

Quantum electrodynamics of resonant energy transfer in condensed matter

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A microscopic many-body QED theory for dipole-dipole resonance energy transfer has been developed from first principles. A distinctive feature of the theory is full incorporation of the dielectric effects of the supporting medium, in the context of an interplay between what have traditionally been regarded as radiationless and radiative excitation transfer. The approach employs the concept of bath polaritons mediating the energy transfer. The transfer rate is derived in terms of the Green's operator corresponding to the polariton matrix Hamiltonian. In contrast to the more common lossless polariton models, the present theory accommodates an arbitrary number of energy levels for each molecule of the medium. This includes, in particular, a case of special interest, where the excitation energy spectrum of the bath molecules is sufficiently dense that it can be treated as a quasicontinuum in the energy region in question, as in the condensed phase normally results from homogeneous and inhomogeneous line broadening. In such a situation, the photon "dressed" by the medium polarization (the polariton) acquires a finite lifetime, the role of the dissipative subsystem being played by bath molecules. It is this which leads to the appearance of the exponential decay factor in the microscopically derived pair transfer rates. Accordingly, the problem associated with potentially infinite total ensemble rates, due to the divergent R^{-2} contribution, is solved from first principles. In addition, the medium modifies the distance dependence of the energy transfer function $A(R)$ and also produces extra modifications due to screening contributions and local field effects. The formalism addresses cases where the surrounding medium is either absorbing or lossless over the range of energies transferred. In the latter case the exponential factor does not appear and the dielectric medium effect in the near zone reduces to that which is familiar from the theory of radiationless (Förster) energy transfer.

I. INTRODUCTION

Over recent years there has been substantial interest in the nonrelativistic applications of quantum electrodynamics (QED). It has covered a broad range of topics such as superradiance,^{1,2} spontaneous emission in dielectric structures,³⁻⁵ anomalous manifestations of QED associated with a photoionic band gap,^{3,6,7} photon pairing in nonlinear crystals,⁸ causality and retardation in energy transfer,⁹⁻¹⁶ the Casimir effect,^{17,18} bimolecular absorption and bimolecular scattering of photons,¹⁹⁻²¹ etc. Among other QED problems, resonant transfer of excitation energy is distinctive for two reasons. First, as the simplest example of interatomic (or intermolecular) interactions mediated by virtual photons, energy transfer is a prime candidate for the application of QED. It provides a test bed for developing concepts such as the possible violation of causality in intermolecular processes.^{10,13,15} Second, energy transfer is an interesting phenomenon *per se*, having considerable importance in nature: the most familiar manifestation is, perhaps, the migration of electronic excitation in photosynthesis.²²

In most of the existing literature, excitation transfer is traditionally described in terms of short-range radiationless and long-range radiative limits (see, e.g., Refs. 23 and 24). The former, which operates over transfer distances $R \ll \lambda$ (λ is a reduced wavelength corresponding to the transfer energy), is assumed to be induced by an instantaneous Coulombic interaction. In the case of dipole-allowed transitions, this mechanism leads to the Förster-

type R^{-6} distance dependence of the pair transfer rate. The latter radiative transfer, operating over distances $R \gg \lambda$, is considered to be a two-stage process consisting of the emission of a (real) photon and its subsequent recapture. The probability of the radiative transfer has the R^{-2} dependence characteristic of a classical spherical wave.

The less familiar QED approach to resonant energy transfer, originating from pioneering studies by Avery²⁵ and also by Gomberoff and Power,²⁶ does not differentiate transfer by the radiative and radiationless mechanisms, as they prove to correspond, respectively, to the far- and near-zone limits of a unified theory. Throughout the whole range of distances, energy transfer is treated as a concerted second-order process mediated by a virtual photon.^{11,12,14-16} Here the pair rate of dipole-dipole energy transfer has both R^{-6} and R^{-2} terms, as well as an R^{-4} contribution which features in the intermediate region of distances where $R \sim \lambda$. However, the standard QED derivation of pair rates involves a quantized electromagnetic field and a pair of molecules or atoms between which the energy is transferred, with no consideration of other species which constitute the medium. Consequently, the R^{-2} contribution present in the pair rates might appear to lead to potentially infinite ensemble rates. For instance, the total rate of energy transfer from an initially excited molecule to any of its surrounding counterparts, calculated as a sum of the corresponding pair rates, would linearly increase with the system dimensions and could therefore grow to infinity.¹⁴

In our previous paper, it was proposed that the distance dependence of the pair rate be modified via the phenomenological introduction of exponential (Beer's law) decay factors to account for energy losses associated with the media molecules.¹⁴ Although that resolved the problems of potentially infinite decay rates and produced physically reasonable rate equations for the ensemble, the phenomenological approach lacked justification at the fundamental microscopic level of QED. Moreover, preexponential refractive factors, such as those associated with local field effects, have not been taken into consideration.

Here a comprehensive many-body formulation of microscopic QED is presented which systematically deals with these issues and thus fully accounts for intermolecular dipole-dipole energy transfer in a dielectric medium. The approach involves the employment of the polariton concept for representing the mediation of energy transfer. In contrast to the lossless polariton model, employed recently by Knoester and Mukamel in dealing with the related problems of intermolecular forces and superradiance in a dielectric medium,¹ the present theory accommodates an arbitrary number of energy levels for each molecule of the medium (bath). This includes, in particular, a case of special interest, where the excitation spectrum of the bath molecules is sufficiently dense and smooth that it can be treated as a quasicontinuum in the energy region of interest. In such a situation, the photon "dressed" by the medium polarization (the polariton) acquires a finite lifetime, the role of the dissipative subsystem being played by bath molecules. It is this which leads to the appearance of the exponential decay factor in the microscopically derived pair transfer rates. The factor coincides, in the limit of low number density for the medium molecules, to that obtained on a phenomenological basis.¹⁴ In addition, the medium modifies the distance dependence of the energy transfer function $A(R)$ and also produces extra modifications due to screening contributions and local field effect, correctly represented through full incorporation of umklapp processes. The formalism addresses cases where the surrounding medium is either absorbing or lossless over the range of energies transferred. In the latter case, the exponential factor does not appear and the dielectric medium effect in the near zone reduces to that which is familiar from the theory of radiationless (Föster) energy transfer.²³

The paper is organized as follows. In the next section, the full system is first defined in terms of two subsystems, one comprising a pair of atoms or molecules between which energy is transferred and the other a bath comprising the surrounding material medium and the radiation field. Section II also introduces the Hamiltonian of the system and defines the pair transfer rate. Section III completes the representation of the bath by invoking the polariton concept through a modified form of a matrix formulation, first suggested by Orrit and Kottis,²⁷ of the second-quantized polariton Hamiltonian. The energy transfer rate is subsequently (Sec. IV) derived in terms of the Green's operator corresponding to the matrix Hamiltonian. As a result, determination of the transfer rate reduces to a problem of finding the appropriate Green's

function. This allows us to bypass the eigenstate problem which frequently features in polariton-related topics (see, for instance, Refs. 1 and 28). Since an arbitrary number of molecular levels is involved in our polariton model, a straightforward diagonalization of the Hamiltonian would be mathematically intractable. Finally, a discussion of the results and their applicability is presented in Sec. V, and the derivations of some of the results are given in two appendices.

II. GENERAL FORMULATION

The system of interest is an ensemble of molecules interacting with a quantized electromagnetic field. The molecular part of the system is comprised of a selected pair of molecules A and B and the surrounding bath molecules. Although for convenience A and B will be referred to as *guest* species, they do not necessarily differ in type from the bath molecules which constitute the host material. Here and hereafter the term "molecule" is used generically to also encompass atoms.

To deal with the field-assisted transfer of excitation energy between A and B , we will make use of the multipolar representation of QED.^{27,29} The term "multipolar" explicitly indicates that the theory originates in a formulation of the coupling which entails the full multipolar expansion of electronic, magnetic, and diamagnetic densities of molecules interacting with the quantized field. For present purposes we will nonetheless restrict ourselves to the electric-dipole approximation. This is sufficient and generally appropriate for the description of dipole-allowed molecular or intermolecular processes provided the molecular dimensions are small enough compared to a characteristic scale of distances. For intermolecular problems of interest, the role of these characteristic lengths is played by the separations between molecules; the characteristic distance for molecular absorption, emission, or scattering processes is the corresponding wavelength of light.

A. Hamiltonian

Let us divide the full system into the guest subsystem and the bath. The latter is chosen to be a coupled system of the electromagnetic field and the host molecules. The total Hamiltonian H^T splits naturally into the zero-order Hamiltonian H^0 and the operator V [to be given explicitly in Eq. (2.5)] representing the mutual guest-bath interaction:

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

where

$$H^0 = H_A + H_B + H_{\text{bath}}, \quad (2.2)$$

$$H_{\text{bath}} = H_{\text{rad}} + H_{\text{host}} + H_{\text{coup}}, \quad (2.3)$$

$$H_{\text{host}} = \sum_{X \neq A, B} H_X. \quad (2.4)$$

Here H_{bath} is a bath Hamiltonian comprising a sum of the free radiation (H_{rad}) and molecular (H_{host}) Hamiltonians, as well as the radiation-matter coupling operator

H_{coup} , to be defined below in Eq. (2.6); H_X are the Hamiltonians of individual molecules, with X being a molecular index which can span both guest and host species.

In accordance with the multipolar QED formulation,²⁹ the total Hamiltonian H_T does not contain terms (such as H_{AB}) to invoke direct intermolecular coupling. The interaction between the radiation and matter originates from contributions by individual molecules. The contributions by the A and B species give rise to the guest-bath interaction V , whereas those due to the host molecules are responsible for the matter-radiation coupling within the bath, H_{coup} :

$$V = H_A^{\text{int}} + H_B^{\text{int}}, \quad (2.5)$$

$$H_{\text{coup}} = \sum_{X \neq A, B} H_X^{\text{int}}, \quad (2.6)$$

where the molecular-radiation interaction operators H_X^{int} are, in the electric-dipole approximation,

$$H_X^{\text{int}} = -\epsilon_0^{-1} \boldsymbol{\mu}(X) \cdot \mathbf{d}^\perp(\mathbf{r}_X). \quad (2.7)$$

The above ϵ_0 is the vacuum dielectric permittivity, $\boldsymbol{\mu}(X)$ and \mathbf{r}_X are, respectively, the dipole moment operator and position vector of the molecule X and $\mathbf{d}^\perp(\mathbf{r})$ is the operator for the transverse electric displacement field. The latter can be cast in terms of a normal-mode expansion,²⁹ expressible as

$$\begin{aligned} \mathbf{d}^\perp(\mathbf{r}) = & \sum_{\mathbf{k}, \mathbf{G}, \lambda} \left[\frac{\hbar c |\mathbf{k} + \mathbf{G}| \epsilon_0}{2V_0} \right]^{1/2} i e^{(\lambda)}(\mathbf{k} + \mathbf{G}) \\ & \times [a^{(\lambda)}(\mathbf{k} + \mathbf{G}) - a^{\dagger(\lambda)}(-\mathbf{k} - \mathbf{G})] \\ & \times e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}. \end{aligned} \quad (2.8)$$

Here $a^{\dagger(\lambda)}(\mathbf{k} + \mathbf{G})$ and $a^{(\lambda)}(\mathbf{k} + \mathbf{G})$ are the photon creation and annihilation operators, V_0 is the quantization volume, and the sum is taken over the radiation modes characterized by the wave vector $\mathbf{k} + \mathbf{G}$ and the unit polarization vector $e^{(\lambda)}(\mathbf{k} + \mathbf{G})$. For convenience, the former wave vector is partitioned into the first Brillouin-zone vector \mathbf{k} and the inverse lattice vector \mathbf{G} in order to anticipate the lattice symmetry to be imposed on the host medium in Sec. III A. The latter polarization vector is considered to be real (corresponding to the field expansion in terms of linearly polarized plane waves) and such that $e^{(\lambda)}(\mathbf{k} + \mathbf{G}) = e^{(\lambda)}(-\mathbf{k} - \mathbf{G})$. On a similar basis, the mode representation of the radiation Hamiltonian reads as

$$H_{\text{rad}} = \sum_{\mathbf{k}, \mathbf{G}, \lambda} a^{\dagger(\lambda)}(\mathbf{k} + \mathbf{G}) a^{(\lambda)}(\mathbf{k} + \mathbf{G}) \hbar c |\mathbf{k} + \mathbf{G}| + e_{\text{vac}}, \quad (2.9)$$

where $\hbar c |\mathbf{k} + \mathbf{G}|$ is a photon energy and e_{vac} is the usual photon vacuum energy.

The detailed definition of the system Hamiltonian will be completed in the Sec. III by choosing a particular form for the host molecular operators H_{host} and $\boldsymbol{\mu}(X)$ ($X \neq A, B$). As regards the guest molecules, only their transition dipole moments, the transfer energy, and the mutual separation distance feature in the theory to be developed below.

B. Definition of the transfer rate

The initial- and final-state vectors, representing the energy transfer between A and B , are constructed as

$$|I\rangle = |A^*\rangle |B\rangle |0\rangle \quad (2.10)$$

and

$$|F\rangle = |A\rangle |B^*\rangle |0\rangle, \quad (2.11)$$

where $|0\rangle$ is the ground-state vector of the bath and $|A^*\rangle$ and $|A\rangle$ ($|B\rangle$ and $|B^*\rangle$) are the initial- and final-state vectors of the molecule A (B). For generality, the molecular state vectors are considered to implicitly contain both electronic and vibrational contributions which are normally separable on the basis of the Born-Oppenheimer principle. The full state vectors, $|I\rangle$ and $|F\rangle$ are eigenvectors of the zero-order Hamiltonian (2.2), with

$$E_I = e_{A^*} + e_B + e_0 \quad (2.12)$$

and

$$E_F = e_A + e_{B^*} + e_0, \quad (2.13)$$

being the eigenenergies. Here e_{A^*} , e_B , e_A , and e_{B^*} are the corresponding energies of the initial and final molecular states and e_0 is the ground-state energy of the bath.

It is worth pointing out that, although Eqs. (2.10) and (2.11) resemble the standard initial conditions featuring in the QED description of energy transfer between an isolated pair of molecules,^{9,11,12,14-16} the state vector $|0\rangle$ here no longer denotes a photon vacuum. Instead, it represents the ground state of a coupled system of photons and host molecules. In other words, the present initial conditions fully take account of the radiation-matter coupling in the bath. It may also be remarked that the initial-state vector $|0\rangle$ of the bath in (2.10) is identical to that which appears in the final state (2.11). Any possible changes in the final bath state would correspond to higher-order bimolecular processes, such as those involving single-photon²⁰ or multi-photon^{19,21} absorption and scattering.

In order to derive the rate equation for intermolecular energy transfer associated with the given initial and final system states, we employ the normal methods of time-dependent perturbation theory with V acting as the perturbation on basis states which are eigenstates of H^0 . The transfer rate is then obtained from the application of the generalized Fermi rule³⁰

$$W_{IF} = \frac{2\pi}{\hbar} |\langle F|T|I\rangle|^2 \delta(E_F - E_I), \quad (2.14)$$

where T is the transition operator, its expansion given by

$$T = T^{(1)} + T^{(2)} + \dots, \quad (2.15)$$

with

$$T^{(1)} = V, \quad (2.16)$$

$$T^{(2)} = V \frac{1}{E_I - H^0 + is} V, \quad s \rightarrow +0, \quad (2.17)$$

and higher terms can for our purposes be neglected. The term “generalized” is used here because (2.16) reduces to the ordinary Fermi golden rule in the first order of perturbation through substituting V for T . Since there is no direct longitudinal interaction between molecules, the energy transfer appears in the second order of perturbation, as represented by the term $T^{(2)}$,

$$\langle F|T^{(2)}|I\rangle = \frac{1}{\hbar} \sum_{\sigma} \sum_{p=1}^2 \frac{\langle F|V|I_p(\sigma)\rangle \langle I_p(\sigma)|V|I\rangle}{(-1)^{p+1}cK - \Pi_{\sigma} + is}, \quad (2.18)$$

where

$$\hbar cK = e_{A^*} - e_A = e_{B^*} - e_B > 0 \quad (2.19)$$

is the transfer energy,

$$|I_1(\sigma)\rangle = |A\rangle|B\rangle|\sigma\rangle \quad (2.20)$$

and

$$|I_2(\sigma)\rangle = |A^*\rangle|B^*\rangle|\sigma\rangle \quad (2.21)$$

are the intermediate states,

$$\hbar \Pi_{\sigma} = e_{\sigma} - e_0 \quad (2.22)$$

is the bath excitation energy (difference in energies between the excited and ground bath states), and the index σ refers to the excited bath states accessible through a single action by the interaction operator V on the ground-state vector $|0\rangle$. Accordingly, the energy transfer is now regarded as being mediated by bath excitations (polaritons) rather than by “pure” photons. The two types of intermediate states correspond to the two possible sequences of the transitions undergone by the guest molecules. In the first case, the transition $A^* \rightarrow A$ precedes the transition $B \rightarrow B^*$ [Fig. 1(a)], whereas in the second case the transition of molecule B takes place first [Fig. 1(b)]. The latter sequence features an apparently anomalous situation in which the upward transition of molecule B is associated with the excitation of the bath (the creation of the polariton) and the subsequent polariton annihilation is accompanied by the deexcitation of A . Nonetheless, both types of diagrams must be accommodated in the theory according to the normal rules of time-dependent perturbation theory. Inclusion of the contributions by Fig. 1(b) is of essential importance at small separations between the guest species, in order to correctly generate the nonretarded quasidelectrostatic intermolecular interactions. The precision with which the

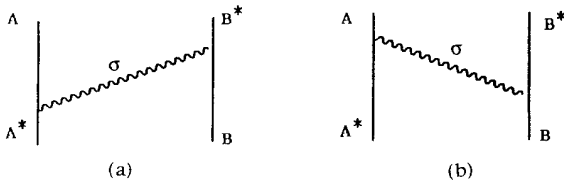


FIG. 1. Time-ordered diagrams for resonant energy transfer mediated by the intermolecular propagation of a virtual bath polariton.

law of energy conservation has to apply for intermediate (virtual) bath polaritons is determined by the time-energy uncertainty principle. At large separations, where the virtual polariton mediating the guest-guest interaction exists for a time appreciably exceeding the duration of the optical cycle, the polariton acquires real character. Consequently, the contributions associated with Fig. 1(b) diminish to a point where they can be considered negligible.

By making use of Eqs. (2.18), (2.5), and (2.7), together with (2.10), (2.11), (2.20), and (2.21), one finds the general expression for the transition matrix element:

$$\langle F|T^{(2)}|I\rangle = \sum_{i,j=1}^3 \mu_{B_i} \theta_{ij} \mu_{A_j}, \quad (2.23)$$

with

$$\theta_{ij} = \frac{1}{\hbar \epsilon_0^2} \sum_{\sigma} \left[\frac{\langle 0|\mathbf{d}_j^{\dagger}(\mathbf{r}_B)|\sigma\rangle \langle \sigma|\mathbf{d}_i^{\dagger}(\mathbf{r}_A)|0\rangle}{cK - \Pi_{\sigma} + is} - \frac{\langle 0|\mathbf{d}_j^{\dagger}(\mathbf{r}_A)|\sigma\rangle \langle \sigma|\mathbf{d}_i^{\dagger}(\mathbf{r}_B)|0\rangle}{cK + \Pi_{\sigma} - is} \right], \quad (2.24)$$

where μ_A and μ_B are the transition dipole moments of the guest species,

$$\mu_A = \langle A|\mu(A)|A^*\rangle, \quad (2.25)$$

$$\mu_B = \langle B^*|\mu(B)|B\rangle, \quad (2.26)$$

and θ_{ij} is the electromagnetic tensor for retarded dipole-dipole coupling between the sites A and B . Unlike the vacuum electromagnetic tensors featuring in the standard QED theories of energy transfer,^{11,12,31} here θ_{ij} is obviously influenced by the material medium, as the bath states and energies (rather than those of the free radiation field) enter Eq. (2.24).

III. POLARITON REPRESENTATION OF THE BATH

A. Second-quantized Hamiltonian

Let us suppose for convenience that the host species are all identical and constitute a simple cubic lattice; the possible significance of this assumption with regard to the generality of the theory will be discussed in Sec. V. Representing the host molecules in terms of a set of Bose-type oscillators, the Hamiltonian (2.4) takes the form

$$H_{\text{host}} = \sum_{n,\gamma} \sum_{j=1}^3 \hbar \omega_{\gamma} B_{n,\gamma,j}^{\dagger} B_{n,\gamma,j}, \quad (3.1)$$

where the vector

$$\mathbf{n} = \sum_{j=1}^3 n_j \mathbf{e}_j \quad (3.2)$$

labels the host molecules in the lattice (i.e., the index X takes the values \mathbf{n}), with \mathbf{e}_j being the unit vector along the Cartesian axis j and n_j taking integer values. The above $B_{n,\gamma,j}^{\dagger}$ and $B_{n,\gamma,j}$ are the Bose operators for

creation and annihilation of the excitation (exciton) at molecule \mathbf{n} . When acting on a ground molecular state, the creation operator $B_{\mathbf{n},\gamma,j}^\dagger$ produces an excited state characterized by the indexes γ and j , $\hbar\omega_\gamma$ being the excitation energy. The index j explicitly indicates that the molecular levels γ are triply degenerate, the corresponding transition dipole moments $\mu_\gamma \mathbf{e}_j$ ($j=1,2,3$) being mutually perpendicular. By properly choosing the phases of molecular wave functions, it is possible to make the values of the transition dipole moments real. The dipole operator of molecule \mathbf{n} is then expressible as

$$\boldsymbol{\mu}(\mathbf{n}) = \sum_\gamma \sum_{j=1}^3 (B_{\mathbf{n},\gamma,j}^\dagger + B_{\mathbf{n},\gamma,j}) \mu_\gamma \mathbf{e}_j. \quad (3.3)$$

At this juncture a couple of remarks should be made concerning the above representation of the material medium. First, the molecular creation and annihilation operators $B_{\mathbf{n},\gamma,j}^\dagger$ and $B_{\mathbf{n},\gamma,j}$ should strictly speaking obey Pauli (not universally Bose) commutation relations, under which the Bose commutation rules apply only for operators belonging to different lattice sites, with Fermi rules applying for operators at the same sites. The latter of course precludes the possibility of any double excitation of individual molecular levels, in accordance with the Pauli exclusion principle. The replacement of the Pauli by Bose commutation rules is nonetheless a common approximation which normally produces good results for three-dimensional molecular systems such as the one considered here. The most significant manifestations of any *kinematic interactions*, originating from the employment of nonexact Bose commutation rules, appear in low-dimensional structures. For instance, the electronic excitations in one-dimensional molecular systems are better represented by Fermi than by Bose operators.³²⁻³⁴ Second, unlike more common lossless polariton models, the present approach accommodates an arbitrary number molecular excitation frequencies ω_γ . To this extent our

polariton model resembles that used by Philpott³⁵ to incorporate vibronic structure in polariton theory by treating the vibronic progressions of the molecular electronic states in terms of well-separated molecular sublevels. However, we are more interested in another case where the molecular excitation spectrum is sufficiently dense that it can be treated as a quasicontinuum in the energy region of interest, as in a condensed phase normally results from homogeneous and inhomogeneous line broadening.³⁶ In this case the bath molecules act as a dissipative subsystem effectively causing the decay of polaritons, which can be visualized as photons "dressed" by the molecular excitations of the absorbing medium. The complex dielectric constant will appear in the Sec. IV, as a result.

Returning to the exciton operators, the standard transformation to the momentum space reads

$$B_{\mathbf{k},\gamma,j} = N^{-1/2} \sum_{\mathbf{n}} B_{\mathbf{n},\gamma,j} e^{-i\mathbf{k}\cdot\mathbf{r}_{\mathbf{n}}}, \quad (3.4)$$

$$B_{\mathbf{k},\gamma,\lambda'} = \sum_j [e^{(\lambda')}(\mathbf{k}) \cdot \mathbf{e}_j] B_{\mathbf{k},\gamma,j}, \quad (3.5)$$

with $\mathbf{r}_{\mathbf{n}} = a\mathbf{n}$ being a lattice vector, a the lattice spacing, and N the number of molecules in a quantization volume $V_0 = Na^3$. The latter V_0 is chosen to coincide with the quantization volume of the radiation field. In other words, the same boundary conditions are imposed on the excitons and on the quantized radiation field. Consequently, the same set of wave vectors applies to both the excitons and the first Brillouin-zone photons. That is a common polariton assumption which is justified unless one is interested in surface effects.^{1,27,28,35} The operators $B_{\mathbf{k},\gamma,\lambda'}$ describe the longitudinal [$\lambda'=3$, $e^{(3)}(\mathbf{k}) = \mathbf{k}/|\mathbf{k}|$] and transverse ($\lambda'=1,2$) excitons: the polarization vectors of the latter coincide with that of the first Brillouin-zone photons in Eq. (2.8). Using Eqs. (3.1)–(3.5) and (2.6)–(2.8), one finds

$$H_{\text{host}} = \sum_{\mathbf{k},\gamma} \sum_{\lambda'=1}^3 \hbar\omega_\gamma B_{\mathbf{k},\gamma,\lambda'}^\dagger B_{\mathbf{k},\gamma,\lambda'}, \quad (3.6)$$

$$H_{\text{coup}} = \sum_{\mathbf{G},\mathbf{k},\gamma} \sum_{\lambda'=1}^3 \sum_{\lambda=1}^2 \hbar [C_{(\mathbf{k},\gamma,\lambda')(\mathbf{k},\mathbf{G},\lambda)} (B_{-\mathbf{k},\gamma,\lambda'} + B_{\mathbf{k},\gamma,\lambda'}^\dagger) a^{(\lambda)}(\mathbf{k}+\mathbf{G}) + C_{(\mathbf{k},\mathbf{G},\lambda')(\mathbf{k},\mathbf{G},\lambda)}^\dagger a^{\dagger(\lambda)}(\mathbf{k}+\mathbf{G}) (B_{-\mathbf{k},\gamma,\lambda'}^\dagger + B_{\mathbf{k},\gamma,\lambda'})], \quad (3.7)$$

$$C_{(\mathbf{k},\gamma,\lambda')(\mathbf{k},\mathbf{G},\lambda)} = -i \left[\frac{c|\mathbf{k}+\mathbf{G}|}{2\epsilon_0\hbar} \rho \right]^{1/2} \mu_\gamma [e^{(\lambda')}(\mathbf{k}) \cdot e^{(\lambda)}(\mathbf{k}+\mathbf{G})], \quad (3.8)$$

with

$$\rho = N/V_0 \quad (3.9)$$

being the mean number density of the host material.

Equations (3.6) and (3.7) together with (2.9) define the bath Hamiltonian (2.3) in terms of molecular and radiative sets of Bose operators. It is more convenient, however, to introduce a single set of annihilation (creation) operators A_α (A_α^\dagger) where α covers both radiative and molecular indexes:

$$A_\alpha = \begin{cases} B_{\mathbf{k},\gamma,\lambda'} & \text{for } \alpha = (\mathbf{k},\gamma,\lambda'), \\ a^{(\lambda)}(\mathbf{k}+\mathbf{G}) & \text{for } \alpha = (\mathbf{k},\mathbf{G},\lambda). \end{cases} \quad (3.10)$$

By adopting the tilde convention

$$\widetilde{(\mathbf{k},\gamma,\lambda')} = (-\mathbf{k},\gamma,\lambda'), \quad (3.11)$$

$$\widetilde{(\mathbf{k},\mathbf{G},\lambda)} = (-\mathbf{k},-\mathbf{G},\lambda), \quad (3.12)$$

the second-quantized bath Hamiltonian then takes the form

$$H_{\text{bath}} = \hbar \sum_{\alpha, \beta} [\Omega_{\alpha\beta} A_{\alpha}^{\dagger} A_{\beta} + \Phi_{\alpha\beta} A_{\alpha} A_{\beta} + \Phi_{\alpha\beta}^{*} A_{\beta}^{\dagger} A_{\alpha}^{\dagger}] + e_{\text{vac}}, \quad (3.13)$$

with the matrixes Ω and Φ having the block structure

$$\Omega = \begin{pmatrix} \omega' & C \\ {}^t C^{*} & \omega \end{pmatrix}, \quad (3.14)$$

$$\Phi = \begin{pmatrix} 0 & C \\ 0 & 0 \end{pmatrix}, \quad (3.15)$$

where ω' and ω are the diagonal matrices of molecular and radiative frequencies (ω_{γ} and $c|\mathbf{k} + \mathbf{G}|$, respectively), C is the radiation-matter coupling matrix defined by Eq. (3.8), and the superscripts $*$ and t refer to the complex-conjugated and transposed matrices, respectively. By making use of the Bose commutation relations

$$[A_{\alpha}, A_{\beta}] = 0, \quad (3.16)$$

$$[A_{\alpha}, A_{\beta}^{\dagger}] = \delta_{\alpha, \beta}, \quad (3.17)$$

and bearing in mind that ${}^t \Omega_{\alpha\beta}^{*} = \Omega_{\alpha\beta} = \Omega_{\alpha\beta}$ and $\Phi_{\alpha\beta}^{*} = \Phi_{\alpha\beta}$, the Hamiltonian (3.13) acquires the symmetric form

$$H_{\text{bath}} = \frac{\hbar}{2} \sum_{\alpha, \beta} [\Omega_{\alpha\beta} A_{\alpha}^{\dagger} A_{\beta} + \Omega_{\alpha\beta}^{*} A_{\alpha} A_{\beta}^{\dagger} + \chi_{\alpha\beta} A_{\alpha} A_{\beta} + \chi_{\alpha\beta}^{*} A_{\alpha}^{\dagger} A_{\beta}^{\dagger}], \quad (3.18)$$

where

$$\chi = \Phi + {}^t \Phi = \begin{pmatrix} 0 & C \\ {}^t C & 0 \end{pmatrix}, \quad (3.19)$$

and the molecular shift in the zero-point energies, $(3N/2) \sum_{\gamma} \hbar \omega_{\gamma}$, has been omitted in Eq. (3.18), since it has no physical significance for the processes under consideration.

B. Matrix Hamiltonian

In the next two subsections, a matrix representation of the polariton problem, first suggested by Orrit and Kottis,²⁷ will be reformulated in a modified form more suitable for the present purposes. To begin, it may be observed that the expansion (3.18) of H_{bath} has been arranged in such a way that tildes stand on the annihilation (creation) operators if and only if they are on the left (right) of the creation (annihilation) operators. Hence H_{bath} can be rewritten in a compact manner involving the matrix product

$$H_{\text{bath}} = \frac{\hbar}{2} (A^{\dagger}, \tilde{A} | h | A, \tilde{A}^{\dagger}). \quad (3.20)$$

Here $|A, \tilde{A}^{\dagger}\rangle$ and $(A^{\dagger}, \tilde{A} |$ are row and column matrix vectors whose elements are the creation and annihilation operators

$$|A, \tilde{A}^{\dagger}\rangle = (A_{\alpha_1}, A_{\alpha_2}, \dots; A_{\alpha_1}^{\dagger}, A_{\alpha_2}^{\dagger}, \dots), \quad (3.21)$$

$$(A^{\dagger}, \tilde{A} | = \begin{pmatrix} A_{\alpha_1}^{\dagger} \\ A_{\alpha_2}^{\dagger} \\ \vdots \\ A_{\alpha_1} \\ A_{\alpha_2} \\ \vdots \end{pmatrix}, \quad (3.22)$$

and h is the matrix Hamiltonian, its block structure being given by

$$h = \begin{pmatrix} \Omega & \chi^{*} \\ \chi & \Omega^{*} \end{pmatrix}. \quad (3.23)$$

By making use of Eqs. (3.14) and (3.19), the matrix h reads more explicitly as

$$h = \begin{pmatrix} \omega' & C & 0 & C^{*} \\ {}^t C^{*} & \omega & {}^t C^{*} & 0 \\ 0 & C & \omega' & C^{*} \\ {}^t C & 0 & {}^t C & \omega \end{pmatrix}. \quad (3.24)$$

In passing, we note that the original matrix formulation²⁷ did not involve any tildes over the radiative and molecular indexes. That was a consequence of operating in the site representation of the material medium. Here the introduction of the tilde designation facilitates the treatment, as the momentum representation of the medium is considered. Returning to the matrix vectors, for present purposes it is more convenient to deal with their expansions in terms of orthogonal sets of unit matrix vectors $|\alpha, i\rangle$ and $\langle\alpha, i|$, $i=1, 2$:

$$|A, \tilde{A}^{\dagger}\rangle = \sum_{\alpha} [|\alpha, 1\rangle A_{\alpha} + |\alpha, 2\rangle A_{\alpha}^{\dagger}], \quad (3.25)$$

$$(A^{\dagger}, \tilde{A} | = \sum_{\alpha} [A_{\alpha}^{\dagger} \langle\alpha, 1| + A_{\alpha} \langle\alpha, 2|], \quad (3.26)$$

where, for example,

$$|\alpha_2, 1\rangle = (0, 1, 0, \dots; 0, 0, \dots), \quad (3.27)$$

$$|\alpha_3, 2\rangle = (0, 0, \dots; 0, 0, 1, \dots). \quad (3.28)$$

Summation over α accommodates all α_t ($t=1, 2, 3, \dots$). The presence of an extra index $i=1, 2$ reflects the fact that the current matrix representation entails a double basis set of the original molecular excitation and radiation modes denoted by α . On a similar basis, the expanded matrix Hamiltonian reads

$$h = \sum_{i, i'=1}^2 \sum_{\alpha, \beta} |\alpha, i\rangle \langle\alpha, i| h |\beta, i'\rangle \langle\beta, i'|, \quad (3.29)$$

with $\langle\alpha, i| h |\beta, i'\rangle$ being the matrix elements of h . By using the explicit form (3.24) for the matrix h , the expansion (3.29) may be represented as

$$h = h_r + h_m + h_{r-m} + h_{m-r}, \quad (3.30)$$

with

$$h_r = \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\lambda=1}^2 \sum_{i=1}^2 |\mathbf{k}, \mathbf{G}, \lambda, i\rangle c |\mathbf{k} + \mathbf{G}\rangle |(\mathbf{k}, \mathbf{G}, \lambda, i)|, \quad (3.31)$$

$$h_m = \sum_{\mathbf{k}} \sum_{\gamma} \sum_{\lambda'=1}^3 \sum_{i=1}^2 |\mathbf{k}, \gamma, \lambda', i\rangle \omega_{\gamma} |\mathbf{k}, \gamma, \lambda', i|, \quad (3.32)$$

$$h_{r-m} = \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\gamma} \sum_{\lambda'=1}^3 \sum_{\lambda=1}^2 \sum_{i=1}^2 [|\mathbf{k}, \mathbf{G}, \lambda, 1\rangle - |\mathbf{k}, \mathbf{G}, \lambda, 2\rangle] C_{(\mathbf{k}, \gamma, \lambda')(\mathbf{k}, \mathbf{G}, \lambda)}^* |\mathbf{k}, \gamma, \lambda', i|, \quad (3.33)$$

$$h_{m-r} = \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\gamma} \sum_{\lambda'=1}^3 \sum_{\lambda=1}^2 \sum_{i=1}^2 |\mathbf{k}, \gamma, \lambda', i\rangle C_{(\mathbf{k}, \gamma, \lambda')(\mathbf{k}, \mathbf{G}, \lambda)} [(\mathbf{k}, \mathbf{G}, \lambda, 1) - (\mathbf{k}, \mathbf{G}, \lambda, 2)]. \quad (3.34)$$

The above matrix Hamiltonian resembles in its form the quantum-mechanical Hamiltonian of a system comprising $2L$ levels, L being the number of original modes α . This analogy will facilitate the derivation of the Green's functions corresponding to the matrix Hamiltonian in Sec. IV. The matrix vectors entering Eqs. (3.30)–(3.34) should not, however, be confused with the usual quantum-mechanical bra and ket state vectors, such as $|I\rangle$ and $\langle F|$, which have already appeared in Sec. II.

C. Diagonal representation

Diagonalization of the second-quantized polariton Hamiltonian implies linear transform to a new set of Bose operators P_{σ}^{\dagger} and P_{σ} . The linear relation between the old and new operators can compactly be expressed in the following way:

$$|P, \tilde{P}^{\dagger}\rangle = S |A, \tilde{A}^{\dagger}\rangle, \quad (3.35)$$

$$\langle P^{\dagger}, \tilde{P} | = \langle A^{\dagger}, \tilde{A} | S^* ; \quad (3.36)$$

where S is the transformation matrix. In analogy to Eqs. (3.25) and (3.26), the transformed matrix vectors may be cast in terms of the orthonormal basis as

$$|P, \tilde{P}^{\dagger}\rangle = \sum_{\sigma} [|\sigma, 1\rangle P_{\sigma}^{\dagger} + |\sigma, 2\rangle P_{\tilde{\sigma}}^{\dagger}], \quad (3.37)$$

$$\langle P^{\dagger}, \tilde{P} | = \sum_{\sigma} [P_{\sigma}^{\dagger}(\sigma, 1) + P_{\tilde{\sigma}}(\sigma, 2)]. \quad (3.38)$$

Expansion of (3.35) produces a more familiar form of the polariton transform which reads

$$P_{\sigma} = \sum_{\alpha} [(\sigma, 1|S|\alpha, 1) A_{\alpha} + (\sigma, 1|S|\alpha, 2) A_{\tilde{\alpha}}^{\dagger}], \quad (3.39)$$

$$P_{\tilde{\sigma}}^{\dagger} = \sum_{\alpha} [(\sigma, 2|S|\alpha, 1) A_{\alpha} + (\sigma, 2|S|\alpha, 2) A_{\tilde{\alpha}}^{\dagger}]. \quad (3.40)$$

The transformation obviously correlates the creation and annihilation operators associated with opposite momenta, as the tildes imply momentum reversal. The following conditions are imposed on the transformation matrix. First, by virtue of translational symmetry and spatial isotropy, one has

$$\langle \tilde{\sigma}, i | S | \tilde{\alpha}, j \rangle = \langle \sigma, i | S | \alpha, j \rangle \quad (i, j = 1, 2). \quad (3.41)$$

Second, by taking the Hermitian conjugate of Eq. (3.39) and comparing the result to Eq. (3.40), it follows that

$$\langle \sigma, 1 | S^* | \alpha, 1 \rangle = \langle \sigma, 2 | S | \alpha, 2 \rangle, \quad (3.42)$$

$$\langle \sigma, 1 | S^* | \alpha, 2 \rangle = \langle \sigma, 2 | S | \alpha, 1 \rangle. \quad (3.43)$$

Last, requiring Bose commutation relations to be satisfied by the transformed operators leads to an extra condition (see Appendix A):

$$S Q^{\dagger} S^* = Q \quad (3.44)$$

and, thus,

$$S^{-1} = Q^{\dagger} S^* Q, \quad (3.45)$$

with Q having the block structure

$$Q = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (3.46)$$

In terms of the new operators, the second-quantized Hamiltonian takes the form

$$H = \frac{\hbar}{2} \sum_{\sigma} \Pi_{\sigma} (P_{\sigma}^{\dagger} P_{\sigma} + P_{\tilde{\sigma}} P_{\tilde{\sigma}}^{\dagger}), \quad (3.47)$$

which can be expressed using the matrix representation as

$$H = \frac{\hbar}{2} \langle P^{\dagger}, \tilde{P} | \Lambda | P, \tilde{P}^{\dagger} \rangle, \quad (3.48)$$

with

$$\Lambda = \begin{pmatrix} \Pi & 0 \\ 0 & \Pi \end{pmatrix} \quad (3.49)$$

being a diagonal matrix Hamiltonian involving the bath excitation frequencies Π_{σ} that have already entered Eqs. (2.18) and (2.24). By making use of Eqs. (3.20), (3.35), (3.36), and (3.48), one finds the following relation between the original and transformed matrix Hamiltonians:

$$h = S^* \Lambda S. \quad (3.50)$$

The above equation, together with Eq. (3.44), defines the diagonalization. Nonetheless, no explicit diagonalization will be involved in the present study, as the physical observables of interest will be directly calculated in terms of the Green's function.

IV. DERIVATION OF THE TRANSFER RATE

A. Green's-function development of the electromagnetic dipole-dipole coupling

In Sec. II the transition matrix element for energy transfer has been expressed by Eq. (2.23) via the electromagnetic tensor θ_{ij} representing dipole-dipole cou-

pling between sites A and B and fully accommodating the effects of the guest medium. The first step toward explicit calculation of this tensor is to cast the electric-field displacement operator \mathbf{d}^\dagger of Eq. (2.24) in terms of polariton creation and annihilation operators. Applying the inverse transform S^{-1} , the expansion of the Bose radiation operators reads

$$a^{(\lambda)}(\mathbf{k}+\mathbf{G}) = \sum_{\sigma} [(\mathbf{k}, \mathbf{G}, \lambda, 1 | S^{-1} | \sigma, 1) P_{\sigma} + (\mathbf{k}, \mathbf{G}, \lambda, 1 | S^{-1} | \sigma, 2) P_{\sigma}^{\dagger}], \quad (4.1)$$

$$a^{\dagger(\lambda)}(-\mathbf{k}-\mathbf{G}) = \sum_{\sigma} [(\mathbf{k}, \mathbf{G}, \lambda, 2 | S^{-1} | \sigma, 1) P_{\sigma} + (\mathbf{k}, \mathbf{G}, \lambda, 2 | S^{-1} | \sigma, 2) P_{\sigma}^{\dagger}], \quad (4.2)$$

which, together with the Eqs. (3.41)–(3.43) and (3.45), gives

$$a^{(\lambda)}(\mathbf{k}+\mathbf{G}) - a^{\dagger(\lambda)}(-\mathbf{k}-\mathbf{G}) = \sum_{\sigma} \{ [(\mathbf{k}, \mathbf{G}, \lambda, 1 | -(\mathbf{k}, \mathbf{G}, \lambda, 2 | S^{-1} | \sigma, 1) P_{\sigma} - (\sigma, 1 | QSQ | -\mathbf{k}, -\mathbf{G}, \lambda, 1) - | -\mathbf{k}, -\mathbf{G}, \lambda, 2) | P_{\sigma}^{\dagger}] \}. \quad (4.3)$$

Substituting the above equation into Eq. (2.8) for \mathbf{d}^\dagger and making an assumption that the guest species occupy the lattice sites [$\exp(i\mathbf{G}\cdot\mathbf{r}_X) = 1$; $X = A, B$], one finds

$$d_j^{\dagger}(\mathbf{r}_X) = i\hbar\epsilon_0 N^{-1/2} \sum_{\mathbf{k}, \sigma} [e^{i\mathbf{k}\cdot\mathbf{r}_X} {}_j(\mathbf{k}, \text{rad} | S^{-1} | \sigma, 1) P_{\sigma} - e^{-i\mathbf{k}\cdot\mathbf{r}_X} (\sigma, 1 | QSQ | \mathbf{k}, \text{rad}) {}_j P_{\sigma}^{\dagger}], \quad (4.4)$$

where the \mathbf{k} -dependent radiation row and column matrices $|\mathbf{k}, \text{rad}\rangle_j$ and ${}_j\langle\mathbf{k}, \text{rad}|$ have been defined as

$$|\mathbf{k}, \text{rad}\rangle_j = \sum_{\mathbf{G}} \sum_{\lambda=1}^2 [|\mathbf{k}, \mathbf{G}, \lambda, 1\rangle - |\mathbf{k}, \mathbf{G}, \lambda, 2\rangle] e_j^{(\lambda)}(\mathbf{k}+\mathbf{G}) \left[\frac{c|\mathbf{k}+\mathbf{G}|}{2\epsilon_0\hbar} \rho \right]^{1/2}, \quad (4.5)$$

$${}_j\langle\mathbf{k}, \text{rad}| = \sum_{\mathbf{G}} \sum_{\lambda=1}^2 e_j^{(\lambda)}(\mathbf{k}+\mathbf{G}) \left[\frac{c|\mathbf{k}+\mathbf{G}|}{2\epsilon_0\hbar} \rho \right]^{1/2} [(\mathbf{k}, \mathbf{G}, \lambda, 1 | -(\mathbf{k}, \mathbf{G}, \lambda, 2 |)]. \quad (4.6)$$

The matrix elements of S entering Eq. (4.4) satisfy the relations

$${}_j\langle\mathbf{k}, \text{rad} | S^{-1} | \sigma, 1\rangle = -(\sigma, 2 | QSQ | \mathbf{k}, \text{rad})_j \quad (4.7)$$

and

$$(\sigma, 1 | QSQ | \mathbf{k}, \text{rad})_j = -{}_j\langle\mathbf{k}, \text{rad} | S^{-1} | \sigma, 2\rangle. \quad (4.8)$$

Thus, as $\langle\sigma' | P_{\sigma}^{\dagger} | 0\rangle = \langle 0 | P_{\sigma} | \sigma'\rangle = \delta_{\sigma, \sigma'}$, the electromagnetic tensor (2.24) takes the following matrix form, free from any second-quantized state vectors and operators:

$$\theta_{ij} = \frac{\hbar}{N} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} e^{i\mathbf{k}\cdot\mathbf{r}_B} {}_i\langle\mathbf{k}, \text{rad} | \ddot{G} | \mathbf{k}', \text{rad}\rangle_j e^{-i\mathbf{k}'\cdot\mathbf{r}_A}, \quad (4.9)$$

with

$$\ddot{G} = S^{-1} \sum_{\sigma} \left[\frac{|\sigma, 1\rangle\langle\sigma, 1|}{cK + is - \Pi_{\sigma}} + \frac{|\sigma, 2\rangle\langle\sigma, 2|}{-(cK + is) - \Pi_{\sigma}} \right] QSQ \quad (4.10)$$

$$= S^{-1} [(cK + is)Q - \Lambda]^{-1} QSQ. \quad (4.11)$$

Here, for convenience, the sign of the infinitesimal $s \rightarrow +0$ has been reversed in the nonresonant term of Eq. (4.10). By making use of Eqs. (3.44) and (3.50), one has

$$\ddot{G} = [(cK + is)Q - h]^{-1}. \quad (4.12)$$

The above \ddot{G} can be identified as the Green's matrix corresponding to the matrix Hamiltonian h , the umlaut serving to differentiate it from the inverse lattice vector \mathbf{G} . Unlike the standard Green's operators featured in solid-state problems, the present \ddot{G} contains the matrix Q

($Q \neq 1$, $Q^2 = 1$) multiplying the argument. That is because the formalism involves a nonunitary transformation S satisfying the condition (3.45). Nonetheless, the Green's matrix can be treated in terms of techniques analogous to the normal solid-state approach³⁷ involving projection operator and local perturbation methods, in an only slightly modified manner. Finally, noting that those matrix elements of \ddot{G} nondiagonal with respect to the index \mathbf{k} are zero, the tensor (4.9) acquires the form

$$\theta_{ij} = \frac{\hbar}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}_B - \mathbf{r}_A)} \ddot{G}_{ij}(\mathbf{k}), \quad (4.13)$$

with

$$\ddot{G}_{ij}(\mathbf{k}) = {}_i\langle\mathbf{k}, \text{rad} | \ddot{G} | \mathbf{k}, \text{rad}\rangle_j \quad (4.14)$$

being the Green's function.

B. Determination of the electromagnetic coupling tensor

Let us initially define the following idempotent matrices projecting onto radiative and molecular subspaces:

$$I_r = \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\lambda=1}^2 \sum_{i=1}^2 |\mathbf{k}, \mathbf{G}, \lambda, i\rangle\langle\mathbf{k}, \mathbf{G}, \lambda, i|, \quad (4.15)$$

$$I_m = \sum_{\mathbf{k}} \sum_{\gamma} \sum_{\lambda'=1}^3 \sum_{i=1}^2 |\mathbf{k}, \gamma, \lambda', i\rangle\langle\mathbf{k}, \gamma, \lambda', i|. \quad (4.16)$$

Since the sum of I_r and I_m constitutes the unit matrix $\mathbf{1}$, any matrix D may be decomposed as

$$D = I_r D I_r + I_m D I_m + I_r D I_m + I_m D I_r \quad (4.17)$$

$$= D_r + D_m + D_{r-m} + D_{m-r}. \quad (4.18)$$

The decomposition of the matrix Hamiltonian h has already been given by Eq. (3.30). At this stage it is convenient to represent the radiation-matter coupling terms of h in the form

$$h_{r-m} = i \sum_{\mathbf{k}} \sum_{j=1}^3 |\mathbf{k}, \text{rad}\rangle_j \langle \mathbf{k}, \text{matt}|, \quad (4.19)$$

$$h_{m-r} = -i \sum_{\mathbf{k}} \sum_{j=1}^3 |\mathbf{k}, \text{matt}\rangle_j \langle \mathbf{k}, \text{rad}|, \quad (4.20)$$

where

$$|\mathbf{k}, \text{matt}\rangle_j = \sum_{\gamma} \sum_{\lambda'=1}^3 \sum_{i=1}^2 |\mathbf{k}, \gamma, \lambda', i\rangle e_j^{(\lambda')}(\mathbf{k}) \mu_{\gamma}, \quad (4.21)$$

${}_j\langle \mathbf{k}, \text{matt}|$ is the corresponding column matrix, and the radiative matrix vectors ${}_j\langle \mathbf{k}, \text{rad}|$ and $|\mathbf{k}, \text{rad}\rangle_j$ are as defined by Eqs. (4.5) and (4.6). Note that umklapp processes $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$ are completely incorporated in the above coupling terms (4.19) and (4.20) to correctly represent the local field effects. The significance of the umklapp processes has been extensively discussed in the literature both for the minimum coupling and the multipolar QED formulation.^{1,35,38,39}

It is obvious that only the radiative component \ddot{G}_r of the full Green's matrix \ddot{G} contributes to the Green's function $\ddot{G}_{ij}(\mathbf{k})$ of Eq. (4.14). As a result, the radiative subsystem of the bath plays a privileged role in the present calculations. To derive a closed equation for \ddot{G}_r and consequently that for $\ddot{G}_{ij}(\mathbf{k})$, we make use of the Dyson equation

$$\ddot{G} = \ddot{G}^0 + \ddot{G}^0 v \ddot{G}, \quad (4.22)$$

where

$$\ddot{G}^0 = [(cK + is)Q - h^0] \quad (4.23)$$

is the zero-order Green's matrix, h^0 and v playing role of the zero-order matrix Hamiltonian and the interaction matrix:

$$h^0 = h_r + h_m, \quad (4.24)$$

$$v = h_{r-m} + h_{m-r}. \quad (4.25)$$

Recursive substitution of the left-hand side of the Dyson equation for G into the right-hand side, with subsequent projection onto the radiative subspace, produces the following Dyson-type equation for \ddot{G}_r :

$$\ddot{G}_r = \ddot{G}_r^0 + \ddot{G}_r^0 v_r^{\text{eff}} \ddot{G}_r, \quad (4.26)$$

where the matrix

$$v_r^{\text{eff}} = h_{r-m} \ddot{G}_m^0 h_{m-r} \quad (4.27)$$

describes the effective (K -dependent) interaction, induced by the host material, between the radiation modes. Explicitly v_r^{eff} is given by

$$v_r^{\text{eff}} = -\hbar\alpha \sum_{\mathbf{k}} \sum_{j=1}^3 |\mathbf{k}, \text{rad}\rangle_j \langle \mathbf{k}, \text{rad}|, \quad (4.28)$$

where

$$\alpha \equiv \alpha(cK) = \frac{1}{\hbar} \sum_{\gamma} \left[\frac{\mu_{\gamma}^2}{\omega_{\gamma} - cK - is} + \frac{\mu_{\gamma}^2}{\omega_{\gamma} + cK + is} \right] \quad (4.29)$$

is the isotropic molecular polarizability at the transfer frequency $cK = (e_A^* - e_A)\hbar$. The matrix v_r^{eff} has the features of a local perturbation,³⁷ since for each value of \mathbf{k} only three different row vectors $|\mathbf{k}, \text{rad}\rangle_j$ ($j=1,2,3$) appear [together with the corresponding column vectors ${}_j\langle \mathbf{k}, \text{rad}|$] in Eq. (4.28). As a result, the following 3×3 system of equations for the Green's function $\ddot{G}_{ij}(\mathbf{k})$ is obtained, using Eqs. (4.14), (4.26), and (4.28):

$$\ddot{G}_{ij}(\mathbf{k}) = \ddot{G}_{ij}^0(\mathbf{k}) - \hbar\alpha [\ddot{G}^0(\mathbf{k}) \ddot{G}(\mathbf{k})]_{ij}, \quad (4.30)$$

where the abbreviated $\ddot{G}(\mathbf{k})$ is a 3×3 matrix. The formal solution of Eq. (4.30) reads

$$\ddot{G}_{ij}(\mathbf{k}) = (\hbar\alpha)^{-1} \{ \delta_{ij} - [1 + \hbar\alpha \ddot{G}^0(\mathbf{k})]_{ij}^{-1} \}, \quad (4.31)$$

which is an exact result.

In what follows, we assume that the A - B separation distance greatly exceeds the lattice constant ($R \gg a$). Under this condition, only radiation modes (\mathbf{k}, G) with $k \ll 2\pi/a$ contribute significantly to the electromagnetic tensor θ_{ij} .⁴⁰ As shown in Appendix B, for $k \ll 2\pi/a$ the Green's function $\ddot{G}_{ij}(\mathbf{k})$ is given by Eq. (B8). Consequently, Eq. (4.13) for θ_{ij} becomes

$$\theta_{ij} = \epsilon_r^{-1} [(\epsilon_r + 2)/3]^2 \theta_{ij}^{\text{vac}}(nK), \quad (4.32)$$

where

$$\epsilon_r = 1 + \frac{\alpha\rho/\epsilon_0}{1 - \alpha\rho/3\epsilon_0}, \quad (4.33)$$

$$n \equiv n' + in'' = \epsilon_r^{1/2} \quad (n'' > 0), \quad (4.34)$$

$$\theta_{ij}^{\text{vac}}(y) = \frac{y^3 e^{iyR}}{4\pi\epsilon_0} \left[(\delta_{ij} - 3\hat{R}_i \hat{R}_j) \left(\frac{1}{y^3 R^3} - \frac{i}{y^2 R^2} \right) - (\delta_{ij} - \hat{R}_i \hat{R}_j) \frac{1}{yR} \right], \quad (4.35)$$

$\hat{\mathbf{R}} = \mathbf{R}/R$ being a unit vector. Thus, as one might anticipate for separations $R \gg a$, the medium effects are described entirely in terms of the frequency-dependent macroscopic relative permittivity, $\epsilon_r(cK) \equiv \epsilon_r = \epsilon/\epsilon_0$, satisfying the Clausius-Mossotti relation. The coupling tensor (4.32) accommodates the screening contribution ϵ_r^{-1} and the local field factor $(\epsilon_r + 2)/3$, as well as the tensor $\theta_{ij}^{\text{vac}}(y)$. The latter has the structure of the vacuum electromagnetic tensor, its argument $y = nK$ being scaled by the complex refractive index n .

C. Transfer rate

Since the transition matrix element $\langle F|T^{(2)}|I\rangle$ is expressible in terms of θ_{ij} through the tensor product (2.23), one finds, from Eq. (4.32),

$$|\langle F|T^{(2)}|I\rangle|^2 = \left| \frac{\mu_A \mu_B}{3n^2} \left[\frac{n^2 + 2}{3} \right]^2 \right|^2 A e^{-2n''KR}, \quad (4.36)$$

where

$$A = \left[\frac{3}{4\pi\epsilon_0} \right]^2 \left| \eta_3 \left[\frac{1}{R^3} - \frac{inK}{R^2} \right] - \eta_1 \frac{n^2 K^2}{R} \right|^2 \quad (4.37)$$

$$= \left[\frac{3}{4\pi\epsilon_0} \right]^2 \left\{ \frac{\eta_3^2}{R^6} + 2\eta_3^2 n'' \frac{K}{R^5} + [\eta_3^2 |n|^2 - 2\eta_1 \eta_3 (n'^2 - n''^2)] \frac{K^2}{R^4} + 2\eta_1 \eta_3 n'' |n|^2 \frac{K^3}{R^3} + \eta_1^2 |n|^4 \frac{K^4}{R^2} \right\}, \quad (4.38)$$

with η_p being the orientational factors defined in terms of the units vectors through

$$\eta_p = \hat{\mu}_A \cdot \hat{\mu}_B - p(\hat{\mu}_A \cdot \hat{\mathbf{R}})(\hat{\mu}_B \cdot \hat{\mathbf{R}}) \quad (p = 1, 3). \quad (4.39)$$

The transfer rate is then determined by the above equations for $|\langle F|T^{(2)}|I \rangle|^2$ together with Eq. (2.14), subject to the standard averaging over the initial and summation over the final substates of the guest molecules.^{14,23} The latter averaging and summation smoothes the contribution by the δ function, as finite spectral widths for the guest molecules are implicitly assumed. The near- and far-zone limits read⁴¹

$$|\langle F|T^{(2)}|I \rangle|^2 = \left| \frac{1}{n^2} \left[\frac{n^2+2}{3} \right]^2 \right|^2 \left[\frac{\mu_A \mu_B}{4\pi\epsilon_0} \right]^2 \frac{\eta_3^2}{R^6}, \quad |n|KR \ll 1, \quad (4.40)$$

$$|\langle F|T^{(2)}|i \rangle|^2 = \left| \frac{n^2+2}{3} \right|^4 \left[\frac{\mu_A \mu_B}{4\pi\epsilon_0} \right]^2 \frac{\eta_1^2 K^4}{R^2} e^{-2n''KR}, \quad |n|KR \gg 1. \quad (4.41)$$

Finally, the corresponding orientationally averaged results are obtained by replacing the function A in Eq. (4.36) by its mean value, giving

$$\bar{A} = 2(4\pi\epsilon_0)^{-2} \left[3/R^6 + 6n''K/R^5 + (n'^2 + 5n''^2)K^2/R^4 + 2n''|n|^2 K^3/R^3 + |n|^4 K^4/R^2 \right]. \quad (4.42)$$

For a unit refractive index ($n=1$), the above reduces to the familiar function $A(K, R)$ for the transfer of energy between molecules in a vacuum.¹²

V. DISCUSSION

It follows from Eq. (4.36) that, besides the screening and local field contributions, medium effects are manifest in the appearance of the exponential decay factor and in the refractivity dependence of the energy transfer function A . The exponential factor arises only in the case of an absorbing medium ($n'' > 0$) and takes account of the associated energy losses. That solves the problem of potentially infinite ensemble rates, as discussed previously.¹⁴ However, in contrast to our earlier study, the appearance of this factor is an intrinsic feature of the present approach based on microscopic many-body QED. Specifically, the factor is associated with the quenching of bath polaritons mediating the energy transfer, the role of the dissipative subsystem being played by molecules of the medium having a dense excitation spectrum. Each photon mode is coupled with a quasicontinuum of molecular states, so that decay ensures when resonance ap-

plies.⁴² In this way, the bath plays a role of both energy mediator and quencher.

It can readily be shown that the exponential factor of Eq. (4.36) reduces to that obtained previously on a phenomenological basis, $\exp(-\sigma_{\text{host}}\rho)$, given that the density of the medium is low enough to ensure linear dependence of the complex refractive index on the number density ρ . Specifically, we have

$$2n''K \approx K\rho \text{Im}\alpha/\epsilon_0 = \sigma_{\text{host}}\rho, \quad (5.1)$$

with

$$\sigma_{\text{host}} = (\pi K/\epsilon_0) \sum_{\gamma} \mu_{\gamma}^2 \delta(\hbar cK - \hbar\omega_{\gamma}) \quad (5.2)$$

being the isotropic absorption cross section per host molecule.

It is interesting to consider in detail the nature of the modifications of the energy transfer function A by the medium, since these are features which previous theories have been unable to accommodate. It is evident from Eq. (4.38) that such modifications are due to both the real and imaginary parts of the complex refractive index n . For $n'' \neq 0$, the transfer function (4.38) contains not only the usual even powers of R , but odd ones (R^{-3} and R^{-5}) as well. However, since normally $n'' \ll n'$, the terms with the odd powers of R contribute to a much lesser extent than the even ones, each of the latter becoming significant over a different range of distances R . The R^{-6} term is dominant in the near zone, $|n|KR \ll 1$, the R^{-2} term prevails in the far zone, $|n|KR \gg 1$, and the R^{-4} term features in the critical retardation region where $R \sim (|n|K)^{-1}$. The near- and far-zone results are given explicitly by Eqs. (4.40) and (4.41). For real values of n , the refractivity effect of the medium reduces in the near zone to that which is familiar from the theory of radiationless energy transfer.²³ The far-zone equation (4.41) represents the classical R^{-2} result for two-stage (emission and reabsorption) radiative energy transfer, the exponential factor expressing the probability for the photon not to be absorbed between the sites A and B . Here the refractivity preexponential factor may, in a sense, be construed as originating from the combined effect of the $n[(n^2+2)/3]^2$ dependence of the emission rate of A and the $n^{-1}[(n^2+2)/3]^2$ dependence of the absorption by B .

The present theory exploits the polariton concept for the bath representation. Although that may seem to be rather specific because of the embodiment of lattice symmetry, the rate of guest-guest energy transfer which is at issue is not sensitive to the possible lack of this symmetry in most important situations. That includes in particular the case where the spectral widths of the host electronic lines, $\hbar\Delta\omega_{\text{host}}$, exceed the characteristic energy V_{host} of

the resonant coupling between the neighboring host molecules. In this situation the electronic excitations of the medium are incoherent,²³ which implies nonsensitivity to the possible introduction of some orientational or energetic disorder in the bath molecules. Specifically, our assumption that these host molecules are characterized by isotropic molecular polarizabilities can approximately represent a situation where nonisotropic molecules are randomly oriented in their sites. Translational symmetry may have essential importance for the opposite (coherent exciton) case, which arises when $V_{\text{host}} > \hbar\Delta\omega_{\text{host}}$ and which thus generally requires low temperatures. The coherent excitons are well represented in terms of spatially delocalized waves of excitation, and any destruction of the translational order results in the scattering of such waves (i.e., losses of the exciton coherence). However, if the energy transferred between the guests species is far removed from any exciton resonances of the medium, the coherence does not play a significant role and the transfer rate is once again insensitive to the lack of translational regularity. To summarize, the employment of the polaron concept is not central to the theory; rather, it is a matter of convenience, offering calculational advantages by imposing lattice symmetry.

It is to be noted that the theory is based on the widely accepted description of energy transfer in terms of rates. In other words, the overall multistep migration process occurs through uncorrelated acts of incoherent energy transfer between the molecules of the system. Hence the coherent transfer manifest at $R < R_c$ (R_c being the characteristic coherence distance) is out of the scope of the present study.^{43,44} Typically $R_c \sim 20 \text{ \AA}$, and so the restriction $R > R_c$ is also consistent with the adoption of the electric dipole approximation: The latter is appropriate for separations R exceeding characteristic molecular dimensions $d \sim 10 \text{ \AA}$. However, in contrast to the standard theory of radiationless energy transfer,^{23,24} in which the same short-range constraints are normally imposed, the present approach has no restrictions at large (far-zone) intermolecular separations.

To conclude, a comprehensive many-body formulation of microscopic QED has been developed to take systematic account of the influence of the medium in dipole-dipole resonance energy transfer. The theory is applicable to a wide range of both ordered and disordered materials, describing the transfer of electronic energy between chromophoric entities in organic, inorganic, and biological system. The results correctly reflect the local field effects and intrinsically embody an exponential decay factor modifying the transfer rate, including the divergent R^{-2} term. Accordingly, the problem associated with potentially infinite ensemble rates has been solved from first principles. Finally, our theory establishes the precise details of the interplay in condensed matter between what have traditionally been regarded as radiationless and radiative energy transfer.

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APPENDIX A: CONDITION ON THE TRANSFORM MATRIX

Consider the $2L \times 2L$ matrix defined by

$$\varphi(A, \tilde{A}^\dagger) = |A, \tilde{A}^\dagger\rangle\langle A^\dagger, \tilde{A}| - \langle A^\dagger, \tilde{A}|(A, \tilde{A}^\dagger)|, \quad (\text{A1})$$

the matrix vectors $|A^\dagger, \tilde{A}\rangle$ and $\langle A, \tilde{A}^\dagger|$ being defined in obvious analogy to $|A, \tilde{A}^\dagger\rangle$ and $\langle A^\dagger, \tilde{A}|$ of Eqs. (3.21) and (3.22). By exploiting the Bose commutation relations (3.16) and (3.17), it is clear that $\varphi(A, \tilde{A}^\dagger)$ takes the diagonal form

$$\varphi(A, \tilde{A}^\dagger) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \equiv Q, \quad (\text{A2})$$

the off-diagonal terms vanishing through commutation of the corresponding $|A^\dagger, \tilde{A}\rangle$ and $\langle A, \tilde{A}^\dagger|$ terms in (A1). The same condition applies after transformation to the new set of operators; from (3.35) and (3.36), we have

$$S\varphi(A, \tilde{A}^\dagger)'S^* = \varphi(P, \tilde{P}^\dagger) = Q. \quad (\text{A3})$$

In this way one obtains the required relation (3.44).

APPENDIX B: CALCULATION OF THE GREEN'S FUNCTION $\ddot{G}_{ij}^0(\mathbf{k})$

To begin, the zero-order Green's function present in Eq. (4.31) is given by

$$\begin{aligned} \ddot{G}_{ij}^0(\mathbf{k}) &\equiv \langle \mathbf{k}, \text{rad} | \ddot{G}^0 | \mathbf{k}, \text{rad} \rangle_j \\ &= \frac{\rho}{\hbar\epsilon_0} \sum_{\mathbf{G}} \frac{|\mathbf{k} + \mathbf{G}|^2 \delta_{ij} - (\mathbf{k} + \mathbf{G})_i (\mathbf{k} + \mathbf{G})_j}{(K + is')^2 - |\mathbf{k} + \mathbf{G}|^2} \\ &\quad (s' \rightarrow +0), \end{aligned} \quad (\text{B1})$$

which can be rewritten as

$$\begin{aligned} \ddot{G}_{ij}^0(\mathbf{k}) &= \frac{1}{\hbar} \sum_{\mathbf{r}_n \neq 0} \left[\frac{\rho}{N\epsilon_0} \sum_{\mathbf{k}'} \frac{k'^2 \delta_{ij} - k'_i k'_j}{(K + is')^2 - k'^2} e^{i\mathbf{k}' \cdot \mathbf{r}_n} \right] \\ &\quad \times e^{-i\mathbf{k} \cdot \mathbf{r}_n}, \end{aligned} \quad (\text{B2})$$

where the summation over \mathbf{k}' is now not restricted to the first Brillouin zone; that is, we have $\mathbf{k}' = \mathbf{k}_1 + \mathbf{G}$, \mathbf{k}_1 being a first Brillouin-zone vector. The term in the square brackets of Eq. (B2) can readily be identified as the retarded vacuum dipole interaction tensor, and the $\mathbf{r}_n = 0$ term is therefore omitted to exclude contributions associated with self-interactions.

In what follows, consideration will be restricted to the case of small $k \equiv |\mathbf{k}| \ll 2\pi/a$. That is sufficient to account for energy transfer over distances R , which substantially exceed the lattice constant a . Replacing the summations over \mathbf{r}_n and \mathbf{k}' in Eq. (B2) by integrations and excluding the δ -function contribution at the origin $\mathbf{r} = 0$, one obtains, from the resulting double Fourier integral,

$$\begin{aligned} \ddot{G}_{ij}^0(\mathbf{k}) &= \frac{\rho}{3\hbar\epsilon_0} \frac{[2(K + is')^2 + k^2] \delta_{ij} - 3k_i k_j}{(K + is')^2 - k^2} \\ &\quad (k \ll 2\pi/a). \end{aligned} \quad (\text{B3})$$

Denoting

$$a = 1 + \frac{\alpha\rho}{3\epsilon_0} \frac{2(K + is')^2 + k^2}{(K + is')^2 - k^2}, \quad (\text{B4})$$

$$b = \frac{\alpha\rho}{\epsilon_0} \frac{k^2}{(K + is')^2 - k^2}, \quad (\text{B5})$$

one has

$$[1 + \hbar\alpha\ddot{G}^0(\mathbf{k})]_{ij} = a\delta_{ij} - b\hat{k}_i\hat{k}_j \quad (\text{B6})$$

and thus

$$[1 + \hbar\alpha\ddot{G}^0(\mathbf{k})]_{ij}^{-1} = \frac{1}{a} \left[\delta_{ij} + \frac{b}{a-b} \hat{k}_i\hat{k}_j \right]. \quad (\text{B7})$$

Substituting Eqs. (B4) and (B5) into (B7) and the result into Eq. (4.31), one finds after performing some algebraic rearrangements the required Green's function

$$\ddot{G}_{ij}(\mathbf{k}) = \frac{\rho}{3\hbar\epsilon_0} \frac{1}{\epsilon_r} \left[\frac{\epsilon_r + 2}{3} \right]^2 \left[\frac{[2\epsilon_r(K + is')^2 + k^2]\delta_{ij} - 3k_ik_j}{\epsilon_r(K + is')^2 - k^2} - \frac{2\alpha\rho}{3\epsilon_0} \delta_{ij} \right] \quad (k \ll 2\pi/a), \quad (\text{B8})$$

where the relative dielectric permittivity ϵ_r is given by Eq. (4.33) of the main text.

Finally, substituting the above Green's function into Eq. (4.13) and replacing the sum over \mathbf{k} by an integral over a continuous variable, one ultimately arrives at Eq. (4.32), the result for the dielectric tensor θ_{ij} . Note that retention of the infinitesimal is' of Eq. (B8), in order to displace the poles of the integrand from the real k axis, is only entirely necessary for a medium which is lossless ($\text{Im}\epsilon_r = 0$).

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⁴⁰That can be proved either mathematically, by inspecting Eq. (B8) of Appendix B together with Eq. (4.13) for θ_{ij} or from physical arguments by applying the wave-vector-distance uncertainty principle $\Delta k R \sim 1$ for a virtual polariton mediating the guest-guest energy transfer.

⁴¹In Eqs. (4.40) and (4.41), it is implicitly assumed that the orientational factors n_1 and n_3 are nonzero, as is normally the case.

⁴²To this extent, the depiction of polariton quenching by an intrinsic molecular capture, as in the present model, is very much in contrast to its more familiar association with a photon escape through the crystal boundaries (Ref. 27). In the

latter case each mode of molecular excitations \mathbf{k} is coupled to the photon continuum.

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