

## Quantum electrodynamics of resonant energy transfer in condensed matter. II. Dynamical aspects

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A microscopic quantum electrodynamical (QED) theory is developed for representing the dynamics of excitation transfer in a dielectric medium between individual species, such as atoms or molecules, at various separations, including both near- and far-zone distances. The theory, built on explicit QED consideration of the time evolution, fully incorporates medium-induced energy renormalizations and damping corrections for the transfer species. In addition, it embodies the local field and screening contributions which have already been featured in a previous paper devoted to the rate description. The influence of the medium is also manifest in the relativistic time-lag (reflecting the delay of the initial arrival of the excitation at the acceptor molecule), which is now shown to be characterized by the group velocity of the light. The phase velocity features in the distance-dependent retardation in phase of the transition matrix element. The theory extends to different transfer regimes. Following a general analysis, the paper reexamines the rate regime, where not only the transition matrix element but also the molecular excitation frequencies for the transfer species are modified by the medium. Another non-rate-regime, occurring in situations that lack an intrinsic molecular density of states, displays oscillatory dynamics over short transfer distances. These oscillations are suppressed by monomolecular damping in the long-range case: here the transfer process is cast in terms of transfer probabilities, rather than rates. In all situations the characteristic parameters of the process properly reflect the influence of the medium, though it is apparent that in the limiting case of an infinitely dilute medium the present results are consistent with those previously obtained for the vacuum case.

### I. INTRODUCTION

The resonance transfer of electronic excitation is a phenomenon familiar from its manifestations at various ranges. For transfer distances  $R$  exceeding the appropriate (reduced) wavelength of light,  $\lambda$ , the process is often understood as being a two-stage event involving emission of a real light quantum by one initially excited molecule (atom, ion, or chromophore group) and its subsequent recapture by another moiety. It leads to the well-known far-zone  $R^{-2}$  distance behavior for the pair transfer probability, the latter being enhanced by the large number of absorbing molecules surrounding the emitter. On the other hand, over distances  $R$  below  $\lambda$  there is another type of transfer, kinetically in competition with the natural decay of the excited states. In dense media, that may lead to fast and effective migration of the photoexcitation energy among the molecules during their excited-state lifetime.<sup>1</sup> This is the feature exploited in photosynthetic light harvesting.<sup>2</sup> The latter near-zone transfer is traditionally considered as being induced by an instantaneous Coulomb interaction and is therefore generally referred to as radiationless.<sup>1,3</sup> For dipole-dipole allowed transitions, the rate of such a radiationless process has the familiar  $R^{-6}$  distance dependence first predicted by Förster.<sup>4</sup>

Since the 1960s, the formalism of quantum electrodynamics (QED) has been used to address, in a number of publications, the problem of resonance excitation transfer, primarily in order to explore the crossover from near- to far-zone behavior.<sup>5-19</sup> Under the QED ap-

proach both far- and near-zone transfer may be equally treated as concerted radiative processes involving the emission of a transverse virtual photon by one molecule and its recapture by another.<sup>8,10-20</sup> From application of the Fermi golden rule, pair transfer rates have been obtained displaying both  $R^{-6}$  and  $R^{-2}$  terms, as well as an extra  $R^{-4}$  contribution,<sup>11-17</sup> the latter featuring at critical retardation distances  $R \sim \lambda$ . In other developments,<sup>5,6,9,21-23</sup> the explicit QED time evolution of the energy transfer has been examined for the case of a pair of two-level species, level broadening arising exclusively due to radiative damping. The result is characterized by damped oscillatory behavior of the transfer kinetics.

Although a sporadic handful of attempts to accommodate medium effects in excitation transfer has appeared,<sup>7,14,17</sup> most existent QED theories totally ignore the influence of such effects. The 1989 treatment by Craig and Thirunamachandran,<sup>14</sup> cast in terms of third-body mediation, led to a new discussion of the way to incorporate dielectric characteristics. It was suggested from macroscopic arguments<sup>14</sup> that the vacuum dielectric permittivity  $\epsilon_0$  entering the equation for the rate of excitation transfer *in vacuo* should be replaced by its medium  $\epsilon$  to represent the screening. Nevertheless, in using this prescriptive approach other important medium effects, such as local fields, energy losses, and changes in character of the medium-induced rate modifications on passing from the near to far zone, have not been considered. It was the main objective of our previous paper<sup>24</sup> to develop a QED theory which systematically dealt with these issues entirely on the basis of a microscopic many-body framework. In contrast to conventional QED theories

(see, e.g., Refs. 8–19) in which energy transfer is cast in terms of the intermolecular propagation of virtual photons, the new theory has been formulated by invoking the concept of bath polaritons (“medium-dressed” photons) mediating the process.<sup>25</sup> To this extent, the approach resembled that employed by Knoester and Mukamel<sup>26</sup> with respect to the related problems of intermolecular forces and superradiance, in which a lossless medium was modeled by an ensemble of two-level species. In our work<sup>24</sup> an arbitrary number of energy levels for each medium molecule has been accommodated, the ensuing mathematical complications being resolved through a development of Green’s-function techniques in order to bypass the explicit eigenvalue problem.

As a result of these deliberations,<sup>24</sup> the theory is now at a stage where it can address both transparent and absorbing media. In the absorbing case, an exponential (Beer’s-law) factor appears as an intrinsic part of the microscopic analysis, thus taking account of the associated energy losses. This solves from first principles the problem of ensemble rates which are potentially infinite due to the divergent far-zone  $R^{-2}$  behavior. On the other hand, the medium modifications in the near zone agree with those familiar from the theory of radiationless energy transfer. It is to be pointed out that the previous theory<sup>24</sup> has been based on a rate description, employing the Fermi golden rule, which left other dynamical aspects out of consideration.

It is the purpose of the current paper to present a detailed study of the transfer dynamics through explicit consideration of the QED time evolution. A distinctive aspect of the theory is that it affords a combined analysis of rate and nonrate regimes in the context of examining the influence of the dielectric medium. The theory is built on the foundation established in our previous work.<sup>24</sup> Again, the approach exploits the concept of transfer mediated by bath polaritons. The theory also makes use of the previously derived tensor for the retarded (electromagnetic) dipole-dipole coupling in a medium,<sup>24</sup> now more with regard to the dynamical behavior. The present study not only extends consideration beyond the rate description, but also reexamines the rate regime itself. It leads to incorporation of an energy renormalization for both the ground and excited states of the transfer species, as a result of the interaction of these species with the medium molecules and also with each other. This is a feature not reflected in direct application of the ordinary Fermi golden rule.

The paper is organized as follows. In Sec. II A the Heitler-Ma method<sup>27,28</sup> for describing the quantum time evolution is first briefly outlined and subsequently reformulated to suit our current purposes. Consequently, the basic equations for time evolution acquire a form more symmetric with respect to the initial and final states. Section II B defines the Hamiltonian of the system comprising the selected pair of transfer species and a bath constituted from the other (medium) molecules and the quantized radiation field. Section III concentrates on the transfer dynamics, starting from general considerations and leading to an analysis of both the rate regime and beyond. The nonrate regime features in situations lack-

ing an intrinsic density of molecular states for the participating species. Section IV summarizes the results.

## II. FORMULATION

### A. General description of time evolution

Consider the quantum dynamics of a system with a time-independent Hamiltonian separable as the sum of a zero-order Hamiltonian  $H^0$  and an interaction term  $V$ :

$$H = H^0 + V, \quad (2.1)$$

where the eigenvectors of  $H^0$  include, *inter alia*, both the initial state  $|I\rangle$  and the final state  $|F\rangle$  of the process. For reasons which will become apparent later, we shall commence work in the Schrödinger representation rather than the more common interaction representation. The state vector of the system then evolves at positive times from the state  $|I\rangle$  at  $t = +0$  as

$$\begin{aligned} S(t)|I\rangle &= \Theta(t)e^{-iHt/\hbar}|I\rangle \\ &= -\frac{1}{2\pi i} \int_{-\infty}^{+\infty} d\epsilon e^{-i\epsilon t/\hbar} (\epsilon - H + i\eta)^{-1} |I\rangle \\ &\quad (\eta \rightarrow +0), \end{aligned} \quad (2.2)$$

$\Theta(t)$  being the unit step function. The Heitler-Ma method<sup>27,28</sup> may now be employed, giving

$$\begin{aligned} \langle F | (\epsilon - H + i\eta)^{-1} | I \rangle \\ = \frac{U_{FI}(\epsilon)}{(\epsilon - E_F + i\eta)[\epsilon - E_I + \frac{1}{2}i\hbar\Gamma_I(\epsilon) + i\eta]}. \end{aligned} \quad (2.4)$$

Here  $U_{FI}(\epsilon)$  and  $\Gamma_I(\epsilon)$  are, respectively, the matrix elements of the off-diagonal transition operator  $U(\epsilon)$  and the diagonal damping operator  $\Gamma(\epsilon)$ , both determined by the recurrent relation

$$U(\epsilon) - \frac{i}{2}\hbar\Gamma(\epsilon) = V + V(\epsilon - H^0 + i\eta)^{-1}U(\epsilon). \quad (2.5)$$

For present purposes it is more convenient to represent the above in a nonrecursive format as

$$\begin{aligned} [U(\epsilon) - (i/2)\hbar\Gamma(\epsilon)]|I\rangle \\ = [V + VP_I(\epsilon - H^0 - P_I VP_I + i\eta)^{-1}P_I V]|I\rangle, \end{aligned} \quad (2.6)$$

where the idempotent operator

$$P_I = 1 - |I\rangle\langle I| \quad (2.7)$$

identifies the exclusion of contributions by the initial state in the perturbation expansion of Eq. (2.6). Recasting the transition matrix element in a form where the perturbational contribution by the final state is no longer explicitly featured, one arrives at

$$U_{FI}(\epsilon) = \frac{\epsilon - E_F + i\eta}{\epsilon - E_F + (i/2)\hbar\Gamma'_F + i\eta} U'_{FI}, \quad (2.8)$$

where the newly defined quantities on the right,  $U'_{FI}$  and  $\Gamma'_F$ , both have implicit  $\epsilon$  dependence and are given by

$$U'_{FI} = \langle F | [V + VP_I P_F (\epsilon - H^0 - P_I P_F V P_I P_F + i\eta)^{-1} P_I P_F V] | I \rangle, \quad (2.9)$$

$$-\frac{i}{2} \hbar \Gamma'_F = \langle F | [V + VP_I P_F (\epsilon - H^0 - P_I P_F V P_I P_F + i\eta)^{-1} P_I P_F V] | F \rangle, \quad (2.10)$$

with

$$P_F = 1 - |F\rangle\langle F|. \quad (2.11)$$

Finally, using Eqs. (2.3), (2.4), and (2.8), one finds, for the transfer probability amplitude,

$$\langle F | S(t) | I \rangle = -\frac{1}{2\pi i} \int_{-\infty}^{+\infty} d\epsilon \frac{U'_{FI} e^{-i\epsilon t/\hbar}}{[\epsilon - E_F + (i/2)\hbar \Gamma'_F + i\eta][\epsilon - E_I + (i/2)\hbar \Gamma_I + i\eta]}, \quad (2.12)$$

which is still an exact result. Here the presence of both  $\Gamma_I$  and  $\Gamma'_F$  in the energy denominators explicitly accommodates the damping corrections and energy renormalization to the initial and final states. Consequently, the transfer amplitude as presented above has a form more obviously symmetric with respect to the initial and final states than would result from direct substitution of Eq. (2.4) into (2.3). Still, there is some asymmetry with respect to these states, reflected by the prime on  $\Gamma'_F$ . The retention of this asymmetry will be of vital importance in the case of sharp energy levels where the transfer species lack an intrinsic density of molecular states; this aspect is to be considered in the final part of Sec. III.

### B. Definition of the system

The dynamical system of interest comprises an ensemble of molecules (atoms or chromophoric groups) and the quantized radiation field. To deal with excitation transfer between a selected pair of molecules  $A$  and  $B$ , the full system will be divided into two parts, one subsystem consisting of species  $A$  and  $B$  and the other the bath. The latter, in turn, is comprised of the quantized electromagnetic field and the remaining molecules which constitute the surrounding medium. Note that the molecules of the medium may, but do not necessarily, differ in type from  $A$  and  $B$ .

In the multipolar QED formulation to be employed here, the electromagnetic coupling entails an interaction between the molecules and radiation field, there being no instantaneous (Coulombic) intermolecular contribution.<sup>29-31</sup> With regard to the chosen partitioning of the system, the zero-order and interaction Hamiltonian terms in the electric dipole approximation are then

$$H^0 = H_A + H_B + H_{\text{bath}}, \quad (2.13)$$

$$V = H_A^{\text{int}} + H_B^{\text{int}}, \quad (2.14)$$

where

$$H_{\text{bath}} = H_{\text{rad}} + \sum_{X \neq A, B} (H_X + H_X^{\text{int}}), \quad (2.15)$$

with

$$H_X^{\text{int}} = -\epsilon_0^{-1} \boldsymbol{\mu}(X) \cdot \mathbf{d}^{\perp}(\mathbf{R}_X). \quad (2.16)$$

Here  $H_{\text{bath}}$  is the bath Hamiltonian,  $H_X$  is the Hamiltonian for molecule  $X$  positioned at  $\mathbf{R}_X$ , and  $H_X^{\text{int}}$  represents the radiation-molecule coupling;  $\boldsymbol{\mu}(X)$  is the electric di-

pole operator, and in each case the molecular index  $X$  spans both  $A$  and  $B$  as well as medium species. Finally,  $H_{\text{rad}}$  and  $\mathbf{d}^{\perp}$  are, respectively, the radiation Hamiltonian and the electric displacement operator, for both of which the explicit mode expansions are given elsewhere (see, for instance, Refs. 15-18, 24, and 31).

For the representation of energy transfer from  $A$  to  $B$ , the initial- and final-state vectors are

$$|I\rangle = |A_n^*, B_m; 0\rangle, \quad |F\rangle = |A_l, B_p^*; 0\rangle, \quad (2.17)$$

the corresponding energies being

$$E_I = e_{A_n} + e_{B_m} + e_0, \quad E_F = e_{A_l} + e_{B_p} + e_0, \quad (2.18)$$

where  $|0\rangle$  is the ground-state vector of the bath,  $e_0$  the corresponding energy, and the asterisk refers to a manifold of the electronically excited state of the transfer species  $A$  and  $B$ . In the following, the vibrational, rotational, etc., sublevels (if any) of the molecules are mostly kept implicit, but are where necessary explicitly denoted by the indices  $n, m, l$ , and  $p$ . Having defined the system, we now turn our attention to the transfer dynamics.

### III. TRANSFER DYNAMICS

Because of the two-center character of the interaction operator (2.14), it is convenient to carry out a corresponding partitioning in Eqs. (2.6) and (2.10), writing

$$-\frac{i}{2} \hbar \Gamma_I(\epsilon) = \Delta e_{A\cdot} + \Delta e_{B\cdot} - \frac{i}{2} \hbar \gamma_{A\cdot} - \frac{i}{2} \hbar \Gamma_{A\cdot B}, \quad (3.1)$$

$$-\frac{i}{2} \hbar \Gamma'_F(\epsilon) = \Delta e_{A\cdot} + \Delta e_{B\cdot} - \frac{i}{2} \hbar \gamma_{B\cdot} - \frac{i}{2} \hbar \Gamma'_{AB\cdot}, \quad (3.2)$$

where the one-center contributions, denoted by a single index  $A$  or  $B$ , have already been separated into real energy shifts and imaginary damping terms; the other (complex) quantities  $\Gamma_{A\cdot B}$  and  $\Gamma'_{AB\cdot}$  are two-center contributions resulting from cross terms (containing both  $V_A$  and  $V_B$ ) in the perturbation expansion of (2.6) and (2.10). Here, for instance,  $\Delta e_{A\cdot}$  and  $\gamma_{A\cdot}$  represent, respectively, the bath-induced level shift (energy renormalization) and the decay factor for the excited molecular state  $|A^*\rangle$ . Each such energy renormalization ( $\Delta e_{A\cdot}$ ,  $\Delta e_{B\cdot}$ ,  $\Delta e_{A\cdot}$ , and  $\Delta e_{B\cdot}$ ) embodies not only the radiative (Lamb) shift,<sup>32</sup> but also the dispersion energy contribution (together with higher-order energy corrections) arising from the interac-

tion of  $A$  or  $B$  with the medium molecules. Note that the dispersion energy now appears in the second order of perturbation, rather than the usual fourth order,<sup>31,33,34</sup> as the coupling of the radiation field with the medium has already been included in the zero-order Hamiltonian  $H^0$ .

In this paper we shall not consider the explicit structure of these energy shifts, which are to be treated as the parameters of the theory.

By making use of Eqs. (3.1) and (3.2), the transfer probability amplitude (2.12) becomes

$$\langle F|\tilde{S}(t)|I\rangle = -\frac{1}{2\pi i\hbar} \int_{-\infty}^{+\infty} d\omega \frac{U'_{FI}(\omega) e^{-i(\omega - \omega_{B'})t}}{[\omega - \omega_{B'} + (i/2)\gamma_{B'} + (i/2)\Gamma'_{AB'} + i\eta'] [\omega - \omega_{A'} + (i/2)\gamma_{A'} + (i/2)\Gamma_{A'B} + i\eta']} \quad (\eta' \rightarrow 0), \quad (3.3)$$

where

$$\omega = (\epsilon - e_A - e_B - \Delta e_A - \Delta e_B - e_0)/\hbar \quad (3.4)$$

is the new variable and

$$\omega_{A'} = (e_{A'} + \Delta e_{A'} - e_A - \Delta e_A)/\hbar, \quad (3.5)$$

$$\omega_{B'} = (e_{B'} + \Delta e_{B'} - e_B - \Delta e_B)/\hbar \quad (3.6)$$

are the excitation frequencies of  $A$  and  $B$ . These now incorporate the level shifts both for the molecular ground and excited states. Finally, in Eq. (3.3) the transformation to a modified interaction representation has been carried out as

$$\langle F|\tilde{S}(t)|I\rangle = \langle F|S(t)|I\rangle \exp[-i(E_F + \Delta E_F)t/\hbar], \quad (3.7)$$

the term "modified" referring to the medium renormalization of the final-state energy  $E_F$  by the amount  $\Delta E_F = \Delta e_A + \Delta e_B$ .

Now we turn our attention to the transition matrix element  $U'_{FI}(\omega)$ , which, in the present study, will be represented through an effective second-order contribution as<sup>35</sup>

$$U'_{FI}(\omega) \approx U_{FI}^{(2)}(\omega) = \mu_{B'} \theta_{ij} \mu_{A'}, \quad (3.8)$$

with

$$\theta_{ij} = \frac{1}{\hbar\epsilon_0^2} \sum_{\sigma} \left[ \frac{\langle 0|\mathbf{d}_i^+(\mathbf{r}_B)|\sigma\rangle \langle \sigma|\mathbf{d}_j^+(\mathbf{r}_A)|0\rangle}{\omega - \Pi_{\sigma} + i\eta'} + \frac{\langle 0|\mathbf{d}_j^+(\mathbf{r}_A)|\sigma\rangle \langle \sigma|\mathbf{d}_i^+(\mathbf{r}_B)|0\rangle}{\omega - \omega_{A'} - \omega_{B'} - \Pi_{\sigma} + i\eta'} \right], \quad (3.9)$$

where  $\mu_A = \langle A|\mu(A)|A^*\rangle$  and  $\mu_B = \langle B^*|\mu(B)|B\rangle$  are the transition dipole moments of  $A$  and  $B$  (chosen to be real),  $\hbar\Pi_{\sigma} = e_{\sigma} - e_0$  is the bath excitation energy, and the index  $\sigma$  denotes excited (single-polariton) states<sup>24</sup> of the bath accessible from the ground state  $|0\rangle$  by single actions of the operator  $\mathbf{d}^+(\mathbf{r})$ . Equation (3.8) is cast in a form which entails the convention of implied summation over repeated indices. Within the range of frequencies  $\omega$  close to molecular transition frequencies  $\omega_{A'}$  and  $\omega_{B'}$ , the energy denominator  $(\omega - \omega_{A'} - \omega_{B'} - \Pi_{\sigma} + i\eta')$  may be

replaced by  $(-\omega - \Pi_{\sigma} + i\eta')$  in the nonresonant term of Eq. (3.9).<sup>36</sup> The tensor (3.9) then reduces to that considered in our previous paper, giving<sup>24</sup>

$$\theta_{ij} = \frac{1}{n^2} \left[ \frac{n^2 + 2}{3} \right]^2 \theta_{ij}^{\text{vac}} \left[ \frac{n\omega}{c} \right], \quad (3.10)$$

$$\theta_{ij}^{\text{vac}}(y) = \frac{y^3 e^{iyR}}{4\pi\epsilon_0} \left[ (\delta_{ij} - 3\hat{R}_i\hat{R}_j) \left[ \frac{1}{y^3 R^3} - \frac{i}{y^2 R^2} \right] - (\delta_{ij} - \hat{R}_i\hat{R}_j) \frac{1}{yR} \right], \quad (3.11)$$

where  $n = n' + in'' = \epsilon_r^{1/2}$ , with  $\epsilon_r$  being the complex relative dielectric permittivity satisfying the Clausius-Mossotti relation, as explicitly presented in Ref. 24; here also  $\mathbf{R} = \mathbf{r}_B - \mathbf{r}_A$  is the  $A$ - $B$  separation vector, a caret referring to the corresponding unit vector. The above  $\theta_{ij}$  represents the tensor for the retarded dipole-dipole electromagnetic interaction in the medium,  $\theta_{ij}^{\text{vac}}(y)$  being its vacuum counterpart: the argument  $(y = n\omega/c)$  of the latter is now scaled by the complex refractive index  $n \equiv n(\omega)$ . The electromagnetic tensor  $\theta_{ij}$  also manifestly accommodates both screening and Lorentz local field factors. It is to be noted that such a description in terms of the macroscopic dielectric constant as featured above is applicable for  $A$ - $B$  separations  $R$  exceeding the intermolecular distances characteristic of the medium.<sup>24</sup> Also note that, although the derivation of the tensor  $\theta_{ij}$  given by Eq. (3.10) has for mathematical convenience invoked a regular lattice arrangement of the medium species, the results are applicable to a wide variety of energetically and positionally disordered media as previously discussed.<sup>24</sup>

In the context of time evolution, the  $\omega$  dependence in the exponential phase factor  $\exp(in\omega R/c)$  of the transition matrix element  $U_{FI}^{(2)}(\omega)$ , through (3.8), (3.10), and (3.11), will lead to appearance of the time lag in the initial arrival of the excitation at molecule  $B$ , as a result of the finite speed of the signal propagation. The remainder of the transition matrix element, together with other  $\omega$ -dependent parameters in Eq. (3.3), will at this stage be evaluated at the resonant transfer frequency,  $\omega = \omega_{B'}$ .

Linearizing the exponent,

$$n(\omega)\omega R/c \approx [n(\omega_B)\omega_B R/c] + [(\omega - \omega_B)R/v_g], \quad (3.12)$$

with

$$\frac{1}{v_g} = \frac{d}{d\omega} \left[ \frac{n\omega}{c} \right] \Big|_{\omega=\omega_B}, \quad (3.13)$$

and defining  $\tau = (t - R/v_g)$ , the transfer amplitude (3.3) then takes the form

$$\langle F | \tilde{S}(t) | I \rangle = -\frac{1}{2\pi\hbar i} \int_{-\infty}^{+\infty} d\omega \frac{U_{FI}^{(2)}(\omega_B) e^{-i(\omega - \omega_B)\tau}}{[\omega - \omega_B + (i/2)\gamma_B + i\eta'] [\omega - \omega_A + (i/2)\gamma_A + i\eta']}, \quad (3.14)$$

$$= \hbar^{-1} U_{FI}^{(2)}(\omega_B) \Theta(\tau) \frac{\exp(-\frac{1}{2}\gamma_B \tau) - \exp\{[-\frac{1}{2}\gamma_A + i(\omega_B - \omega_A)]\tau\}}{(\omega_B - \omega_A) + \frac{1}{2}i(\gamma_A - \gamma_B)}, \quad (3.15)$$

which takes account of damping for both sites  $A$  and  $B$ . Here the two-center contributions  $\Gamma_{A \cdot B}$  and  $\Gamma'_{AB}$  are for the present omitted; the physical basis of this approximation will be clarified in due course.

To make a brief comment on Eq. (3.15), the radiative group velocity  $v_g$  is here featured in the delay time for the initial arrival of the excitation at molecule  $B$ , whereas the phase velocity  $v_\phi = c/n$ , entering the exponential factor  $\exp(i\omega_B R/v_\phi)$  of the transition matrix element  $U_{FI}^{(2)}(\omega_B)$ , characterizes the distance-dependent retardation in phase. It is also to be noted that incorporation of the time lag in the above manner implies that the refractive index, and hence also the group velocity, takes real values. Nonetheless, the following general expressions (3.16) and (3.17) for the transfer rates hold both for lossless and absorbing media.

#### A. Transfer rates

Let us consider first the case where the spectral widths of the species participating in the transfer exceed the magnitude of the corresponding transition matrix elements. The overall migration is then incoherent, described as a multistep process involving uncorrelated events of excitation transfer between the molecules of the system. With regards to the selected pair  $A$ - $B$ , by omitting the relaxation terms  $\gamma_A$  and  $\gamma_B$  in Eq. (3.14) and for times in excess of the transit time  $R/v_g$ , the resultant rate equation reads

$$\begin{aligned} W_{FI} &= \frac{d}{dt} |\langle F | \tilde{S}(t) | I \rangle|^2 \\ &= \frac{2\pi}{\hbar} |U_{FI}^{(2)}(\omega_B)|^2 \delta(\hbar\omega_A - \hbar\omega_B). \end{aligned} \quad (3.16)$$

The pair transfer rate  $W_{B \leftarrow A}$  is subsequently obtained by means of the standard procedure involving averaging over initial and summing over final molecular states, as in Refs. 1 and 16:

$$W_{B \leftarrow A} = \sum_{I, F} \rho_I W_{FI}. \quad (3.17)$$

As discussed previously,<sup>24,37</sup>  $|U_{FI}^{(2)}|^2$  entering Eq. (3.16) is obviously influenced by the surrounding medium

through local field and screening contributions, as well as in the medium-induced (refractive) modifications to the distance dependence. The latter include, *inter alia*, the appearance of an exponential decay factor  $\exp(-2n''\omega R/c)$  in the case of a lossy medium ( $n'' \neq 0$ ). That regularizes the potentially divergent  $R^{-2}$  term.<sup>24</sup> A new feature arising from the present dynamical consideration is that the excitation frequencies  $\omega_A$  and  $\omega_B$  have now been modified (renormalized) as a result of the interaction of the transfer species with the molecules of the surrounding medium. The mutual interaction of  $A$  with  $B$  may also be taken into account by retaining the omitted terms  $\Gamma_{A \cdot B}$  and  $\Gamma'_{AB}$  in Eq. (3.14). It alters the molecular excitation frequencies  $\omega_A$  and  $\omega_B$  featured in the energy conservation  $\delta$  function of Eq. (3.16) by the amounts  $\text{Im}\Gamma_{A \cdot B}/2$  and  $\text{Im}\Gamma'_{AB}/2$ , respectively: These represent changes in the excitation energy of each transfer species due to its interaction with the other. Such corrections decrease with distance, and over the separations of interest where  $R$  is greater than typical intermolecular distances within the medium, they contribute negligibly.

At this juncture, a remark should be made concerning some asymmetry of the formalism with regard to the initial and final states, as reflected by the prime on  $\Gamma'_{AB}$ . The rate regime generally implies the presence of a dense structure of (vibrational) molecular energy levels within the electronic manifolds of  $A$  and  $B$ . Hence the asymmetry in question vanishes, as either inclusion or exclusion of the individual states (such as  $|I\rangle$  or  $|F\rangle$ ) in the intermediate-state summation does not significantly alter  $\Gamma_{A \cdot B}$  and  $\Gamma'_{AB}$ . It is a different story in the case where there is no intrinsic density of molecular states for the participating species, as is to be considered next.

#### B. Nonrate regime

Suppose now that each of the ground- and excited-state manifolds of  $A$  and  $B$  is characterized by only one molecular sublevel, so that the subsystem  $A$ - $B$  may be treated as a pair of two-level species. Ignoring contributions from states with two or more mediating bath excitations (polaritons), the exchange of energy between  $A$  and  $B$  now occurs exclusively through intermediate states in

which both transfer species are either in their ground or excited states, the bath being in a one-polariton excited state. Under these conditions,  $\Gamma_{A'B}$  and  $\Gamma'_{AB}$  of Eqs. (3.1) and (3.2) are

$$-\frac{i}{2}\Gamma_{A'B} = \frac{[U_{FI}^{(2)}(\omega)]^2/\hbar^2}{\omega - \omega_{B'} + (i/2)\Gamma_{B'} + i\eta'}, \quad (3.18)$$

$$\langle F|\tilde{S}(t)|I\rangle = -\frac{1}{2\pi\hbar i} \int_{-\infty}^{+\infty} d\omega \frac{U_{FI}^{(2)}(\omega) e^{-i(\omega - \omega_{B'})t}}{[\omega - \omega_{B'} + (i/2)\Gamma_{B'} + i\eta'][\omega - \omega_{A'} + (i/2)\Gamma_{A'} + i\eta'] - [U_{FI}^{(2)}/\hbar]^2}. \quad (3.20)$$

To illustrate the precise form of the time evolution for one specific application, one finds for the case of identical species ( $\omega_{A'} = \omega_{B'}$ ,  $\gamma_{A'} = \gamma_{B'}$ ), and without regard to the time delay  $R/v_g$ ,<sup>38</sup> the following:

$$|\langle F|\tilde{S}(t)|I\rangle|^2 = \frac{1}{2} [\cosh(\gamma_{AB}t) - \cos(2\Omega_{AB}t)] e^{-\gamma_{B'}t}, \quad (3.21)$$

where the transfer frequency  $\Omega_{AB}$  and the inverse time  $\gamma_{AB}$ , respectively, represent the real and imaginary parts of the transition matrix element:

$$\hbar^{-1}U_{FI}^{(2)}(\hbar\omega_{B'}) = \Omega_{AB} - \frac{i}{2}\gamma_{AB}. \quad (3.22)$$

Equation (3.21) has a form familiar from the case of energy transfer between molecules *in vacuo*,<sup>6,21-23</sup> although the parameters  $\gamma_{AB}$ ,  $\gamma_{B'}$ , and  $\Omega_{AB}$  here display the influence of the medium. Note that although the transfer species *A* and *B* have been modeled as two-level systems, the formulation still allows each of the surrounding molecules to possess an arbitrary number of energy levels, thus accommodating the cases of both absorbing and lossless media.

Expression (3.21) represents the oscillatory to and fro exchange of excitation accompanied by damping. This type of dynamical behavior is a direct consequence of the absence of a density of final states, a feature which obviously makes the rate description inadequate. Nonetheless, a distinction should be made between the short-range reversible Rabi-type oscillatory behavior, which does not represent any real flow of energy from *A* to *B*, and the long-range behavior. In the latter case, the excitation energy of *A* is irreversibly passed to *B*. Under such circumstances it is appropriate to introduce transfer probabilities (rather than rates), as will be shown below.

In the long-range limit, the contribution  $[U_{FI}^{(2)}]^2$ , associated with the mutual coupling between *A* and *B*, may legitimately be omitted in the denominator of the integrand in Eq. (3.20). The system then again follows the same time evolution as described through the earlier Eq. (3.15), where the two-level species *A* and *B* are now not necessarily identical. Here the transfer dynamics reflect both the initial arrival of excitation at molecule *B* commencing from time  $t = R/v_g$  and the subsequent decay of

$$\Gamma'_{AB} = 0, \quad (3.19)$$

where use has been made of Eqs. (2.6) and (2.10). Substituting these results for  $\Gamma_{A'B}$  and  $\Gamma'_{AB}$  into the general dynamical equation (3.3), the probability amplitude becomes

the resulting excited state. The rate of the latter decay may be considered the same as that for the free molecule *B*,  $\gamma_{B'}$ , as at large distances the influence of *A* is minimal. Accordingly, the total transfer probability *P* may be defined as the probability for irreversible trapping of the excitation by molecule *B*. Integrating the population-weighted rate of decay of the excited state of *B*, we obtain, for *P*,

$$P = \int_{R/v_g}^{\infty} |\langle F|\tilde{S}(t)|I\rangle|^2 \gamma_{B'} dt \quad (3.23)$$

$$= (\Omega_{AB}^2 + \gamma_{AB}^2) \gamma_{A'}^{-1} \frac{(\gamma_{A'} + \gamma_{B'})}{(\omega_{B'} - \omega_{A'})^2 + (\gamma_{A'} + \gamma_{B'})^2/4}. \quad (3.24)$$

which is in agreement with the previous far-zone result for the transfer of energy between a pair of molecules *in vacuo*.<sup>9</sup> The explicit expression for the natural decay rates featured in the above is, for the specific consideration at this stage of a nonabsorbing medium,

$$\gamma_{X'} = n \left[ \frac{n^2 + 2}{3} \right]^2 \left[ \frac{\mu_{X'}^2 \omega_{X'}^3}{3\pi\epsilon_0 \hbar c^3} \right] \quad (X = A, B). \quad (3.25)$$

Hence, using Eqs. (3.8), (3.10), (3.11), and (3.22), the long-range result (3.24) assumes the form

$$P = \frac{9}{8\pi} \langle \sigma_B \rangle [(\hat{\mu}_A \cdot \hat{\mu}_B) - (\hat{\mu}_A \cdot \hat{\mathbf{R}})(\hat{\mu}_B \cdot \hat{\mathbf{R}})]^2 / R^2, \quad (3.26)$$

with

$$\langle \sigma_B \rangle = \frac{1}{n} \left[ \frac{n^2 + 2}{3} \right]^2 \frac{\mu_B^2 \omega_B}{3\epsilon_0 \hbar c} \times \left[ \frac{(\gamma_{A'} + \gamma_{B'})/2}{(\omega_{B'} - \omega_{A'})^2 + (\gamma_{A'} + \gamma_{B'})^2/4} \right]. \quad (3.27)$$

Here, in addition to the appearance of the refractive prefactors, the influence of the medium also extends both to the transfer frequency  $\omega_{B'}$  and to the decay parameters  $\gamma_{A'}$  and  $\gamma_{B'}$  through Eq. (3.25). The above  $\langle \sigma_B \rangle$  may be identified as the isotropic absorption section of *B*,  $\sigma_B(\omega)$ ,

averaged over the normalized emission spectrum of  $A^*$ ,  $I_{A^*}(\omega)$ :

$$\langle \sigma_B \rangle = \int_{-\infty}^{+\infty} \sigma_B(\omega) I_{A^*}(\omega) d\omega, \quad (3.28)$$

with  $\sigma_B(\omega)$  and  $I_{A^*}(\omega)$  given by

$$\sigma_B(\omega) = \frac{1}{n} \left[ \frac{n^2 + 2}{3} \right]^2 \frac{\mu_B^2 \omega_B}{3\epsilon_0 \hbar c} \left[ \frac{\gamma_B / 2}{(\omega - \omega_B)^2 + (\gamma_B / 2)^2} \right] \quad (3.29)$$

and

$$I_{A^*}(\omega) = \frac{1}{\pi} \left[ \frac{\gamma_{A^*} / 2}{(\omega - \omega_{A^*})^2 + (\gamma_{A^*} / 2)^2} \right]. \quad (3.30)$$

Finally, one obtains, for the orientationally averaged probability,

$$\bar{P} = \langle \sigma_B \rangle / 4\pi R^2, \quad (3.31)$$

which is the ratio of the spectrally averaged isotropic absorption cross section to the spherical surface at distance  $R$ ,  $4\pi R^2$ . In the case of an absorbing medium, an exponential decay factor of the form  $\exp(-2n''\omega R/c)$  would also be featured in the above.

#### IV. CONCLUSION

A microscopic quantum electrodynamical (QED) theory has been developed for representing the dynamics of excitation transfer in both lossless and absorbing

dielectric media. The theory, built on explicit QED considerations of the time evolution, fully incorporates medium-induced energy renormalizations and damping corrections for the transfer species. In addition, it embodies local field and screening contributions, together with changes in the character of the medium influence on passing from the near to the far zone. The effect of the medium is also manifest in a modification of the relativistic time lag, now shown to be characterized by the group velocity of light. On the other hand, the phase velocity is featured in the distance-dependent retardation in the phase of the transition matrix element  $U_{FI}^{(2)}$ .

The theory extends to different transfer regimes. In the rate regime, not only the transition matrix element, but also the molecular excitation frequencies for the transfer species are now modified by the medium. In other situations that lack an intrinsic molecular density of states, a nonrate regime applies in which oscillatory dynamical behavior is displayed over short transfer distances. Such oscillations are suppressed by monomolecular damping in the long-range case. Here the transfer process is cast in terms of transfer probabilities,  $P \propto |U_{FI}^{(2)}|^2$ , rather than rates. In all the situations considered, the characteristic parameters of the transfer process properly reflect the influence of the medium, although it is apparent that in the limiting case of an infinitely dilute medium the present results are consistent with those previously obtained for the vacuum case.

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- <sup>35</sup>Here the required energy shifts are incorporated in the intermediate states through the appropriate summation of an infinite set of diagrams.
- <sup>36</sup>It follows from the time-energy uncertainty principle that retention of the original form (3.9) is important only for times which are less than the inverse molecular transition frequency  $\omega_B^{-1}$  generally on the femtosecond time scale.
- <sup>37</sup>In the earlier paper (Ref. 24), the transition matrix element analogous to  $U_{fi}^{(2)}$  was represented as  $\langle F|T^{(2)}|I\rangle$ .
- <sup>38</sup>In this respect, detailed consideration of the case of a pair of nonidentical species *in vacuo* has been made by Ficek, Tanas, and Kielich (Ref. 23).