \), Eqs. (65)–(67) just give the Green tensor whose imaginary part determines the influence of the interface on the rate of spontaneous decay of a single molecule [21,24]. (For some special cases, see also Ref. [15].) Under the assumptions made, the main contribution to \( G^\text{refl} \) comes from \( G^\text{refl}_{zz} \). Hence surface-guided waves (including decaying waves) play an important role and can noticeably influence the resonant energy transfer. In particular, when medium 2 is a metal or a dielectric with \( \varepsilon_2 < 0 \), (and typically \( \varepsilon_2 \ll |\varepsilon_2| \)), then a strong effect is observed for \( \varepsilon_2(\omega) = -\varepsilon_1(\omega) \), which is nothing but the condition for best excitation of surface-guided waves [26].

In the numerical calculation of \( \tilde{w}(\omega) \) [Eq. (44)], which contains the relevant information about the influence of the interface on the rate of energy transfer [see Eqs. (13)–(14)], we have assumed that the two molecules are situated in vacuum \( \varepsilon_1(\omega) = 1 \) above a half-space medium of Drude–Lorentz type and restricted our attention to a single-resonance medium,

\[ \varepsilon_2(\omega) = \varepsilon(\omega) = 1 + \frac{\omega_p^2}{\omega^2 - \omega^2 - i\gamma}. \]  

(68)

Here, \( \omega_p \) corresponds to the coupling constant, and \( \omega_T \) and \( \gamma \) are respectively the medium oscillation frequency and the linewidth. Recall that the Drude–Lorentz model covers both metallic \( \omega_T = 0 \) and dielectric \( \omega_T \neq 0 \) matter and features a band gap between \( \omega_T \) and \( \omega_L = \sqrt{\omega_T^2 + \gamma^2} \). We have performed the calculations using the exact Green tensor [Eqs. (24)–(24)]. Comparing the results with those obtained by using the approximately valid Green tensor [Eq. (24) together with Eqs. (25)–(27)], we have found good agreement.

The behavior of \( \tilde{w}(\omega) \) is illustrated in Fig. 3. It is seen that outside the band gap \( \omega < \omega_T \) where \( \varepsilon_2 > 0 \) the modification of \( \tilde{w}(\omega) \) due to the presence of the interface is small even for small distances of the molecules from the interface. Since in this frequency domain \( \tilde{w}(\omega) \) may be regarded as being slowly varying on a frequency scale defined by the vibrational frequencies of the molecules, Eq. (44) applies. Thus, the energy transfer rate is simply proportional to \( \tilde{w}(\omega_A) \).

Inside the band gap, however, the interface can significantly affect \( \tilde{w}(\omega) \) if, according to Eqs. (63)–(67),
Finally, the large-distance reduction of \( \tilde{w}(\omega) \) below the free-space level results from material absorption. As already mentioned, the behavior of \( \tilde{w}(\omega) \) in Fig. 3 is dominated by surface-guided waves that decay exponentially along the \( \pm z \)-directions. With increasing material absorption the penetration depths decrease, so that on average \( \tilde{w}(\omega) \) becomes closer to the free-space level. The possibility of controlling the ultrashort-range energy transfer by varying the distance of the molecule from the surface is illustrated in the inset.

In Fig. 4 the dependence of \( \tilde{w}(\omega) \) (again for \( \omega \approx 1.062 \omega_T \)) on the molecule–surface distance is plotted, and the contributions to \( \tilde{w}(\omega) \) from ordinary waves having a propagating component in \( z \)-direction (\( G_1^{\text{eff}} \)) and surface-guided waves (\( G_2^{\text{eff}} \)) are shown. It is clearly seen that when the two molecules are very near the surface, then energy transfer between them is mediated by surface-guided waves, whereas for larger distances ordinary waves play the dominant role. Note that the oscillatory behavior is typical of the latter case. Clearly, for very large distances \( (z_A, z_B \gg \lambda_T) \) the free-space behavior is observed.

2. Comparison with experiments

Recently, experiments have been carried out to study the transfer of excitation energy between dye molecules confined within planar optical microcavities \( 8 \). In the experiments, donors (Eu\(^{3+} \) complex) and acceptors (1,1'-dioctadecyl-3,3',3'-tetramethylindodicarbocyanine) embedded within a transparent material (22-tricosenoic acid) bounded by no (weak-cavity structure), one (half-cavity structure), or two (full-cavity structure) silver mirrors are considered. To compare the experimental results with the theoretical ones, we have modeled the half-cavity structure by a planar four-layered system and the full-cavity structure by a five-layered system. The former consists of vacuum, dielectric matter (22-tricosenoic acid, \( \varepsilon = 2.49 \) \( 26 \), thickness \( d \), metal (silver, \( \varepsilon = -16.0 + 0.6i \) \( 26 \), thickness 25 nm), and vacuum, and the latter consists of vacuum, metal (silver, thickness 20 nm), dielectric matter (the same as above, thickness \( d \), metal (silver, thickness 25 nm), and vacuum. In each system, the donor is situated in the middle of the dielectric layer, while the position of the acceptor is shifted towards the silver mirror of 25 nm thickness. The Green tensors of the two systems can be calculated according to Eqs. (54)–(55). Assigning to silver a Drude–Lorentz-type permittivity \( 27 \), it can be proven that in the relevant frequency interval (of overlapping donor emission and acceptor absorption spectra) \( \tilde{w}(\omega) \) and \( \tilde{\Gamma}_A(\omega) \) sufficiently slowly vary with \( \omega \), so that [cf. Eq. (17)] \( \tilde{w} \sim \tilde{w}(\omega_A) \) and, similarly, \( \tilde{\Gamma}_A \sim \tilde{\Gamma}_A(\omega_A) \). Thus, \( \tilde{w}(\omega_A) \) and \( \tilde{\Gamma}_A(\omega_A) \) can be viewed as measures of the energy transfer rate and the donor decay rate, respectively.
FIG. 5. The electronic parts of the donor decay rate (a) and the donor–acceptor energy transfer rate (b) (averaged over the dipole orientations) of molecules in cavity-like systems are shown as functions of the cavity length for the four-layered system (dashed line) and the five-layered system (full line) considered in Section III B 2 (λ_A = 614 nm; R = −R_z = 24 nm).

Figure 5 shows the dependence on d of \( \tilde{\Gamma}_A(\omega_A) \) and \( \tilde{w}(\omega_A) \) (averaged over the dipole orientations). From Fig. 5(a) it is seen that at \( d/\lambda_A \sim 0.21 \) (i.e., \( d \sim 130 \) nm for \( \lambda_A = 614 \) nm) the ratio of the donor decay rates for the five- and four-layered systems is \( \tilde{\Gamma}_A(\omega_A)|_5/\tilde{\Gamma}_A(\omega_A)|_4 \sim 1.3 \), which (within the measurement accuracy) is in sufficiently good agreement with experimental result (see Fig. 2D in Ref. [8]). Note that in the vicinity of \( d/\lambda_A \sim 0.21 \) the ratio of the two rates sensitively responds to a change of \( d/\lambda_A \).

Comparing \( \hat{\Gamma}_A(\omega_A) \) [Fig. 5(a)] with \( \hat{w}(\omega_A) \) [Fig. 5(b)], we see that for the four-layered system and \( d/\lambda_A \sim 0.16...0.33 \) (i.e., \( d \sim 100...200 \) nm for \( \lambda_A = 614 \) nm) both \( \hat{\Gamma}_A(\omega_A) \) and \( \hat{w}(\omega_A) \) decrease with increasing \( d \) and an approximately valid linear relation between the energy transfer rate and the donor decay rate can be established in agreement with experimental results in Ref. [8]. From the data reported in Ref. [8] it could be expected that the linear relation between the two rates is generally valid. This is of course not the case. Since the energy transfer rate is determined by the full (two-point) Green tensor, whereas the donor decay rate is only determined by the imaginary part of the (one-point) Green tensor, the two rates can behave quite differently, as it is demonstrated in Fig. 5. In particular, the increase of the donor decay rate at the cavity resonances can be accompanied with a decrease of the energy transfer rate, because of destructive interferences.

In the experiments in Ref. [8], the measurements are performed on an ensemble of donors and acceptors whose distance is fixed in the z-direction but variable in the x-direction (\( \Delta R_x \sim 1 \) nm). The question thus arises of whether the measured data refer to a single nearest-neighboring donor–acceptor pair (\( R_z = 0 \)) or not. In Fig. 6 we have plotted the dependence on d of \( \tilde{w}(\omega_A) \) (averaged over the dipole orientations) for the five-layered system and various values of \( R_z \), with \( R_z \) being fixed. We see that the rates of energy transfer between molecules whose distances are larger than that of nearest-neighboring molecules can be quite comparable with those of the latter. Moreover there are also cases where the energy transfer rate increases with the donor–acceptor distance. The experimentally determined energy transfer rates are thus averaged rates, which not necessarily show the characteristic features of single-pair transfer rates. Averaging in Fig. 6 \( \tilde{w}(\omega_A) \) over all values of \( R_z \), the resulting curve is expected to be substantially flatter than the solid-line curve (\( R_z = 0 \)), particularly when d sweeps through \( \lambda_A \).

An analysis of the contributions of \( G_1^\text{refl} \) [Eq. (63)] and \( G_2^\text{refl} \) [Eq. (64)] to \( G^\text{refl} \) [Eq. (62)] reveals that for cavity
lengths of \( d/\lambda_A \lesssim 0.16 \) (i.e., \( d \lesssim 100 \) nm for \( \lambda_A = 614 \) nm) evanescent waves dominate the influence of the cavity system on both the rate of intermolecular energy transfer and the donor decay rate and lead to a strong increase of them. Whereas for cavities lengths of \( d/\lambda_A \gtrsim 0.81 \) (i.e., \( d \gtrsim 500 \) nm for \( \lambda_A = 614 \) nm) evanescent waves only weakly affect the donor decay rate, they can strongly affect the intermolecular energy transfer up to cavity lengths of a few micrometers. Note that the resonance lengths seen in Fig. 7 originate from propagating waves.

### C. Microsphere

Microspheres have been of increasing interest, because of the whispering-gallery (WG) and surface-guided (SG) waves, which may be employed, e.g., for reducing the thresholds of nonlinear optical processes \([23,24]\). Intermolecular energy transfer in the presence of microspheres has been considered for molecules near a small metallic spheroid (spheroid's linear extension \( \ll \lambda_A \)) in the non-retardation limit, for molecules embedded within a dielectric microsphere \([112]\), and for the case where one molecule is inside a dielectric microsphere and the other outside it \([3]\). Here we restrict our attention to the influence of WG and SG waves on the energy transfer between two molecules outside a microsphere, taking fully into account retardation effects.

Let \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) be respectively the permittivities outside and inside the sphere. If the transition dipole moments are parallel to each other and tangentially oriented with respect to the sphere, the relevant (spherical-coordinate) components of \( G^{\text{refl}} \) are \((\phi_A = \phi_B = 0, \theta_A = 0)\)

\[
G^{\text{refl}}_{\phi_B \phi_A}(r_B, r_A, \omega) = \frac{ik_1}{4\pi} \sum_{l=1}^{\infty} \frac{(2l + 1)}{l(l+1)} \left[ B^M_l h^{(1)}_l(k_1 r_A) h^{(1)}_l(k_1 r_B) \right.
\]
\[
\times \left[ l(l+1) P_l(\cos \theta_B) - \cos \theta_B P'_l(\cos \theta_B) \right]
\]
\[
+ B^N_l \left\{ \frac{k_1 r_A h^{(1)}_l(k_1 r_A)}{k_1 r_B} \right\}
\]
\[
\times \left[ \frac{k_1 r_B h^{(1)}_l(k_1 r_B)}{k_1 r_B} \right] P'_l(\cos \theta_B) \right] \}
\]

(69)

(for the Green tensor of a sphere, see, e.g., \([23]\), and for radially oriented dipoles the relevant components are \((\phi_A = \phi_B = 0, \theta_A = 0)\)

\[
G^{\text{refl}}_{\phi_B \phi_A}(r_B, r_A, \omega) = \frac{ik_1}{4\pi} \sum_{l=1}^{\infty} \frac{(2l + 1)}{l(l+1)} \frac{l(l+1)}{r_A r_B} \left[ B^M_l h^{(1)}_l(k_1 r_A) h^{(1)}_l(k_1 r_B) P'_l(\cos \theta_B) \right],
\]

(70)

where

\[
B^M_l(\omega) = - \frac{[a_2 j_l(a_2)'] j_l(a_1) - [a_1 j_l(a_1)]' j_l(a_2)}{[a_2 j_l(a_2)]' h^{(1)}_l(a_1) - j_l(a_2) [a_1 h^{(1)}_l(a_1)]'},
\]

(71)

\[
B^N_l(\omega) = - \frac{\varepsilon_1(\omega) j_l(a_2) [a_1 j_l(a_1)]'}{\varepsilon_1(\omega) j_l(a_2) [a_2 j_l(a_2)]'} - \frac{\varepsilon_2(\omega) j_l(a_1) [a_2 j_l(a_2)]'}{\varepsilon_2(\omega) j_l(a_2) [a_2 j_l(a_2)]'} h^{(1)}_l(a_1)
\]

(72)

\([a_1, 2 = k_1, 2 a]; a, \) microsphere radius; \( j_l(z), \) spherical Bessel function; \( h^{(1)}_l(z), \) spherical Hankel function; \( P'_l(x), \) associated Legendre function).

In Fig. 7 the dependence on frequency of \( \tilde{\omega}(\omega) \) is illustrated for the case where vacuum is outside the sphere and the two molecules are placed at diametrically opposite positions \((r_A = -r_B), \) with the transition dipole moments being radially oriented. It is clearly seen that the energy transfer can greatly be facilitated at the positions of the sphere-assisted field resonances, the enhancement of \( \tilde{\omega}(\omega) \) at the positions of SG resonances (inside the band gap) being larger than those at the positions of WG resonances (outside the band gap). Maximum values of \( \tilde{\omega}(\omega) \) are observed where the SG resonances overlap.

The energy transfer rate for tangentially oriented dipoles (not shown) is in general smaller than that for radially oriented dipoles. Note that when \( \tilde{\omega}(\omega) \) is sharply peaked at the sphere-assisted field resonances, such that it is not slowly varying in the frequency interval where the (image-space) donor emission and acceptor absorption spectra overlap, then it cannot be taken at the electronic energy transfer frequency and put in front of the integral in Eq. (43). In this case, the change of the energy transfer...
rate will be less pronounced than it might be expected from the frequency response of the electronic part, because of the frequency integration.

IV. CONCLUSIONS

We have given a rigorous, strictly quantum mechanical derivation of the rate of intermolecular energy transfer in the presence of dispersing and absorbing material bodies of arbitrary shapes, showing that both the minimal-coupling scheme and the multipolar coupling scheme lead to rate formulas of exactly the same form. The dependence on the material bodies of the energy transfer rate is fully expressed in terms of the Green tensor of the macroscopic Maxwell equations for the medium-assisted electromagnetic field. In the macroscopic approach, the dispersing and absorbing material bodies are described, from the very beginning, in terms of a spatially varying permittivity, which is a complex function of frequency. The macroscopic approach has – similar to classical optics – the benefit of being universally valid, without the need of involved ab initio microscopic calculations. In so far as such calculations for simple model systems have been performed, the results agree with those obtained from the microscopic approach. Clearly, macroscopic electrodynamics is valid only to some approximately fixed length scale which exceeds the average interatomic distance in the material bodies.

Whereas the donor spontaneous decay rate is determined by the imaginary part of the Green tensor in the coincidence limit, the donor–acceptor energy transfer rate depends on the full two-point Green tensor. Hence, the decay rate and the energy transfer rate can be affected by the presence of material substances quite differently. Our calculations for planar multilayer structures have shown that enhancement (inhibition) of spontaneous decay and inhibition (enhancement) of energy transfer can appear simultaneously. They have further shown that surface-guided waves can strongly affect the energy transfer, thus being very suitable for controlling it.

In free space it is often distinguished between two limiting cases, namely the short-distance nonradiative (Förster) energy transfer and the long-distance radiative energy transfer. The former is characterized by the $R^{-6}$ distance dependence of the transfer rate, and the latter by the $R^{-2}$ dependence. In particular, in the short-distance limit the energy transfer rate rapidly decreases with increasing distance between the molecules. Therefore, the distance between the molecules is the limiting case, namely the short-distance nonradiative energy transfer. The former is characterized by the (Förster) energy transfer and the long-distance radiative energy transfer. The latter is given by the (multipolar) energy transfer.

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APPENDIX A: DERIVATION OF THE TRANSFER RATE IN THE MULTIPOLAR-COUPLING SCHEME

The multipolar-coupling Hamiltonian can be obtained from the minimal-coupling Hamiltonian by means of the Power–Zienau transformation [34],

$$\hat{H} = \hat{U}^\dagger \hat{H} \hat{U},$$

(A1)

where

$$\hat{U} = \exp \left[ \sum_M \frac{i}{\hbar} \int d^3 r \hat{P}_M(r) \hat{A}(r) \right],$$

(A2)

with

$$\hat{P}_M(r) = \sum_{\alpha M} q_{\alpha M} (\hat{r}_{\alpha M} - r_M)$$

(A3)

being the polarization associated with the $M$th molecule.

Using $\hat{H}$ from Eq. (1), we derive (see, for details, [17])

$$\hat{H} = \int d^3 r \int_0^\infty d\omega \, h\omega \hat{f}^\dagger(r, \omega) \hat{f}(r, \omega)$$

$$+ \sum_M \sum_{\alpha M} \int_0^\infty \frac{d\omega}{2\pi} \{ \hat{P}_M(r) \hat{A}(r) \}$$

$$+ \sum_{\alpha M} \int_0^\infty d\omega \lambda (\hat{r}_{\alpha M} - r_M) \times \hat{B} [\hat{r}_M + \lambda (\hat{r}_{\alpha M} - r_M)]$$

$$+ \sum_M \int d^3 r \left[ \frac{1}{2\varepsilon_0} \hat{P}_M(r) \hat{E}(r) \right]$$

$$- \sum_M \int d^3 r \left[ \hat{P}_M(r) \hat{E}(r) \right],$$

(A4)

where $\hat{B}(r) = \nabla \times \hat{A}(r)$ [with $\hat{A}(r)$ from Eq. (5)], and

$$\hat{E}(r) = \int_0^\infty d\omega \hat{\mathbf{E}}(r, \omega) + \text{H.c.},$$

(A5)

and neutral molecules with non-overlapping charge distributions are again assumed. Note that in the multipolar-coupling scheme the operator of the electric field strength is defined according to

$$\hat{\mathbf{E}}(r) = -\frac{1}{i\hbar} \left[ \hat{A}(r), \hat{H} \right] - \nabla \hat{\phi}(r) - \nabla \hat{\phi}(r),$$

(A6)
which implies the following relation between $\hat{E}(\mathbf{r})$ and $\hat{E}(\mathbf{r})$:

$$\varepsilon_0 \hat{E}(\mathbf{r}) = \varepsilon_0 \hat{E}(\mathbf{r}) + \sum_M \hat{P}_M(r). \quad (A7)$$

Hence, $\varepsilon_0 \hat{E}(\mathbf{r})$ has the meaning of the displacement field with respect to the molecular polarization.

From Eq. (A4) it is seen that the molecules now interact only via the medium-assisted electromagnetic field. In particular, in the (electric-)dipole approximation Eq. (A4) simplifies to

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad (A8)$$

where

$$\hat{H}_0 = \int d^3r \int_0^\infty d\omega \hat{H}_0^{\dagger}(\mathbf{r}, \omega) \hat{H}(\mathbf{r}, \omega) + \sum_M \hat{H}_M \quad (A9)$$

is the unperturbed Hamiltonian of the medium-assisted electromagnetic field and the molecules, and

$$\hat{H}_{\text{int}} = \sum_M \hat{H}_{\text{int}}^{(M)} = -\sum_M \hat{d}_M \hat{E}(\mathbf{r}_M) \quad (A10)$$

is the interaction energy between them.

Comparing the multipolar-coupling energy given by Eq. (A11), with the minimal-coupling energy $\hat{H}_{\text{int}}$ given by Eq. (A10) together with Eqs. (7)–(8), we see that the two energies (formally) become equal to each other, if we remove in the latter the Coulomb term and replace $-\{d_M, \hat{H}_M\}/\hbar$ with $\hat{d}_M$. Having these changes in mind, we now follow step by step the derivation of Eq. (41) in Section 13. Starting from the corresponding eigenstates of the unperturbed multipolar-coupling Hamiltonian (instead of those of the unperturbed minimal-coupling Hamiltonian), it is not difficult to see that the result is again Eq. (41). It should be pointed out that the above mentioned difference between $\hat{E}(\mathbf{r})$ and $\hat{E}(\mathbf{r})$ [Eq. (A7)] does not affect the energy transfer rate.

**APPENDIX B: SINGLE-MOLECULE EMISSION SPECTRUM**

In the electric-dipole approximation and the rotating-wave approximation, the Hamiltonian for a single molecule (at position $\mathbf{r}_A$) that (with regard to the vibronic transitions $|a'\rangle \leftrightarrow |a\rangle$) resonantly interacts with the medium-assisted electromagnetic field reads, by appropriately specifying Eqs. (13)–(20), [8]

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad (B1)$$

$$\hat{H}_0 = \int d^3r \int_0^\infty d\omega \hbar \omega \hat{f}(\mathbf{r}, \omega) \hat{f}(\mathbf{r}, \omega)$$

$$+ \sum_a \hbar \omega_a |a\rangle \langle a| + \sum_{a'} \hbar \omega_{a'} |a'\rangle \langle a'|, \quad (B2)$$

$$\hat{H}_{\text{int}} = -\sum_{a,a'} \{ |a'\rangle \langle a| \hat{E}(\mathbf{r}_A) d_{a\prime} + \text{H.c.} \}. \quad (B3)$$

where $\hat{E}^{(\dagger)}(\mathbf{r})$ is the positive-frequency part of $\hat{E}(\mathbf{r})$ defined by Eq. (A3), and the vibronic transition-dipole matrix elements $d_{a\prime}$ of the vibronic transitions are given, in the Born–Oppenheimer approximation, by Eq. (41). Let us assume that the molecule is initially (at time $t = 0$) prepared in a statistical mixture of vibrational states in the upper electronic state and the medium-assisted electromagnetic field is in the vacuum state, i.e.,

$$\hat{\rho}(t = 0) = \sum_{a,a'} |a\rangle \langle a| \otimes |\{0\}\rangle \langle\{0\}|. \quad (B4)$$

The time-dependent spectrum of light observed at position $\mathbf{r}$ (in free space) by means of a spectral apparatus of sufficiently small passband width can be given by (see, e.g., [11])

$$S(\mathbf{r}, \omega_S, T) = \int_0^T dt_2 \int_0^T dt_1 \left[ e^{-i\omega_S(t_2-t_1)} \times (E^{(-)}(\mathbf{r}, t_2) E^{(\dagger)}(\mathbf{r}, t_1)) \right]. \quad (B5)$$

where $\omega_S$ and $T$ are respectively the setting frequency and the operating time of the spectral apparatus. In order to calculate the electric-field correlation function associated with the light emitted by the molecule during the spontaneous decay of the upper electronic state, we may restrict our attention to the perturbative expansion of the time evolution operator up to the first order in $\hat{H}_{\text{int}}$ [14],

$$e^{-i\hat{H}_0 t/\hbar} e^{-i\hat{H}_0 t'/\hbar} + \frac{1}{i\hbar} \int_0^t dt' e^{-i\hat{H}_0 (t-t')/\hbar} \hat{H}_{\text{int}} e^{-i\hat{H}_0 t'/\hbar}. \quad (B6)$$

We make use of Eqs. (B3), (A7) [together with Eq. (4)], (B4), and (B6), apply Eq. (B3), and derive after some calculation, on recalling the relation (30), (see also [52])

$$\lim_{T \to \infty} T^{-1} S(\mathbf{r}, \omega_S, T)$$

$$= 2\pi \sum_{a,a'} p_a |a\rangle \langle a| |F(\mathbf{r}, \mathbf{r}_A, \omega_S)|^2 \delta(\omega_S - \omega_{a'}), \quad (B7)$$

where
\[ F(r, r_A, \omega' \alpha) = \frac{1}{\pi \varepsilon_0} \int_0^\infty \frac{\omega'^2}{c^2} \text{Im} G(r, r_A, \omega) dA \zeta(\omega' \alpha - \omega) \]
\[ \approx -\frac{i \omega'^2}{\varepsilon_0 c^2} G(r, r_A, \omega' \alpha) dA \quad \text{(B8)} \]
\[
[\zeta(x) = \pi \delta(x) + i \mathcal{P}/x; \mathcal{P}, \text{principal value}] \text{ In the derivation of Eq. (B7), retardation has been ignored and the relation}
\]
\[
\lim_{T \to \infty} \frac{1}{T} \int_0^T dt_2 \int_0^T dt_1 e^{-i \omega(t_2 - t_1)} = \frac{\sin^2(\omega T/2)}{T(\omega/2)^2} = 2\pi \delta(\omega) \quad \text{(B9)}
\]

has been used.

* on leave from the Institute of Physics, National Center for Sciences and Technology, 1 Mac Dinh Chi Street, District 1, Ho Chi Minh city, Vietnam.

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