

Intermolecular forces, spontaneous emission, and superradiance in a dielectric medium: Polariton-mediated interactions

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A reduced equation of motion that describes the excited-state dynamics of interacting two-level impurity molecules in a dielectric host crystal is derived starting from a microscopic model for the total system. Our theory generalizes the derivation of the conventional superradiance master equation for molecules in vacuum; the role of photons in the conventional theory is played by polaritons (mixed crystal-radiation excitations) in our approach. Our final equation thus contains dispersive and superradiant polariton-mediated intermolecular interactions. The effect of the dielectric host is completely contained within a rescaling of these interactions with the transverse dielectric function $\epsilon(\omega)$ of the crystal taken at the impurity's transition frequency. Our theory yields all local field and screening factors for both the dispersive and the dissipative couplings from a single, unified starting point. Known scaling laws for the spontaneous-emission rate and the instantaneous dipole-dipole interaction are extended to the frequency region where the dispersion of $\epsilon(\omega)$ is important.

I. INTRODUCTION

Currently, many optical experiments are carried out on molecules in a condensed phase; examples of typical systems are disordered crystals, molecules embedded in glasses, or solutions.¹⁻³ The excited-state dynamics of the molecules studied is affected by the host medium. The simplest manifestations of the interaction with the medium are spectral shifts and line broadening, resulting from homogeneous and inhomogeneous dephasing processes. In addition, quantities that appear to be intrinsic to the molecules under study may be altered by the environment. For example, the spontaneous decay rate of an excited molecule in a dielectric host differs from the rate for the same molecule in vacuum.⁴⁻⁶ Many experimental and theoretical studies have been dedicated to the effect of the environment on the radiative lifetime. Apart from molecules in a bulk dielectric, systems that have received much attention in this context include molecules (dipoles) near a dielectric or metallic surface,⁷ in high- Q cavities,⁸ in or near small dielectric particles,^{9,10} or in an artificial superlattice with a periodicity in the dielectric constant.¹¹ The basic principle underlying all these examples is that the density of radiation modes is changed by the presence of a medium and (or) by restriction of the geometry. Because the spontaneous decay rate of a molecular excited state into radiation modes is proportional to this density of states (Fermi golden rule), it is clear that spontaneous emission may be enhanced or inhibited by changing the environment. A total absence of spontaneous emission may, in principle, occur if in certain frequency intervals no radiation modes exist at all (band gaps).^{11,12} Not only radiative decay rates, but also intermolecular interactions are sensitive to the molecular environment.^{3,12} A well-known consequence of this is that the resonant Förster rate of energy transfer between two molecules depends on the index of refraction of the host medium.^{4,6} The role of

the medium on cooperative radiative phenomena occurring in optically dense systems (e.g., superradiance), is less well studied. In view of the current interest in linear and nonlinear optical properties of molecular systems in condensed phases, it is extremely valuable to give a microscopic treatment of all these medium effects. This may be done by deriving a reduced equation of motion for the excited-state dynamics of the molecules starting from a microscopic model that includes the host. Not only would such an approach clarify the microscopic origin of various medium effects, the reduced equation of motion could also serve to properly incorporate these effects in the description of nonlinear optical processes in a dielectric host.

The excited-state dynamics of a collection of two-level molecules is described in an elegant way by the superradiance master equation derived by many authors.¹³ This equation describes the evolution of a general operator working in the Hilbert space of the molecules and contains the effects of single-molecule radiative decay, the Lamb shift, dispersive intermolecular interactions, and superradiant interactions. The equation can be used to describe a great variety of optical phenomena, e.g., photon echoes and superradiance.¹⁴ Usually the equation is derived for molecules in vacuum, starting from the multipolar Hamiltonian, in which no direct intermolecular interactions are present;¹⁵ retarded interactions are instead mediated by exchange of photons between two molecules. For molecules in a dielectric medium, heuristic arguments may be used to include the effect of the medium dielectric constant on the coefficients (the interactions and decay rates) occurring in the master equation (see Sec. V). In this paper we show how this can be done from first principles, where we even include the frequency dispersion of the dielectric function. The model system that we consider consists of a collection of two-level molecules (impurities) randomly substituted in an atomic

crystal. The basic idea behind our calculation is that the impurities do not interact through exchange of photons, but rather through exchange of exciton-polaritons, which are the proper elementary excitations (mixtures of photons and excitons) of the host crystal.^{16,17} We recover the conventional master equation with interactions and decay rates which are scaled by the *frequency-dependent* dielectric function of the host crystal. This dielectric function is obtained within the same calculation, namely, through the dispersion relation of the polaritons. The unique feature of our approach is that it yields from a unified microscopic starting point in an unambiguous way all local-field factors and screening factors which scale the interactions and decay rates.

The outline of this paper is as follows. In Sec. II we further specify the model, define pertinent quantities, and present the Hamiltonian. The form of the polaritons for the pure host crystal is derived in Sec. III. In this derivation, we *do not* neglect umklapp processes, which leads to an infinite number of polariton branches in the first Brillouin zone (in contrast to the usual two branches when umklapp is neglected¹⁶.) These polaritons are used in Sec. IV to derive the master equation for a general operator acting in the Hilbert space of the impurities. Finally, we discuss our results in Sec. V. Some technical details of the derivation presented in Sec. IV are contained in Appendixes A and B.

II. MODEL AND HAMILTONIAN

We consider an infinite simple-cubic crystal with sites occupied by atoms. One atomic *sp* transition of frequency Ω is considered explicitly. The transition dipole moments between the atomic ground state and the three degenerate excited states form an orthogonal set and have magnitude μ . On a small fraction of the lattice sites, the atoms have been replaced by two-level impurity molecules with transition frequency Ω_0 and transition dipole μ_α (α labels the impurities.). The μ_α are not necessarily oriented in the same direction. We work within the multipolar Hamiltonian¹⁵ in the dipole approximation, in which the fully retarded interaction between the radiation field and a particle with transition dipole operator $\hat{\mu}$ at point \mathbf{r} is given by $-\hat{\mu} \cdot \hat{\mathbf{D}}(\mathbf{r})$, with $\hat{\mathbf{D}}(\mathbf{r})$ the transverse electric displacement field at position \mathbf{r} . Furthermore, there are no direct Coulomb forces between particles in this Hamiltonian; all interactions are instead mediated by exchange of photons. The total Hamiltonian for our system may now be written

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{pol}} + \hat{H}_{\text{int}}. \quad (2.1)$$

The first term in this equation represents the electronic energy of the impurity molecules

$$\hat{H}_{\text{mol}} = \hbar\Omega_0 \sum_{\alpha} \hat{b}_{\alpha}^{\dagger} \hat{b}_{\alpha}, \quad (2.2)$$

where $\hat{b}_{\alpha}^{\dagger}$ (\hat{b}_{α}) is the creation (annihilation) operator for an excitation on molecule α . These operators obey the Pauli anticommutation relations

$$[\hat{b}_{\alpha}^{\dagger}, \hat{b}_{\beta}]_{+} = \delta_{\alpha\beta} + 2\hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta} (1 - \delta_{\alpha\beta}). \quad (2.3)$$

The second term in Eq. (2.1) consists of three contributions: the electronic energy of the atoms in the crystal, the Hamiltonian of the radiation field, and the atom-radiation interactions. We have

$$\begin{aligned} \hat{H}_{\text{pol}} = & \hbar\Omega \sum_m \sum_{i=1}^3 \hat{B}_{mi}^{\dagger} \hat{B}_{mi} \\ & + \hbar \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\lambda=1}^2 \omega_{\mathbf{k}+\mathbf{G}} \hat{a}_{\mathbf{k}+\mathbf{G}\lambda}^{\dagger} \hat{a}_{\mathbf{k}+\mathbf{G}\lambda} - \sum_m \hat{\mu}_m \cdot \hat{\mathbf{D}}(\mathbf{r}_m). \end{aligned} \quad (2.4)$$

The index i labels the three Cartesian axes and \hat{B}_{mi}^{\dagger} (\hat{B}_{mi}) is the creation (annihilation) operator for the excited state on atom m with transition dipole in the i direction. The operator \hat{B}_{mi}^{\dagger} , when acting on the ground state of atom m , yields the excited state of this atom with transition dipole in the i direction and gives zero when acting on any other state. The operator \hat{B}_{mi} gives the ground state of atom m when acting on its excited state with transition dipole in the i direction and yields zero when acting on any other state. In the second term of Eq. (2.4), $\hat{a}_{\mathbf{k}+\mathbf{G}\lambda}^{\dagger}$ and $\hat{a}_{\mathbf{k}+\mathbf{G}\lambda}$ denote the usual creation and annihilation operators for a photon of wave vector $\mathbf{k}+\mathbf{G}$ and transverse polarization λ . They obey the Bose commutation relations $[\hat{a}_{\mathbf{k}+\mathbf{G}\lambda}, \hat{a}_{\mathbf{k}'+\mathbf{G}'\lambda'}^{\dagger}] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{G}\mathbf{G}'} \delta_{\lambda\lambda'}$. Throughout this paper, \mathbf{k} runs over the first Brillouin zone only, unless explicitly stated otherwise, and \mathbf{G} runs over the reciprocal lattice. $\omega_{\mathbf{k}+\mathbf{G}} \equiv |\mathbf{k}+\mathbf{G}|c$ is the vacuum photon dispersion relation. In the last term of Eq. (2.4), $\hat{\mu}_m$ denotes the dipole operator of atom m given by

$$\hat{\mu}_m = \sum_i \mu \mathbf{e}_i (\hat{B}_{mi} + \hat{B}_{mi}^{\dagger}), \quad (2.5)$$

with \mathbf{e}_i the unit vector along the i axis, and the displacement field $\hat{\mathbf{D}}(\mathbf{r})$ at position \mathbf{r} is written in second quantization as¹⁵

$$\begin{aligned} \hat{\mathbf{D}}(\mathbf{r}) = & i \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\lambda=1}^2 \left[\frac{2\pi\hbar\omega_{\mathbf{k}+\mathbf{G}}}{V} \right]^{1/2} \\ & \times [\hat{a}_{\mathbf{k}+\mathbf{G}\lambda} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \\ & - \hat{a}_{\mathbf{k}+\mathbf{G}\lambda}^{\dagger} e^{-i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}] \mathbf{e}_{\mathbf{k}+\mathbf{G}\lambda}. \end{aligned} \quad (2.6)$$

Here V is the volume of the quantization box of the radiation, which is taken equal to the crystal volume and will eventually be sent to infinity, and the unit polarization vectors $\mathbf{e}_{\mathbf{k}+\mathbf{G}\lambda}$ are chosen real and such that $\mathbf{e}_{-\mathbf{k}-\mathbf{G}\lambda} = \mathbf{e}_{\mathbf{k}+\mathbf{G}\lambda}$. Finally, the last term in the total Hamiltonian Eq. (2.1) is the interaction between the radiation field and the impurities, which reads

$$\hat{H}_{\text{int}} = - \sum_{\alpha} \hat{\mu}_{\alpha} \cdot \hat{\mathbf{D}}(\mathbf{r}_{\alpha}), \quad (2.7)$$

with $\mu_{\alpha} = \mu_{\alpha} (\hat{b}_{\alpha} + \hat{b}_{\alpha}^{\dagger})$ the dipole operator of the α th impurity.

The reason to combine the three terms in Eq. (2.4) to one term in the total Hamiltonian is that, as is well known, for the perfect crystal it is possible to transform from the radiation and atomic creation and annihilation

operators to a set of polariton creation and annihilation operators that diagonalize \hat{H}_{pol} .^{16,17} We then obtain

$$\hat{H}_{\text{pol}} = \hbar \sum_{\mathbf{k}, \nu} \omega_{\mathbf{k}\nu} \hat{S}_{\mathbf{k}\nu}^\dagger \hat{S}_{\mathbf{k}\nu}, \quad (2.8)$$

where $\hat{S}_{\mathbf{k}\nu}^\dagger$ ($\hat{S}_{\mathbf{k}\nu}$) is the creation (annihilation) operator of a polariton with wave vector \mathbf{k} in branch ν with frequency $\omega_{\mathbf{k}\nu}$. These operators obey the Bose commutation relations

$$[\hat{S}_{\mathbf{k}\nu}, \hat{S}_{\mathbf{k}'\nu'}^\dagger] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\nu\nu'}. \quad (2.9)$$

The transformation to these new operators and the dispersion relation for the polaritons will be worked out explicitly in Sec. III. We note that there are two approximations involved in using Eqs. (2.8) and (2.9). First, the atoms in our system do not occupy a perfect lattice, but, strictly speaking, holes should be considered at sites where impurities have been substituted. These holes would result in scattering of the perfect crystal polaritons, giving them a finite lifetime. We will not consider this perturbation, assuming that the density of impurities is low enough to make its effect negligible. Second, the use of Bose commutation relations is a common approximation which is valid for a low degree of excitation in the atomic crystal and suffices to treat the linear optics of the crystal.¹⁶⁻¹⁸ Even though we may be interested in the nonlinear optics of the impurities, we will assume that the nonlinear optics of the atomic system is weak enough to be neglected, so that we may safely use Eq. (2.9).

The introduction of polaritons is a matter of convenience. If we write the interaction Eq. (2.7) between the impurities and the radiation field in terms of polariton operators, and we use the form Eq. (2.8) for \hat{H}_{pol} , the total Hamiltonian Eq. (2.1) is expressed in terms of impurity and polariton creation and annihilation operators. It is then no longer necessary to address the atomic system and the radiation field explicitly; their coupled dynamics has been formally solved by introducing the polaritons. We may thus describe the complete excited-state dynamics of the impurities by considering them as interacting with the polariton field. At this point we note a strong analogy of our starting Hamiltonian and the Hamiltonian for molecules in vacuum.¹³ Both contain completely equivalent unperturbed molecular parts. Also, in both cases there is a contribution of the same formal form which describes the elementary excitations of the space surrounding the molecules: the photons in vacuum case and the polaritons in ours. Finally, both Hamiltonians contain an interaction between the molecules and these elementary excitations, which can also formally be brought in the same form (Sec. IV). The two Hamiltonians differ in that the dispersion relation and the coefficients occurring in the interaction with the impurities are much more complicated for polaritons than for photons.

III. POLARITON TRANSFORMATION

In this section, we derive the polariton transformation for the perfect atomic crystal. Because of the technical character of this derivation, it is useful to point out its

importance. The transformation is needed to obtain the dispersion relation ($\omega_{\mathbf{k}\nu}$) of the polaritons and to translate the interaction Eq. (2.7) in terms of polariton operators. Hopfield derived this transformation within the minimal coupling ($\mathbf{p} \cdot \mathbf{A}$) Hamiltonian¹⁵ for the crystal and the radiation field.¹⁶ We prefer to work with the multipolar Hamiltonian, however, because there the interaction between the impurities and the polaritons takes a simple form, as it only occurs through the radiation field component of the polaritons. In the minimal coupling Hamiltonian, on the other hand, there is also an interaction between the impurities and the exciton component of the polaritons, arising from the Coulomb interactions between the impurities and the crystal atoms. Although the polariton problem within the multipolar Hamiltonian has also been addressed in the literature, results have so far been limited to the calculation of only the dispersion relation for some of the branches.¹⁹ A complete dispersion diagram *and* the explicit derivation of all of the transformation coefficients between the polariton operators and the atomic and radiation field operators will be given in this section. The main results are comprised within the expressions Eqs. (3.6), (3.11), (3.20), and (3.23) and are depicted in the Figs. 1 and 2. The reader who is willing to take these results for granted is advised to skip this section.

Our starting point is the multipolar Hamiltonian for the perfect atomic crystal and the radiation field as given in Eq. (2.4). Since in an infinite crystal it is natural to work in momentum space, we transform the exciton operators as follows:

$$\hat{B}_{\mathbf{k}+\mathbf{G}i} = \frac{1}{\sqrt{N}} \sum_m \hat{B}_{mi} e^{-i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}_m}, \quad (3.1a)$$

$$\hat{B}_{\mathbf{k}+\mathbf{G}\lambda} = \sum_i (e_{\mathbf{k}+\mathbf{G}\lambda})_i \hat{B}_{\mathbf{k}+\mathbf{G}i}, \quad (3.1b)$$

where $(e_{\mathbf{k}+\mathbf{G}\lambda})_i$ is the i th Cartesian component of $\mathbf{e}_{\mathbf{k}+\mathbf{G}\lambda}$

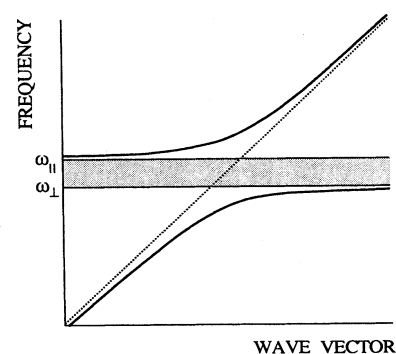


FIG. 1. Typical polariton dispersion curves in the optical region (thick solid curves). The diagonal line represents the pure photon dispersion curve ($\omega_k = kc$). The shaded region between the transverse (ω_{\perp}) and longitudinal (ω_{\parallel}) crystal exciton frequencies is the stopgap, where no polariton modes exist.

and N is the number of lattice sites, which is to be sent to infinity together with the volume such that $N/V \equiv \rho$ is the average atomic density. We also define $\hat{B}_{\mathbf{k}+\mathbf{G}\lambda}$ for

$$\hat{H}_0 = \hbar\Omega \sum_{\mathbf{k}} \sum_{\lambda=1}^3 \hat{B}_{\mathbf{k}\lambda}^\dagger \hat{B}_{\mathbf{k}\lambda} + \hbar \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\lambda=1}^2 \omega_{\mathbf{k}+\mathbf{G}} \hat{a}_{\mathbf{k}+\mathbf{G}\lambda}^\dagger \hat{a}_{\mathbf{k}+\mathbf{G}\lambda} - i \sum_{\mathbf{k}} \sum_{\mathbf{G}} \sum_{\lambda=1}^2 \sum_{\lambda'=1}^3 \hbar C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') (\hat{B}_{-\mathbf{k}\lambda'} \hat{a}_{\mathbf{k}+\mathbf{G}\lambda} - \hat{B}_{\mathbf{k}\lambda} \hat{a}_{\mathbf{k}+\mathbf{G}\lambda}^\dagger + \hat{B}_{\mathbf{k}\lambda}^\dagger \hat{a}_{\mathbf{k}+\mathbf{G}\lambda} - \hat{B}_{-\mathbf{k}\lambda'}^\dagger \hat{a}_{\mathbf{k}+\mathbf{G}\lambda}^\dagger), \quad (3.2)$$

where

$$\hbar C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') \equiv (2\pi\hbar\rho\omega_{\mathbf{k}+\mathbf{G}})^{1/2} \mu \mathbf{e}_{\mathbf{k}+\mathbf{G}\lambda} \cdot \mathbf{e}_{\mathbf{k}\lambda'}. \quad (3.3)$$

As usual we will assume Bose commutators for the excitation operators in \mathbf{k} space

$$[\hat{B}_{\mathbf{k}\lambda}, \hat{B}_{\mathbf{k}'\lambda'}^\dagger] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\lambda\lambda'}, \quad (3.4)$$

which is a good approximation for crystals with a low degree of excitation.^{16,17} Since the photon operators also obey Bose commutation relations, the Hamiltonian Eq. (3.2) is harmonic and may be diagonalized, i.e., brought in the form of Eq. (2.8).²⁰ The eigenmodes are the polaritons. In order to find the polaritons we evaluate the Heisenberg equations of motion for the photon and the exciton operators (the time dependence is implicit)

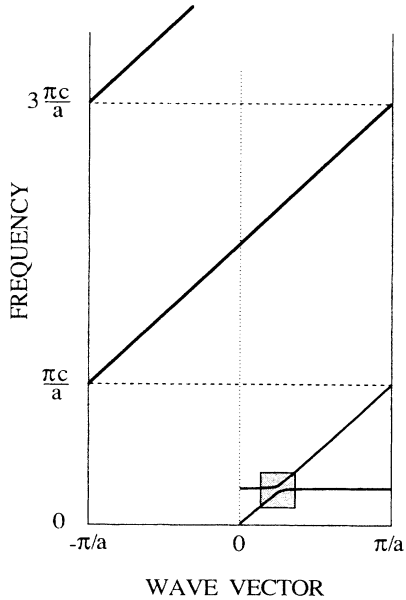


FIG. 2. Schematic representation of the polariton dispersion diagram including the very high frequency polaritons discussed in the text. For convenience, a one-dimensional crystal is assumed, with lattice constant a . All curves should also be reflected with respect to $k=0$ (dotted line) to obtain the full diagram; these additional curves have been omitted for clarity. The most familiar part of this diagram is indicated by the shaded box and is shown in more detail in Fig. 1. To facilitate the presentation, an unrealistically large value for the atomic transition frequency Ω has been used.

$\lambda=3$, corresponding to the longitudinal polarization: $\mathbf{e}_{\mathbf{k}+\mathbf{G}3}$ is parallel to $\mathbf{k}+\mathbf{G}$. Using Eqs. (2.4)–(2.6) and realizing that $\hat{B}_{\mathbf{k}+\mathbf{G}i} = \hat{B}_{\mathbf{k}i}$, we find

$$\frac{1}{i} \frac{d}{dt} \hat{a}_{\mathbf{k}+\mathbf{G}\lambda} = -\omega_{\mathbf{k}+\mathbf{G}} \hat{a}_{\mathbf{k}+\mathbf{G}\lambda} - i \sum_{\lambda'=1}^3 C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') (\hat{B}_{\mathbf{k}\lambda'} + \hat{B}_{-\mathbf{k}\lambda'}^\dagger), \quad (3.5a)$$

$$\frac{1}{i} \frac{d}{dt} \hat{B}_{\mathbf{k}\lambda'} = -\Omega \hat{B}_{\mathbf{k}\lambda'} + i \sum_{\mathbf{G}} \sum_{\lambda=1}^2 C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') \times (\hat{a}_{\mathbf{k}+\mathbf{G}\lambda} - \hat{a}_{-\mathbf{k}-\mathbf{G}\lambda}^\dagger). \quad (3.5b)$$

When this set is supplemented with the equations for $\hat{a}_{-\mathbf{k}-\mathbf{G}\lambda}^\dagger$ and $\hat{B}_{-\mathbf{k}\lambda'}^\dagger$ [which are easily obtained from Eqs. (3.5) by Hermitian conjugation], we obtain for every \mathbf{k} a closed (infinite) set of linear equations coupling $\hat{a}_{\mathbf{k}+\mathbf{G}\lambda}$, $\hat{a}_{-\mathbf{k}-\mathbf{G}\lambda}^\dagger$, $\hat{B}_{\mathbf{k}\lambda'}$, and $\hat{B}_{-\mathbf{k}\lambda'}^\dagger$ (all \mathbf{G} ; $\lambda=1,2$; $\lambda'=1,2,3$). The set is infinitely dimensional, because umklapp processes ($\mathbf{G} \neq 0$ photon operators) are not neglected. We note that in Hopfield's original derivation of polaritons from the minimal coupling $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian, these processes were neglected.¹⁶ When working with the multipolar Hamiltonian, the high wave-vector photons are essential to mediate the interatomic interactions. In the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian, on the other hand, the umklapp processes are only necessary to account for retardation in the interatomic interactions. This point has been addressed in the literature,^{21–23} but a polariton transformation accounting for umklapp has not been worked out in detail.

In analogy with Hopfield,^{16,22} we search for polariton annihilation operators

$$\hat{\xi}_{\mathbf{k}\nu} = \sum_{\mathbf{G}} \sum_{\lambda=1}^2 [w_{\mathbf{G}\lambda\nu}(\mathbf{k}) \hat{a}_{\mathbf{k}+\mathbf{G}\lambda} + y_{\mathbf{G}\lambda\nu}(\mathbf{k}) \hat{a}_{-\mathbf{k}-\mathbf{G}\lambda}^\dagger] + \sum_{\lambda'=1}^3 [x_{\lambda'\nu}(\mathbf{k}) \hat{B}_{\mathbf{k}\lambda'} + z_{\lambda'\nu}(\mathbf{k}) \hat{B}_{-\mathbf{k}\lambda'}^\dagger], \quad (3.6)$$

obeying

$$\frac{1}{i} \frac{d}{dt} \hat{\xi}_{\mathbf{k}\nu} = -\omega_{\mathbf{k}\nu} \hat{\xi}_{\mathbf{k}\nu}. \quad (3.7)$$

Equations (3.6) and (3.7) together with the Heisenberg equations of motion (3.5) define an infinitely dimensional eigenvalue problem. The polariton dispersion $\omega_{\mathbf{k}\nu}$ follows from the associated secular equation, whereas the eigenvectors yield the polariton transformation coefficients w , x , y , and z . Before going into the details of actually solv-

ing the problem, it is useful to mention two general results.²⁰ (i) The condition that the polaritons obey Bose commutation relations (or alternatively, that the polariton transformation is canonical) yields a *normalization relation* for the transformation coefficients

$$\sum_{\mathbf{G}} \sum_{\lambda=1}^2 [|w_{\mathbf{G}\lambda\nu}(\mathbf{k})|^2 - |y_{\mathbf{G}\lambda\nu}(\mathbf{k})|^2] + \sum_{\lambda=1}^3 [|x_{\lambda\nu}(\mathbf{k})|^2 - |z_{\lambda\nu}(\mathbf{k})|^2] = 1. \quad (3.8)$$

(ii) It can be shown quite generally that the *inverse transformation* to Eq. (3.6) reads

$$\hat{a}_{\mathbf{k}+\mathbf{G}\lambda} = \sum_{\nu} [w_{\mathbf{G}\lambda\nu}^*(\mathbf{k}) \hat{\xi}_{\mathbf{k}\nu} - y_{\mathbf{G}\lambda\nu}(\mathbf{k}) \hat{\xi}_{-\mathbf{k}\nu}^{\dagger}], \quad (3.9a)$$

$$\hat{B}_{\mathbf{k}\lambda} = \sum_{\nu} [x_{\lambda\nu}^*(\mathbf{k}) \hat{\xi}_{\mathbf{k}\nu} - z_{\lambda\nu}(\mathbf{k}) \hat{\xi}_{-\mathbf{k}\nu}^{\dagger}], \quad (3.9b)$$

with the asterisk denoting complex conjugation. The complete eigenvalue problem to be solved reads explicitly

$$(\omega_{\mathbf{k}\nu} - \omega_{\mathbf{k}+\mathbf{G}}) w_{\mathbf{G}\lambda\nu}(\mathbf{k}) + i \sum_{\lambda'=1}^3 C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') [x_{\lambda'\nu}(\mathbf{k}) - z_{\lambda'\nu}(\mathbf{k})] = 0, \quad (3.10a)$$

$$(\omega_{\mathbf{k}\nu} + \omega_{\mathbf{k}+\mathbf{G}}) y_{\mathbf{G}\lambda\nu}(\mathbf{k}) - i \sum_{\lambda'=1}^3 C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') [x_{\lambda'\nu}(\mathbf{k}) - z_{\lambda'\nu}(\mathbf{k})] = 0, \quad (3.10b)$$

$$-i \sum_{\mathbf{G}} \sum_{\lambda=1}^2 C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') [w_{\mathbf{G}\lambda\nu}(\mathbf{k}) + y_{\mathbf{G}\lambda\nu}(\mathbf{k})] + (\omega_{\mathbf{k}\nu} - \Omega) x_{\lambda'\nu}(\mathbf{k}) = 0, \quad (3.10c)$$

$$-i \sum_{\mathbf{G}} \sum_{\lambda=1}^2 C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') [w_{\mathbf{G}\lambda\nu}(\mathbf{k}) + y_{\mathbf{G}\lambda\nu}(\mathbf{k})] + (\omega_{\mathbf{k}\nu} + \Omega) z_{\lambda'\nu}(\mathbf{k}) = 0. \quad (3.10d)$$

The first two equations hold for any \mathbf{G} and for $\lambda=1$ and $\lambda=2$, whereas the last two hold for $\lambda'=1, 2, 3$. The coefficients w and y can easily be eliminated from the problem by solving formally for them from Eqs. (3.10a) and (3.10b) and substituting the solutions into the last two equations. We then obtain a 6×6 eigenvalue problem, which (of course) still contains the complete physics; the complexity is buried in an interatomic interaction that depends on the frequency $\omega_{\mathbf{k}\nu}$.¹⁹ We shall not follow this approach right away because it eventually poses great algebraic difficulties related to dipole sums over the lattice (see below). Instead, we use physical intuition to determine the majority of the polariton branches. We start by making the observation that if there were no photon-exciton coupling [$C(\mathbf{k}, \mathbf{G}, \lambda, \lambda')=0$], we would have polariton branches with frequency $\omega_{\mathbf{k}\nu} = \omega_{\mathbf{k}+\mathbf{G}}$ (pure photons). For $\mathbf{G} \neq 0$, this frequency is orders of magnitude higher than the exciton frequency Ω , so that even if the photon-exciton coupling is switched on, the pure photons for $\mathbf{G} \neq 0$ must still be good approximations to polaritons. In fact, if we neglect Ω with respect to $\omega_{\mathbf{k}+\mathbf{G}}$ ($\mathbf{G} \neq 0$), we find consistent solutions to Eqs. (3.10) of

which we will label the branches as $\nu \equiv (\mathbf{G}' \neq 0, \lambda' = 1, 2)$. These solutions have frequencies

$$\omega_{\mathbf{k}\nu} = \omega_{\mathbf{k}+\mathbf{G}'} \quad (3.11a)$$

and transformation coefficients

$$w_{\mathbf{G}\lambda\nu}(\mathbf{k}) = \delta_{\mathbf{G}\mathbf{G}'} \delta_{\lambda\lambda'}, \quad (3.11b)$$

$$y_{\mathbf{G}\lambda\nu}(\mathbf{k}) = 0, \quad (3.11b)$$

$$x_{\lambda\nu}(\mathbf{k}) = z_{\lambda\nu}(\mathbf{k}) = i \left[\frac{2\pi\rho}{\hbar\omega_{\mathbf{k}+\mathbf{G}'}} \right]^{1/2} \mu \mathbf{e}_{\mathbf{k}+\mathbf{G}'\lambda'} \cdot \mathbf{e}_{\mathbf{k}\lambda},$$

which obey the normalization condition Eq. (3.8). We will accept Eqs. (3.11) as a good approximation to polariton branches with "high energy" (i.e., branches which are associated with umklapp processes). Of course, it is possible to search for systematic improvement of this approximation by using perturbation theory in $\Omega/\omega_{\mathbf{k}+\mathbf{G}'}$, but we will not do this here.

Now there are five more polariton branches left to determine. These are possibly strong combinations of the two (transverse) first Brillouin zone photon branches and the three (two transverse, one longitudinal) exciton branches, with a further small contribution of higher Brillouin zone photons. For these polariton branches Ω may not necessarily be neglected with respect to $\omega_{\mathbf{k}\nu}$, so that a more careful solution to the eigenvalue problem must be sought. We first eliminate the coefficients $w_{\mathbf{G}\lambda\nu}$ and $y_{\mathbf{G}\lambda\nu}$ for $\mathbf{G} \neq 0$ from Eqs. (3.10)

$$(\omega - \omega_{\mathbf{k}+\mathbf{G}}) w_{\mathbf{G}\lambda\nu}(\mathbf{k}) = -(\omega + \omega_{\mathbf{k}+\mathbf{G}}) y_{\mathbf{G}\lambda\nu}(\mathbf{k})$$

$$= -i \sum_{\lambda'=1}^3 C(\mathbf{k}, \mathbf{G}, \lambda, \lambda') \times [x_{\lambda'\nu}(\mathbf{k}) - z_{\lambda'\nu}(\mathbf{k})]. \quad (3.12)$$

Substituting Eq. (3.12) back into Eqs. (3.10) yields the following 10×10 eigenvalue problem:

$$(\omega_{\mathbf{k}\nu} - \omega_{\mathbf{k}}) w_{0\lambda\nu}(\mathbf{k}) + iC(k) [x_{\lambda\nu}(\mathbf{k}) - z_{\lambda\nu}(\mathbf{k})] = 0, \quad (3.13a)$$

$$(\omega_{\mathbf{k}\nu} + \omega_{\mathbf{k}}) y_{0\lambda\nu}(\mathbf{k}) - iC(k) [x_{\lambda\nu}(\mathbf{k}) - z_{\lambda\nu}(\mathbf{k})] = 0, \quad (3.13b)$$

$$-iC(k) [w_{0\lambda\nu}(\mathbf{k}) + y_{0\lambda\nu}(\mathbf{k})] + (\omega_{\mathbf{k}\nu} - \Omega) x_{\lambda\nu}(\mathbf{k}) - \sum_{\lambda'=1}^3 R_{\lambda\lambda'}(\mathbf{k}, \omega_{\mathbf{k}\nu}) [x_{\lambda'\nu}(\mathbf{k}) - z_{\lambda'\nu}(\mathbf{k})] = 0, \quad (3.13c)$$

$$-iC(k) [w_{0\lambda\nu}(\mathbf{k}) + y_{0\lambda\nu}(\mathbf{k})] + (\omega_{\mathbf{k}\nu} + \Omega) z_{\lambda\nu}(\mathbf{k}) - \sum_{\lambda'=1}^3 R_{\lambda\lambda'}(\mathbf{k}, \omega_{\mathbf{k}\nu}) [x_{\lambda'\nu}(\mathbf{k}) - z_{\lambda'\nu}(\mathbf{k})] = 0. \quad (3.13d)$$

The first two of these equations hold for $\lambda=1$ and $\lambda=2$; the last two hold for $\lambda=1, 2$, and 3 , where the coefficients w and y must be set zero for $\lambda=3$. $C(k)$ is defined as

$$C(k) = \left[\frac{2\pi\rho\omega_{\mathbf{k}}}{\hbar} \right]^{1/2} \mu, \quad (3.14)$$

and $R_{\lambda\lambda'}(\mathbf{k}, \omega)$ is the frequency-dependent effective interatomic interaction which is mediated by photons outside the first Brillouin zone. It is defined by

$$R_{\lambda\lambda'}(\mathbf{k}, \omega) = \sum_{\mathbf{G} (\neq 0)} \sum_{\lambda''=1}^2 \frac{2\omega_{\mathbf{k}+\mathbf{G}}}{\omega^2 - \omega_{\mathbf{k}+\mathbf{G}}^2} C(\mathbf{k}, \mathbf{G}, \lambda'', \lambda) \times C(\mathbf{k}, \mathbf{G}, \lambda'', \lambda'), \quad (3.15a)$$

which, using Eq. (3.3), may be written in tensor notation as $R_{\lambda\lambda'}(\mathbf{k}, \omega) = \mathbf{e}_{\mathbf{k}\lambda} \cdot \vec{\mathbf{R}}(\mathbf{k}, \omega) \cdot \mathbf{e}_{\mathbf{k}\lambda'}$, with

$$\vec{\mathbf{R}}(\mathbf{k}, \omega) = \frac{4\pi\rho\mu^2}{\hbar} \sum_{\mathbf{G} (\neq 0)} \frac{(\mathbf{k}+\mathbf{G})^2 - (\mathbf{k}+\mathbf{G})(\mathbf{k}+\mathbf{G})}{(\omega/c)^2 - (\mathbf{k}+\mathbf{G})^2}. \quad (3.15b)$$

The summand in Eq. (3.15b) is closely related to the Fourier transform of the retarded dipole field tensor $\vec{\mathbf{F}}(\mathbf{r}, \omega)$,^{24,25} so that the sum over all but the central point in the reciprocal lattice yields a difference between the lattice [$\vec{\mathbf{F}}_l(\mathbf{k}, \omega)$] and continuum [$\vec{\mathbf{F}}_c(\mathbf{k}, \omega)$] Fourier transforms of $\vec{\mathbf{F}}(\mathbf{r}, \omega)$

$$\vec{\mathbf{R}}(\mathbf{k}, \omega) = -\frac{\rho\mu^2}{\hbar} \left[-\frac{8\pi}{3} + \text{Re}[\vec{\mathbf{F}}_l(\mathbf{k}, \omega) - \vec{\mathbf{F}}_c(\mathbf{k}, \omega)] \right], \quad (3.16)$$

with

$$\vec{\mathbf{F}}_l(\mathbf{k}, \omega) = \frac{1}{\rho} \sum_{m (\neq 0)} \vec{\mathbf{F}}(\mathbf{r}_m, \omega) e^{-i\mathbf{k}\cdot\mathbf{r}_m}, \quad (3.17a)$$

$$\vec{\mathbf{F}}_c(\mathbf{k}, \omega) = \int d\mathbf{r} \vec{\mathbf{F}}(\mathbf{r}, \omega) e^{-i\mathbf{k}\cdot\mathbf{r}}, \quad (3.17b)$$

$$\vec{\mathbf{F}}(\mathbf{r}, \omega) \left\{ \left[3 - 3\frac{i\omega r}{c} - \left[\frac{\omega r}{c} \right]^2 \right] \frac{\mathbf{r}\mathbf{r}}{r^2} - \left[1 - \frac{i\omega r}{c} - \left[\frac{\omega r}{c} \right]^2 \right] \vec{\mathbf{1}} \right\} \frac{e^{i\omega r/c}}{r^3}. \quad (3.17c)$$

The real part should be taken in Eq. (3.16) because $\vec{\mathbf{R}}(\mathbf{k}, \omega)$ as defined in Eq. (3.15b) is real, even though ω contains an infinitesimal imaginary part ($\omega \rightarrow \omega + i0^+$) in order to obtain a retarded, instead of an advanced, interaction. In principle, this $i0^+$ generates imaginary parts in the summation of Eq. (3.15b) proportional to $\delta(\omega/c \pm |\mathbf{k}+\mathbf{G}|)$. Since, however, we are in this specific part of the calculation only interested in low-frequency

polaritons ($\omega_{\mathbf{k}_v}/c$ within the first Brillouin zone), and the sum excludes $\mathbf{G}=\mathbf{0}$, $\vec{\mathbf{R}}(\mathbf{k}, \omega)$ is real. We also note that in deriving Eq. (3.16), real self interactions (Lamb shifts) have been neglected; they are assumed to be accounted for in the exciton frequency Ω .

The interaction $\vec{\mathbf{R}}(\mathbf{k}, \omega)$ is, in general, a nondiagonal matrix with a complicated \mathbf{k} and ω dependence, so that the eigenvalue problem Eq. (3.13) is, in general, too difficult to solve analytically. The problem may be simplified appreciably by neglecting the off-diagonal components of $\vec{\mathbf{R}}(\mathbf{k}, \omega)$,²¹ assuming a diagonal matrix with transverse components $R_{\perp}(\mathbf{k}, \omega)$ and longitudinal component $R_{\parallel}(\mathbf{k}, \omega)$. The 10×10 eigenvalue problem then separates into two (identical) 4×4 problems for the transverse polaritons and one 2×2 problem for the longitudinal polariton (exciton). The neglect of off-diagonal $\vec{\mathbf{R}}$ components is justified for small (optical) \mathbf{k} and ω , where the polariton transformation is the least trivial (strong mixture of photons and excitons). In this region, we may approximate²⁶

$$\vec{\mathbf{F}}_l(\mathbf{k}, \omega) - \vec{\mathbf{F}}_c(\mathbf{k}, \omega) \approx - \int_0^{R_c} \vec{\mathbf{F}}(\mathbf{r}, \omega) e^{-i\mathbf{k}\cdot\mathbf{r}}, \quad (3.18a)$$

with R_c of the order of the lattice constant ($4\pi R_c^3 \rho / 3 \approx 1$). In this approximation we find (along the lines used in Ref. 27)

$$\begin{aligned} \text{Re}[\vec{\mathbf{F}}_l(\mathbf{k}, \omega) - \vec{\mathbf{F}}_c(\mathbf{k}, \omega)]_{\parallel} \\ = \frac{4\pi}{3} \left[\frac{1}{5}(kR_c)^2 - \left[\frac{\omega R_c}{c} \right]^2 \right], \end{aligned} \quad (3.18b)$$

$$\begin{aligned} \text{Re}[\vec{\mathbf{F}}_l(\mathbf{k}, \omega) - \vec{\mathbf{F}}_c(\mathbf{k}, \omega)]_{\perp} \\ = \frac{4\pi}{3} \left[-\frac{1}{10}(kR_c)^2 - \left[\frac{\omega R_c}{c} \right]^2 \right], \end{aligned} \quad (3.18c)$$

up to order $(kR_c)^4$ and $(\omega R_c/c)^4$. An important and often used further approximation is to neglect $\vec{\mathbf{F}}_l(\mathbf{k}, \omega) - \vec{\mathbf{F}}_c(\mathbf{k}, \omega)$ completely, which is justified for optical wave vectors and frequencies as can be seen from Eqs. (3.18b) and (3.18c). This leads to $\vec{\mathbf{R}}(\mathbf{k}, \omega) \approx 4\pi\beta\Omega/3$, with $\beta \equiv 2\rho\mu^2/\hbar\Omega$ (as introduced by Hopfield) a parameter that is small compared to unity for typical cases.

For the transverse polaritons we have the following eigenvalue problem

$$\begin{pmatrix} \omega_{\mathbf{k}_v} - \omega_k & 0 & iC(k) & -iC(k) \\ 0 & \omega_{\mathbf{k}_v} + \omega_k & -iC(k) & iC(k) \\ -iC(k) & -iC(k) & \omega_{\mathbf{k}_v} - \Omega - R_{\perp}(\mathbf{k}, \omega) & R_{\perp}(\mathbf{k}, \omega) \\ -iC(k) & -iC(k) & -R_{\perp}(\mathbf{k}, \omega) & \omega_{\mathbf{k}_v} + \Omega + R_{\perp}(\mathbf{k}, \omega) \end{pmatrix} \begin{pmatrix} w_{0\lambda_v}(\mathbf{k}) \\ y_{0\lambda_v}(\mathbf{k}) \\ x_{\lambda_v}(\mathbf{k}) \\ z_{\lambda_v}(\mathbf{k}) \end{pmatrix} = 0, \quad (3.19)$$

for which the secular equation reads:

$$\begin{aligned} (\omega_k^2 - \omega_{\mathbf{k}_v}^2) [\Omega^2 (1 - 4\pi\beta) + 2\Omega R_{\perp}(\mathbf{k}, \omega_{\mathbf{k}_v}) - \omega_{\mathbf{k}_v}^2] \\ = 4\pi\beta\Omega^2 \omega_{\mathbf{k}_v}^2. \end{aligned} \quad (3.20)$$

In the approximation $\vec{\mathbf{R}}(\mathbf{k}, \omega) = 4\pi\beta\Omega/3$ this dispersion relation is a quartic equation for $\omega_{\mathbf{k}_v}$, yielding the usual upper and lower polariton branches separated by the stopgap^{16,28} ranging from the transverse dipolar exciton frequency

$$\omega_{\perp} = \Omega(1 - 4\pi\beta/3)^{1/2}, \quad (3.21a)$$

to the longitudinal one

$$\omega_{\parallel} = \Omega(1 + 8\pi\beta/3)^{1/2}, \quad (3.21b)$$

(Fig. 1). Inclusion of $\text{Re}(\vec{F}_l - \vec{F}_c)$ in $\vec{R}(\mathbf{k}, \omega)$ accounts for effective exciton mass effects and for retardation in the interatomic interactions.^{21,26} In the limit $c \rightarrow \infty$, Eq. (3.20) yields the dispersion curve for the transverse dipolar excitons. The frequency- and wave-vector-dependent transverse dielectric function follows directly from Eq. (3.20) and reads ($\omega \equiv \omega_{\mathbf{k}\nu}$)

$$\epsilon(\mathbf{k}, \omega) \equiv \frac{\omega_k^2}{\omega^2} = 1 + \frac{4\pi\beta\Omega^2}{-\omega^2 + \Omega^2(1 - 4\pi\beta) + 2\Omega R_{\perp}(\mathbf{k}, \omega)}. \quad (3.22)$$

We note that the denominator in Eq. (3.22) is real, implying that the polariton has an infinite radiative lifetime. This conclusion is in agreement with the existing literature.^{16,29,30} We have earlier^{25,27} derived an expression for $\epsilon(\mathbf{k}, \omega)$ that very closely resembles Eq. (3.22) combined with Eq. (3.16), except that ω^2 is replaced by $\omega^2 + i\gamma\omega$ (with γ the single-atom radiative decay rate) and that the real part is not taken in Eq. (3.16). A careful analysis of our previous result shows that the imaginary part in $[\vec{F}_l(\mathbf{k}, \omega) - \vec{F}_c(\mathbf{k}, \omega)]_{\perp}$ cancels the extra decay term, so that there, too, an infinite polariton lifetime is predicted.

Finally, we give the polariton transformation coefficients that follow from Eqs. (3.19) and (3.12). The branch label ν takes on four values, given by $\nu = (b, \lambda')$, with $b = \text{upper or lower}$ and $\lambda' = 1 \text{ or } 2$. At frequency $\omega = \omega_{\mathbf{k}\nu}$ we have

$$w_{0\lambda\nu}(\mathbf{k}) = \frac{(\omega + \omega_k)(\omega^2 - \Omega^2 - 2R_{\perp}(\mathbf{k}, \omega)\Omega)}{2(\omega_k \omega)^{1/2} [(\omega^2 - \Omega^2 - 2R_{\perp}(\mathbf{k}, \omega)\Omega)^2 + 4\pi\beta\Omega^2\omega_k^2]^{1/2}} \delta_{\lambda\lambda'}, \quad (3.23a)$$

$$y_{0\lambda\nu}(\mathbf{k}) = \frac{\omega_k - \omega}{\omega_k + \omega} w_{0\lambda\nu}(\mathbf{k}), \quad (3.23b)$$

$$x_{\lambda\nu}(\mathbf{k}) = i \left[\frac{\pi\beta\Omega}{\omega} \right]^{1/2} \frac{(\omega + \Omega)\omega_k}{[(\omega^2 - \Omega^2 - 2R_{\perp}(\mathbf{k}, \omega)\Omega)^2 + 4\pi\beta\Omega^2\omega_k^2]^{1/2}} \delta_{\lambda\lambda'}, \quad (3.23c)$$

$$z_{\lambda\nu}(\mathbf{k}) = \frac{\omega - \Omega}{\omega + \Omega} x_{\lambda\nu}(\mathbf{k}), \quad (3.23d)$$

$$w_{\mathbf{G}\lambda\nu}(\mathbf{k}) = \left[\frac{\pi\beta\Omega^3}{\omega} \right]^{1/2} \frac{2\omega_k C(\mathbf{k}, \mathbf{G}, \lambda, \lambda')}{(\omega - \omega_{\mathbf{k}+\mathbf{G}}) [(\omega^2 - \Omega^2 - 2R_{\perp}(\mathbf{k}, \omega)\Omega)^2 + 4\pi\beta\Omega^2\omega_k^2]^{1/2}} \quad (\mathbf{G} \neq \mathbf{0}), \quad (3.23e)$$

$$y_{\mathbf{G}\lambda\nu}(\mathbf{k}) = \frac{\omega_{\mathbf{k}+\mathbf{G}} - \omega}{\omega_{\mathbf{k}+\mathbf{G}} + \omega} w_{\mathbf{G}\lambda\nu}(\mathbf{k}) \quad (\mathbf{G} \neq \mathbf{0}). \quad (3.23f)$$

The normalization condition Eq. (3.8) is obeyed exactly if only the first four of the above coefficients are taken into account. The error in the normalization, which is thus due to the contributions of the small $\mathbf{G} \neq \mathbf{0}$ coefficients given in Eqs. (3.23e) and (3.23f), can be shown to equal

$$\Delta(\mathbf{k}, \omega) = - \frac{4\pi\beta\Omega^3 \omega_k^2 \partial R_{\perp}(\mathbf{k}, \omega) / \partial \omega}{\omega \{ [\omega^2 - \Omega^2 - 2\Omega R_{\perp}(\mathbf{k}, \omega)]^2 + 4\pi\beta\Omega^2 \omega_k^2 \}}. \quad (3.24)$$

An estimate for the derivative of $R_{\perp}(\mathbf{k}, \omega)$ with respect to ω in the optical region may be obtained from Eq. (3.18c) in combination with Eq. (3.16). We then find $\Delta(\mathbf{k}, \omega) < 4\pi\beta(\Omega R_c / c)^2$, which is much smaller than unity for realistic cases. We believe that also for (\mathbf{k}, ω) outside the optical region, the derivative of $R_{\perp}(\mathbf{k}, \omega)$ is sufficiently well behaved to justify neglecting $\Delta(\mathbf{k}, \omega)$. The transformation coefficients are only determined up to an overall phase factor, which has no physical significance and has been chosen unity for all branches. Equations (3.11), (3.20), and (3.23) together define all

transverse polariton branches. The total dispersion diagram is depicted in Fig. 2.

At this point, we would like to summarize and explain once again our method of solving for the polaritons. We separated the derivation into the approximate solution for high-energy polaritons [Eqs. (3.11)] and the solution of the four polariton branches with low frequencies [Eqs. (3.20) and (3.23)]. It should be stressed that the method used to obtain the latter solutions is, in principle, also suited to treat the high-frequency branches because the formal solution Eq. (3.12) is valid for all frequencies. Therefore, apart from the separation into transverse and longitudinal parts, the dispersion relation [Eq. (3.20)] is valid for all branches, i.e., solving this equation for $\omega_{\mathbf{k}\nu}$ should yield all polariton branches in Fig. 2. This is a consequence of the frequency dependence of $\vec{F}_l - \vec{F}_c$. Since, however, $\vec{F}_l - \vec{F}_c$ is, in general, a very complicated function of frequency and wave vector, the only roots that can actually be found easily from Eq. (3.20) are the lowest ones, for which $\vec{F}_l - \vec{F}_c$ may be neglected, leading to the familiar quartic dispersion relation. Fortunately,

the remaining polaritons, which are intimately connected with umklapp processes, are easily found using physical intuition, as was shown above. A different way of solving the polariton problem would have consisted of eliminating all ω and y coefficients as in Eq. (3.12), i.e., also for $\mathbf{G}=\mathbf{0}$. This method has already been mentioned above. A 6×6 eigenvalue problem is obtained with an interatomic interaction like in Eq. (3.15b), except that the sum now extends over the complete reciprocal lattice. This interaction is therefore just the lattice Fourier transform [Eq. (3.17a)] of the retarded dipole-dipole interaction.¹⁹ Again neglecting off-diagonal matrix elements in the interaction, the problem separates into three 2×2 problems

$$\begin{pmatrix} \omega_{k\nu} - \Omega - R_{\parallel}(\mathbf{k}, \omega_{k\nu}) & R_{\parallel}(\mathbf{k}, \omega_{k\nu}) \\ -R_{\parallel}(\mathbf{k}, \omega_{k\nu}) & \omega_{k\nu} + \Omega + R_{\parallel}(\mathbf{k}, \omega_{k\nu}) \end{pmatrix} \begin{pmatrix} x_{3\nu}(\mathbf{k}) \\ z_{3\nu}(\mathbf{k}) \end{pmatrix} = 0. \quad (3.25)$$

Using, again, the approximation $\vec{R}(\mathbf{k}, \omega) = 4\pi\beta\Omega/3$, the usual longitudinal dipolar exciton frequency ω_{\parallel} , as defined in Eq. (3.21b), is found from the secular equation. Since we will neglect the role of longitudinal polaritons in the remainder of this paper, we do not derive the transformation coefficients for this branch.

IV. MASTER EQUATION FOR IMPURITY OPERATORS

Having found the polaritons for the atomic crystal, we will now return to the excited-state dynamics of the impurities substituted into the crystal. Our derivation of the master equation that couples different impurity operators follows to a large extent the derivation of the conventional master equation for molecules in vacuum as given by Lehmborg.^{13(b)} The difference is that in our case the molecules interact with the transverse polariton field instead of the photon field. This causes a considerable technical complication, but, as we will see, yields the dependence of the dynamics on the dielectric function of the crystal in a natural way. Our starting point is the Hamiltonian Eq. (2.1) expressed in polariton operators. \hat{H}_{pol} then takes by definition, the form of Eq. (2.8) and, using Eq. (2.6) and the inverse polariton transformation Eq. (3.9), it is easily shown that

$$\hat{H}_{\text{int}} = -\frac{i\hbar}{\sqrt{V}} \sum_{\alpha} \sum_{\mathbf{k}} \sum_{\nu} [K_{k\nu}(\alpha) \hat{\xi}_{k\nu} - K_{k\nu}^*(\alpha) \hat{\xi}_{k\nu}^{\dagger}] \hat{s}_{\alpha}, \quad (4.1)$$

where the \mathbf{k} summation extends over the first Brillouin zone and ν runs over all branches except the longitudinal one. In Eq. (4.1) we have defined

$$\hat{s}_{\alpha} = \hat{b}_{\alpha} + \hat{b}_{\alpha}^{\dagger} \quad (4.2a)$$

$$K_{k\nu}(\alpha) = \sum_{\mathbf{G}} \sum_{\lambda=1}^2 \left[\frac{2\pi\omega_{\mathbf{k}+\mathbf{G}}}{\hbar} \right]^{1/2} [w_{\mathbf{G}\lambda\nu}^*(\mathbf{k}) + y_{\mathbf{G}\lambda\nu}^*(\mathbf{k})] \times (\boldsymbol{\mu}_{\alpha} \cdot \mathbf{e}_{\mathbf{k}+\mathbf{G}\lambda}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}_{\alpha}}. \quad (4.2b)$$

with frequency-dependent interactions. In order to obtain the quartic transverse polariton dispersion relation, part of this frequency dependence has to be known very well, forcing one to address the details of retarded dipole sums on the lattice.^{19,30-32} Our way of solving, namely, by explicitly keeping the central Brillouin zone photons in the calculation, avoids this problem and allows us to neglect the frequency dependence of the effective interaction.

For completeness, we will finally discuss the longitudinal exciton branch. The eigenvalue problem to be solved reads

Substituting Eqs. (3.23) into Eq. (4.2b), we find for the four lowest polariton branches [$\nu=(b, \lambda')$]

$$K_{k\nu}(\alpha) = \left[\frac{2\pi}{\hbar} \right]^{1/2} \frac{\omega_{\mathbf{k}}}{\omega^{1/2}} \times \frac{(\omega^2 - \Omega^2)(\boldsymbol{\mu}_{\alpha} \cdot \mathbf{e}_{\mathbf{k}\lambda'}) e^{i\mathbf{k}\cdot\mathbf{r}_{\alpha}}}{\{[\omega^2 - \Omega^2 - 2\Omega R_{\parallel}(\mathbf{k}, \omega)]^2 + 4\pi\beta\Omega^2\omega_{\mathbf{k}}^2\}^{1/2}}, \quad (4.3a)$$

where ω stands for $\omega_{k\nu}$ (see Appendix A). Analogously, we get for the higher branches [$\nu=(\mathbf{G}', \lambda')$] with the aid of Eqs. (3.11)

$$K_{k\nu}(\alpha) = \left[\frac{2\pi\omega_{\mathbf{k}+\mathbf{G}'}}{\hbar} \right]^{1/2} (\boldsymbol{\mu}_{\alpha} \cdot \mathbf{e}_{\mathbf{k}+\mathbf{G}'\lambda'}) e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}_{\alpha}}. \quad (4.3b)$$

The Heisenberg equation of motion for a polariton destruction operator reads now

$$\frac{d}{dt} \hat{\xi}_{k\nu} = -i\omega_{k\nu} \hat{\xi}_{k\nu} + \frac{1}{\sqrt{V}} \sum_{\alpha} K_{k\nu}^*(\alpha) \hat{s}_{\alpha}, \quad (4.4)$$

which has as solution

$$\hat{\xi}_{k\nu}(t) = \hat{\xi}_{k\nu}(t_0) e^{-i\omega_{k\nu}(t-t_0)} + \frac{1}{\sqrt{V}} \sum_{\alpha} \int_{t_0}^t dt' K_{k\nu}^*(\alpha) \hat{s}_{\alpha}(t') e^{-i\omega_{k\nu}(t-t')}. \quad (4.5)$$

Here t_0 is an initial time, which we will eventually choose in the infinite past. It should be kept in mind that in order for Eq. (4.5) to be the retarded solution, the frequency $\omega_{k\nu}$ under the integral actually stands for $\omega_{k\nu} - i0^+$. Now consider an arbitrary operator \hat{Q} working in the Hilbert space of the impurity molecules. Its Heisenberg equation of motion reads (with the definition $[\hat{A}, \hat{B}]_t \equiv [\hat{A}(t), \hat{B}(t)]$)

$$\begin{aligned} \frac{d}{dt} \hat{Q}(t) = & i\Omega_0 \sum_{\alpha} [\hat{b}_{\alpha}^{\dagger} \hat{b}_{\alpha}, \hat{Q}]_t \\ & + \sum_{\alpha} [\hat{s}_{\alpha}, \hat{Q}]_t \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{\nu} K_{\mathbf{k}\nu}(\alpha) \hat{\xi}_{\mathbf{k}\nu}(t) \\ & - \sum_{\alpha} \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{\nu} K_{\mathbf{k}\nu}^*(\alpha) \hat{\xi}_{\mathbf{k}\nu}^{\dagger}(t) [\hat{s}_{\alpha}, \hat{Q}]_t, \quad (4.6) \end{aligned}$$

$$\begin{aligned} & \frac{1}{\sqrt{V}} \sum_{\alpha} [\hat{s}_{\alpha}, \hat{Q}]_t \sum_{\mathbf{k}} \sum_{\nu} K_{\mathbf{k}\nu}(\alpha) \hat{\xi}_{\mathbf{k}\nu}(t) \\ & = -\frac{i}{\hbar} \sum_{\alpha} [\hat{s}_{\alpha}, \hat{Q}]_t \mu_{\alpha} \cdot \hat{\mathbf{D}}_+^c(\mathbf{r}_{\alpha}, t) + \sum_{\alpha, \beta} [\hat{s}_{\alpha}, \hat{Q}]_t \int_{t_0}^t dt' \hat{s}_{\beta}(t') \frac{1}{V} \sum_{\mathbf{k}} \sum_{\nu} K_{\mathbf{k}\nu}(\alpha) K_{\mathbf{k}\nu}^*(\beta) e^{-i\omega_{\mathbf{k}\nu}(t-t')}. \quad (4.7) \end{aligned}$$

The first right-hand-side term in this equation represents the interaction of the impurities with the positive-frequency part of the pure crystal displacement field defined by

$$\mu_{\alpha} \cdot \hat{\mathbf{D}}_+^c(\mathbf{r}_{\alpha}, t) = \frac{i\hbar}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{\nu} K_{\mathbf{k}\nu}(\alpha) \hat{\xi}_{\mathbf{k}\nu}(t_0) e^{i\omega_{\mathbf{k}\nu}(t-t_0)}. \quad (4.8)$$

This field is not affected by the impurities and propagates according to the pure crystal dispersion relation. The second right-hand-side term in Eq. (4.7) contains polariton-mediated interactions between the impurities, which we will now work out in a more explicit form. In Appendix B we show that within the approximation $\vec{\mathbf{R}}(\mathbf{k}, \omega) = 4\pi\beta\Omega/3$ introduced in Sec. III,

$$\begin{aligned} & \frac{1}{V} \sum_{\mathbf{k}} \sum_{\nu} K_{\mathbf{k}\nu}(\alpha) K_{\mathbf{k}\nu}^*(\beta) e^{-i\omega_{\mathbf{k}\nu}(t-t')} \\ & = \frac{1}{\pi} \int_0^{\infty} d\omega f_{\alpha\beta}(\omega) e^{-i\omega(t-t')}, \quad (4.9a) \end{aligned}$$

with

$$\begin{aligned} f_{\alpha\beta}(\omega) = & \frac{1}{\hbar} \left[\frac{\omega}{c} \right]^3 \sqrt{\epsilon(\omega)} \left[\frac{\epsilon(\omega)+2}{3} \right]^2 \\ & \times \mu_{\alpha} \cdot \vec{\tau} \left[\sqrt{\epsilon(\omega)} \frac{\omega}{c} r_{\alpha\beta} \right] \cdot \mu_{\beta}. \quad (4.9b) \end{aligned}$$

In the ω integration in Eq. (4.9a) the polariton stopgap is excluded from the integration path. In Eq. (4.9b), $\epsilon(\omega)$ is the transverse dielectric function in the infinite effective mass approximation, which follows from Eq. (3.22) with $\vec{\mathbf{R}} = 4\pi\beta\Omega/3$:

$$\epsilon(\omega) = 1 + \frac{4\pi\beta\Omega^2}{-\omega^2 + \Omega^2 \left[1 - \frac{4\pi}{3}\beta \right]}. \quad (4.10)$$

where normal ordering with respect to the polariton operators is used. This equation does not only involve impurity operators at time t , but also polariton operators. The latter can be eliminated by substituting the solution Eq. (4.5), leading to an equation of motion involving impurity operators at all times $t' \leq t$ and polariton operators at the initial time t_0 only. We will first work out the second term in Eq. (4.6)

Furthermore,

$$\vec{\tau}(x) = \vec{u} \frac{\sin x}{x} + \vec{v} \left[\frac{\cos x}{x^2} - \frac{\sin x}{x^3} \right], \quad (4.11a)$$

with

$$\vec{u} = 1 - \mathbf{r}_{\alpha\beta} \mathbf{r}_{\alpha\beta} / r_{\alpha\beta}^2, \quad \vec{v} = 1 - 3\mathbf{r}_{\alpha\beta} \mathbf{r}_{\alpha\beta} / r_{\alpha\beta}^2 \quad (4.11b)$$

$[r_{\alpha\beta} = |\mathbf{r}_{\alpha\beta}| = |\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|]$. The appearance of the functions of $\epsilon(\omega)$ in Eq. (4.9b) is, of course, of utmost importance in this paper. As shown in Appendix B, these functions arise in a nontrivial way from (i) a change of variable from \mathbf{k} to ω (density of states) and (ii) the functional dependence of the coupling coefficient $K_{\mathbf{k}\nu}(\alpha)$ on the polariton frequency, combined with the form of $\epsilon(\omega)$.

We now substitute Eq. (4.9a) into Eq. (4.7), interchange the integrals over ω and t' , and then apply the Markov approximation¹³ to the resulting t' integral

$$\begin{aligned} & \int_{-\infty}^t dt' [\hat{b}_{\beta}(t') + \hat{b}_{\beta}^{\dagger}(t')] e^{-i(\omega-i\eta)(t-t')} \\ & \approx \frac{i\hat{b}_{\beta}(t)}{\Omega_0 - \omega + i\eta} - \frac{i\hat{b}_{\beta}^{\dagger}(t)}{\Omega_0 + \omega - i\eta}. \quad (4.12) \end{aligned}$$

Here we used our choice $t_0 \rightarrow -\infty$ and we indicated explicitly the infinitesimal imaginary part $\eta \rightarrow 0+$ of the frequency. Equation (4.12) is derived by factoring from $\hat{b}_{\beta}(t')$ and $\hat{b}_{\beta}^{\dagger}(t')$ their high-frequency components $\exp(-i\Omega_0 t')$ and $\exp(i\Omega_0 t')$, respectively, and assuming that the remaining operators vary so slowly that they can be approximated by their values at time t . We thus obtain for the second right-hand-side term of Eq. (4.6)

$$\begin{aligned} & \frac{1}{\sqrt{V}} \sum_{\alpha} [\hat{s}_{\alpha}, \hat{Q}]_t \sum_{\mathbf{k}} \sum_{\nu} K_{\mathbf{k}\nu}(\alpha) \hat{\xi}_{\mathbf{k}\nu}(t) \\ & = -\frac{i}{\hbar} \sum_{\alpha} [\hat{s}_{\alpha}, \hat{Q}]_t \mu_{\alpha} \cdot \hat{\mathbf{D}}_+^c(\mathbf{r}_{\alpha}, t) \\ & \quad + \frac{i}{\pi} \sum_{\alpha, \beta} \int_0^{\infty} d\omega f_{\alpha\beta}(\omega) [\hat{s}_{\alpha}, \hat{Q}]_t \\ & \quad \times \left[\frac{\hat{b}_{\beta}(t)}{\Omega_0 - \omega + i\eta} - \frac{\hat{b}_{\beta}^{\dagger}(t)}{\Omega_0 + \omega - i\eta} \right]. \quad (4.13) \end{aligned}$$

The third right-hand-side term of Eq. (4.6) follows easily from this by taking the Hermitian conjugate and replacing \hat{Q}^\dagger by \hat{Q} . If we ignore high-frequency operators, such as $[\hat{b}_\alpha, \hat{Q}]_t \hat{b}_\beta(t)$,^{13,14} and define $\hat{\mathbf{D}}_-^c(\mathbf{r}, t) = [\hat{\mathbf{D}}_+^c(\mathbf{r}, t)]^\dagger$, we obtain as total equation of motion for \hat{Q}

$$\begin{aligned} \frac{d\hat{Q}}{dt} = & i\Omega_0 \sum_\alpha [\hat{b}_\alpha^\dagger \hat{b}_\alpha, \hat{Q}] - \frac{i}{\hbar} \sum_\alpha [\hat{s}_\alpha, \hat{Q}] \mu_\alpha \cdot \hat{\mathbf{D}}_+^c(\mathbf{r}_\alpha, t) - \frac{i}{\hbar} \sum_\alpha \mu_\alpha \cdot \hat{\mathbf{D}}_-^c(\mathbf{r}_\alpha, t) [\hat{s}_\alpha, \hat{Q}] \\ & + \frac{i}{\pi} \sum_{\alpha, \beta} \int_0^\infty d\omega f_{\alpha\beta}(\omega) \left(\frac{[\hat{b}_\alpha^\dagger, \hat{Q}] \hat{b}_\beta}{\Omega_0 - \omega + i\eta} - \frac{[\hat{b}_\alpha, \hat{Q}] \hat{b}_\beta^\dagger}{\Omega_0 + \omega - i\eta} + \frac{\hat{b}_\beta^\dagger [\hat{b}_\alpha, \hat{Q}]}{\Omega_0 - \omega - i\eta} - \frac{\hat{b}_\beta [\hat{b}_\alpha^\dagger, \hat{Q}]}{\Omega_0 + \omega + i\eta} \right). \end{aligned} \quad (4.14)$$

Due to the Markov approximation, this equation is time local: all impurity operators are to be taken at time t .

The last term of Eq. (4.14) can still be worked out further. We use $(x - i\eta)^{-1} = \text{P}(x^{-1}) + i\pi\delta(x)$ for $\eta \rightarrow 0^+$, where P denotes the Cauchy principal part and $\delta(x)$ is the Dirac delta function. The contributions due to the delta functions are easily calculated. They represent radiative loss terms (see Sec. V) and, assuming that Ω_0 does not fall inside the polariton stopgap, we have

$$\left(\frac{d\hat{Q}}{dt} \right)_{\text{loss}} = \sum_{\alpha, \beta} \gamma_{\alpha\beta} [\hat{b}_\alpha^\dagger \hat{Q} \hat{b}_\beta - \frac{1}{2} (\hat{b}_\alpha^\dagger \hat{b}_\beta \hat{Q} + \hat{Q} \hat{b}_\alpha^\dagger \hat{b}_\beta)], \quad (4.15a)$$

with

$$\begin{aligned} \gamma_{\alpha\beta} = & 2f_{\alpha\beta}(\Omega_0) = \frac{2}{\hbar} \left(\frac{\Omega_0}{c} \right)^3 \sqrt{\epsilon(\Omega_0)} \left[\frac{\epsilon(\Omega_0) + 2}{3} \right]^2 \\ & \times \mu_\alpha \cdot \vec{\tau} \left[\sqrt{\epsilon(\Omega_0)} \frac{\Omega_0}{c} r_{\alpha\beta} \right] \cdot \mu_\beta. \end{aligned} \quad (4.15b)$$

The evaluation of the principal part contributions requires more algebra. The term for $\alpha = \beta$ is due to the Lambshift of the impurity transition frequency, which we will neglect henceforth. The terms for $\alpha \neq \beta$ represent the real (dispersive) dipole-dipole interactions between the impurities (see Sec. V). After some straightforward manipulations, we obtain

$$\begin{aligned} \left(\frac{d\hat{Q}}{dt} \right)_{\text{disp}} = & \frac{i}{\pi} \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \text{P} \int_0^\infty d\omega f_{\alpha\beta}(\omega) \left[\frac{1}{\Omega_0 - \omega} - \frac{1}{\Omega_0 + \omega} \right] \\ & \times [\hat{b}_\alpha^\dagger \hat{b}_\beta, \hat{Q}] \end{aligned} \quad (4.16)$$

(use $[\hat{b}_\alpha^\dagger, \hat{b}_\beta] = 0$ for $\alpha \neq \beta$). Since both $\epsilon(\omega)$ and $\vec{\tau}(x)$ are even functions of their arguments, the ω integration may be extended from $-\infty$ to $+\infty$, yielding

$$\left(\frac{d\hat{Q}}{dt} \right)_{\text{disp}} = \frac{i}{\pi} \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \text{P} \int_{-\infty}^\infty d\omega \frac{f_{\alpha\beta}(\omega)}{\Omega_0 - \omega} [\hat{b}_\alpha^\dagger \hat{b}_\beta, \hat{Q}]. \quad (4.17)$$

Here, not only the stopgap, but also the interval from

$-\omega_{\parallel}$ to $-\omega_{\perp}$ [cf. Eqs. (3.21)] is excluded from the ω integration. If we assume that $f_{\alpha\beta}(\omega)$ is an analytic function of ω and extend the integration path to include the stopgap regions, we may easily calculate the principal value integral in Eq. (4.17) using contour integration. To this end the tensor $\vec{\tau}$ contained in $f_{\alpha\beta}(\omega)$ must be split into parts with positive and negative imaginary exponents, for which the integration contour has to be closed in the upper and lower complex half plane, respectively. We then obtain

$$\left(\frac{d\hat{Q}}{dt} \right)_{\text{disp}} = i \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \Omega_{\alpha\beta} [\hat{b}_\alpha^\dagger \hat{b}_\beta, \hat{Q}], \quad (4.18a)$$

with

$$\begin{aligned} \Omega_{\alpha\beta} = & -\frac{1}{\hbar} \left(\frac{\Omega_0}{c} \right)^2 \sqrt{\epsilon(\Omega_0)} \left[\frac{\epsilon(\Omega_0) + 2}{3} \right]^2 \\ & \times \mu_\alpha \cdot \vec{\sigma} \left[\sqrt{\epsilon(\Omega_0)} \frac{\Omega_0}{c} r_{\alpha\beta} \right] \cdot \mu_\beta, \end{aligned} \quad (4.18b)$$

$$\vec{\sigma}(x) \equiv \vec{u} \frac{\cos x}{x} - \vec{v} \left[\frac{\sin x}{x^2} + \frac{\cos x}{x^3} \right]. \quad (4.18c)$$

The tensors \vec{u} and \vec{v} have been defined in Eq. (4.11b).

It should be noted that the assumption that $f_{\alpha\beta}(\omega)$ is analytic is an oversimplification, and that there are more poles that contribute to the integral of Eq. (4.17) than the one at $\omega = \Omega_0$. First of all, the integration path includes singularities at $\pm\omega_{\perp}$ [poles of $\epsilon(\omega)$]. Second, the integrand contains $[\epsilon(\omega)]^{1/2}$ and $[\epsilon(\omega)]^{3/2}$, which give rise to branch cuts. We will not investigate the consequences of these singularities and cuts on the integral. It should be noted, however, that the fact that the integration path hits the poles at $\pm\omega_{\perp}$ is an artifact, resulting from the approximate extension of the \mathbf{k} integral for the lower polariton branch in Appendix B to infinity. In reality, the integration stops slightly outside the stopgap, yielding a convergent integral.

The total equation of motion for the operator \hat{Q} may now be summarized as follows:

$$\begin{aligned}
\frac{d\hat{Q}}{dt} = & i\Omega_0 \sum_{\alpha} [\hat{b}_{\alpha}^{\dagger} \hat{b}_{\alpha}, \hat{Q}] + i \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \Omega_{\alpha\beta} [\hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta}, \hat{Q}] \\
& + \sum_{\alpha, \beta} \gamma_{\alpha\beta} [\hat{b}_{\alpha}^{\dagger} \hat{Q} \hat{b}_{\beta} - \frac{1}{2} (\hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta} \hat{Q} + \hat{Q} \hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta})] \\
& - \frac{i}{\hbar} \sum_{\alpha} [\hat{s}_{\alpha}, \hat{Q}] \mu_{\alpha} \cdot \hat{\mathbf{D}}^c(\mathbf{r}_{\alpha}, t) \\
& - \frac{i}{\hbar} \sum_{\alpha} \mu_{\alpha} \cdot \hat{\mathbf{D}}^c(\mathbf{r}_{\alpha}, t) [\hat{s}_{\alpha}, \hat{Q}]. \quad (4.19)
\end{aligned}$$

V. DISCUSSION

In this paper we derived an equation of motion that describes the excited-state dynamics of impurity molecules embedded in an atomic crystal. In our picture, the intermolecular interactions are mediated by the exchange of polaritons between the molecules. The main motivation for this work is to account in a fully microscopic way for the effect of the dielectric function of a host medium on the excited-state dynamics of molecules embedded in it. Our final result Eq. (4.19) is a time local equation for an arbitrary molecular operator which contains the initial condition of the polariton field as the only operator outside the Hilbert space of the impurities. As argued in Sec. II, our theory generalizes the usual description of the excited-state dynamics of a collection of molecules in vacuum which are interacting through exchange of photons. Our final equation of motion has the same structure as the vacuum superradiance master equation,¹³ the effect of the host crystal is contained within the coefficients $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$, which are scaled by the crystal's dielectric function and within the field $\hat{\mathbf{D}}^c(\mathbf{r}, t)$ with which the molecules interact. If, in order to mimic a vacuum environment, the dielectric function is set equal to unity, the conventional superradiance equation of motion is indeed exactly recovered. The equation of motion Eq. (4.19) provides a general starting point to study nonlinear optical phenomena in a condensed phase. The equation may be written in a more compact way, which better illustrates the significance of its different terms. First we note that in order to calculate observables, we are eventually only interested in expectation values of molecular operators. Taking the expectation value of Eq. (4.19) and assuming that at time t_0 the density operator for the total system is a direct product of an arbitrary molecular density operator and a coherent state³³ density operator for the polaritons, we obtain

$$\frac{d\langle \hat{Q} \rangle}{dt} = \frac{i}{\hbar} \langle \hat{H}_{\text{eff}}(t) \hat{Q} - \hat{Q} \hat{H}_{\text{eff}}^{\dagger}(t) \rangle + i \langle \Gamma \hat{Q} \rangle. \quad (5.1)$$

Here we defined a non-Hermitian time-dependent effective molecular Hamiltonian

$$\begin{aligned}
\hat{H}_{\text{eff}}(t) = & \hbar\Omega_0 \sum_{\alpha} \hat{b}_{\alpha}^{\dagger} \hat{b}_{\alpha} - \mu_{\alpha} \cdot \mathbf{D}^c(\mathbf{r}_{\alpha}, t) (\hat{b}_{\alpha} + \hat{b}_{\alpha}^{\dagger}) \\
& + \hbar \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \Omega_{\alpha\beta} \hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta} + \frac{i\hbar}{2} \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \gamma_{\alpha\beta} \hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta}, \quad (5.2a)
\end{aligned}$$

and

$$\Gamma \hat{Q} \equiv -i \sum_{\alpha, \beta} \gamma_{\alpha\beta} \hat{b}_{\alpha}^{\dagger} \hat{Q} \hat{b}_{\beta} \quad (5.2b)$$

is a term which cannot be interpreted as arising from an effective Hamiltonian. We concentrate on $\hat{H}_{\text{eff}}(t)$. Its first term is just the Hamiltonian Eq. (2.2) of the isolated impurities. The second term is the coupling between the impurities and the expectation value $\mathbf{D}^c(\mathbf{r}, t) \equiv \langle \hat{\mathbf{D}}^c_+(\mathbf{r}, t) + \hat{\mathbf{D}}^c_-(\mathbf{r}, t) \rangle$ of the total electric displacement field in the perfect crystal, i.e., without the impurities, at time t . This field is thus an external, classical quantity. It should be noted that the last two terms in Eq. (4.19) may only be combined in Eq. (5.2a) to obtain this interaction with an external field, as a consequence of the assumed initial condition for the polaritons and the use of normal ordering of the polariton operators. The interaction with the external field may be omitted completely in the special case that the polariton field is initially in the vacuum state.¹³ This situation pertains to spontaneous-emission problems. The third term in the effective Hamiltonian is a Hermitian or dispersive intermolecular interaction (as anticipated in Sec. IV). As is easily shown from Eqs. (3.17c) and (4.18b), the coefficient $\Omega_{\alpha\beta}$ is proportional to the real part of the retarded dipole-dipole interaction $\mu_{\alpha} \cdot \bar{\mathbf{F}}(\mathbf{r}_{\alpha\beta}, \Omega_0) \cdot \mu_{\beta}$, where the presence of the dielectric host is completely contained in a rescaling with functions of $\epsilon(\Omega_0)$. Finally, the last term in Eq. (5.2a) is an anti-Hermitian interaction, causing loss of energy from the impurity system. The coefficient $\gamma_{\alpha\beta}$ equals the imaginary part of the retarded dipole-dipole interaction, again with a rescaling involving $\epsilon(\Omega_0)$, and describes the superradiant intermolecular coupling for $\alpha \neq \beta$ and the single-molecule spontaneous decay rate for $\alpha = \beta$. Equation (5.1) generates a hierarchy of equations of motion for expectation values of impurity operators only, because of the special initial condition for the polaritons. We note that only in this situation the equation of motion derived in this paper (and analogous for the equation in Ref. 13) is useful for a systematic calculation of nonlinear optical processes. For other initial conditions, the operator nature of $\hat{\mathbf{D}}^c(\mathbf{r}, t)$ must be retained, forcing one to build a hierarchy which also involves mixed impurity-polariton operators.

We proceed by concentrating on the intermolecular interactions $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$. Our theory shows from a microscopic starting point how these are changed by the surrounding dielectric. It is instructive to study some special cases and to compare them with other theories. We start by considering the near-zone limit $\sqrt{\epsilon(\Omega_0)} \Omega_0 r_{\alpha\beta} / c \ll 1$. Then

$$\gamma_{\alpha\beta}^{\text{near}} = \frac{4}{3} \left[\frac{\Omega_0}{c} \right]^3 \frac{\mu_{\alpha} \cdot \mu_{\beta}}{\hbar} \sqrt{\epsilon(\Omega_0)} \left[\frac{\epsilon(\Omega_0) + 2}{3} \right]^2. \quad (5.3)$$

From this it follows, in particular, that the single-molecule spontaneous decay rate is given by

$$\gamma_{\alpha\alpha} = \gamma_{\alpha\alpha}^{\text{vac}} \sqrt{\epsilon(\Omega_0)} \left[\frac{\epsilon(\Omega_0) + 2}{3} \right]^2, \quad (5.4a)$$

with

$$\gamma_{\alpha\alpha}^{\text{vac}} = \frac{4\mu_{\alpha}^2}{3\hbar} \left[\frac{\Omega_0}{c} \right]^3 \quad (5.4b)$$

the decay rate of the same molecule in vacuum. We note that the rate Eq. (5.4a) can also be obtained using the Fermi golden rule

$$\gamma_{\alpha\alpha} = \frac{2\pi}{\hbar} |\mathcal{C}|^2 d, \quad (5.5)$$

with \mathcal{C} the coupling between the molecule and the polaritons and d the polariton density of states (in fact, as far as the single-molecule decay rate is concerned, our calculation is completely equivalent to evaluating this Fermi golden rule). In the crystal an excited molecule loses its energy by emitting polaritons rather than photons. There is considerable current interest in studying the spontaneous emission of a chromophore in a finite size environment (a solvent cluster or a microcrystallite). It is clear from our present derivation that Eq. (5.4) is expected to hold only if the cluster size is at least of the order of an optical wavelength. For smaller clusters we cannot invoke the notion of polaritons. This conclusion provides an explanation for recent supersonic beam experiments in which it was observed that the radiative lifetime of 9, 10-dichloroanthracene embedded in Ar clusters does not reach its bulk value [Eq. (5.4)] even for cluster sizes of a few thousand Ar atoms.³⁴

If the impurity transition frequency Ω_0 is far enough from all atomic transition frequencies so that the frequency dispersion of the dielectric function may be neglected [$\epsilon(\omega) = \epsilon$], we may derive the scaling in Eq. (5.4) from heuristic (macroscopic) arguments. In this derivation we also use the Fermi golden rule, but now we simply consider the impurity coupled to an effective (macroscopic) radiation field with a modified velocity of light given by $c/\epsilon^{1/2}$ instead of coupled to the microscopic polariton field. In the frequency domain, the density of modes of this effective field scales as $\epsilon^{3/2}$, as may be seen, for instance, from Eq. (B8) using $\omega_k^2 = \epsilon\omega^2$. Furthermore, the coupling scales as $\epsilon^{-1/2}$ because the plane-wave amplitude of the macroscopic electric field scales in this way. The inclusion of these two effects in the Fermi golden rule leads to a decay rate proportional to $\epsilon^{1/2}$, which is commonly given as the only dependence on the dielectric constant.⁵ The appearance of the last factor in Eq. (5.4a) may be interpreted as a rescaling of the impurity's transition dipole due to the reaction field or local field from the polarized environment. Using electrostatics, there is a dilemma of how to account for this effect. On the one hand, a rescaling of μ_α with a factor $(\epsilon+2)/3$ is obtained by considering the impurity as residing in a *virtual* cavity inside the dielectric, whereas the consideration of a *real* cavity leads to a factor $3\epsilon/(2\epsilon+1)$. This dilemma has been pointed out by Agranovich, who adopted the virtual cavity.⁶ In our microscopic calculation, we do not face this ambiguity at all; the factor $\{[\epsilon(\Omega_0)+2]/3\}^2$ emerges naturally, justifying Agranovich's choice.³⁵ Moreover, our theory properly accounts for frequency dispersion. It should be pointed out that in the presence of frequency dispersion the derivative of $\epsilon(\omega)$ enters the density of states [cf. Eq. (B8)], which, therefore, no longer scales as $[\epsilon(\omega)]^{3/2}$. The apparent simplicity of Eq. (5.4a) is the re-

sult of delicate cancellations of factors in the coupling and the density of states of the polaritons.

The phenomenological arguments given above may in fact be used to explain the dependence of both $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ on ϵ for all values of $\Omega_0 r_{\alpha\beta}/c$. To this end, we repeat the derivation of the master equation for molecules interacting with the effective radiation field, which scales as $\epsilon^{-1/2}$, instead of with polaritons. Both $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ involve two interactions with the field, giving a factor ϵ^{-1} ; the density of states yields a factor $\epsilon^{3/2}$ and the local-field scaling of the dipoles gives $\{(\epsilon+2)/3\}^2$. Furthermore, if we realize that the argument of the tensor $\vec{\tau}$ and $\vec{\sigma}$ is kr and that the wave number k scales like $\sqrt{\epsilon}$ at constant frequency, the ϵ dependences of Eqs. (4.15b) and (4.18b) are obtained.

We now concentrate on the near-zone limit of the dispersive interaction

$$\Omega_{\alpha\beta}^{\text{near}} = \frac{1}{\epsilon(\Omega_0)} \left[\frac{\epsilon(\Omega_0)+2}{3} \right]^2 \times \frac{1}{\hbar} \mu_\alpha \cdot \left[\frac{\vec{1}}{r_{\alpha\beta}^3} - 3 \frac{r_{\alpha\beta} r_{\alpha\beta}}{r_{\alpha\beta}^5} \right] \cdot \mu_\beta, \quad (5.6)$$

which is easily recognized as the instantaneous dipole-dipole interaction scaled by the screening factor $1/\epsilon(\Omega_0)$ and the local field factor $\{[\epsilon(\Omega_0)+2]/3\}^2$. This scaling has also been obtained by Agranovich, starting from molecules with (vacuum) instantaneous Coulomb interactions ($\mathbf{p} \cdot \mathbf{A}$ Hamiltonian), between which exchange of lattice excitons takes place.⁶ We note that Agranovich's starting point is completely unretarded, in contrast to our theory in which we account for retardation through the polaritons. Nevertheless, both approaches yield the same result for the near-zone real interaction because this quantity is, by definition, not sensitive to retardation. Of course, effects related to retardation, in particular, the coefficients $\gamma_{\alpha\beta}$, cannot be obtained by just considering excitons. A well-known consequence of the result Eq. (5.6) is that the Förster rate of energy transfer between two molecules, which is proportional to $|\Omega_{\alpha\beta}^{\text{near}}|^2$, scales like $[(n^2+2)/3]^4 n^{-4}$, with $n = \sqrt{\epsilon}$ the index of refraction of the surrounding medium.^{4,6}

Finally, we give the far-zone results [$\sqrt{\epsilon(\Omega_0)}\Omega_0 r_{\alpha\beta}/c \gg 1$]

$$\gamma_{\alpha\beta}^{\text{far}} = \frac{2}{\hbar} \left[\frac{\Omega_0}{c} \right]^2 \left[\frac{\epsilon(\Omega_0)+2}{3} \right]^2 \times \frac{\sin[\sqrt{\epsilon(\Omega_0)}\Omega_0 r_{\alpha\beta}/c]}{r_{\alpha\beta}} \mu_\alpha \cdot \vec{u} \cdot \mu_\beta, \quad (5.7a)$$

$$\Omega_{\alpha\beta}^{\text{far}} = -\frac{1}{\hbar} \left[\frac{\Omega_0}{c} \right]^2 \left[\frac{\epsilon(\Omega_0)+2}{3} \right]^2 \times \frac{\cos[\sqrt{\epsilon(\Omega_0)}\Omega_0 r_{\alpha\beta}/c]}{r_{\alpha\beta}} \mu_\alpha \cdot \vec{u} \cdot \mu_\beta, \quad (5.7b)$$

from which it is seen that the screening factor $1/\epsilon$ disappears over large distances.

Because of the fundamental role the crystal polaritons play in our theory, it is useful to address the key points

on their calculation once again. First, we did not neglect umklapp processes, leading to an infinite number of polariton branches and the complete recovery of the retarded dipole-dipole interactions in the crystal. We mention, without proof, that a theory starting from the multipolar ($\boldsymbol{\mu} \cdot \mathbf{D}$) Hamiltonian in which umklapp processes are neglected does not yield the local field factor $[(\epsilon+2)/3]^2$ as, for instance, in Eqs. (5.3) and (5.6), but instead gives ϵ^2 . This may be understood because in such a theory $\mathbf{D} = \epsilon \mathbf{E}$ is the local field, instead of $(\epsilon+2)\mathbf{E}/3$ (\mathbf{E} being the Maxwell electric field). Neglecting umklapp processes, one would therefore predict a scaling of, for instance, the single-molecule spontaneous decay rate with a factor $\epsilon^{5/2}$. The most serious approximation in our derivation of the polaritons is that, in order to obtain analytic results, we approximated the interaction tensor Eq. (3.15b) by a constant diagonal tensor $\bar{\mathbf{R}}(\mathbf{k}, \omega) = 4\pi\beta\Omega/3$. This is only correct if $\omega R_c/c \ll 1$ and $kR_c \ll 1$ [cf. Eqs. (3.18)]. We note, however, that this approximation has no effect on the result for the imaginary interaction $\gamma_{\alpha\beta}$, provided that the impurity transition frequency does not approach the stopgap from below. This can be understood as follows: the calculation of $\gamma_{\alpha\beta}$ involves a delta function at $\omega = \Omega_0$ so that the polariton transformation coefficients and dispersion relation are only needed at frequency Ω_0 and wave number $k_0 = \sqrt{\epsilon(\Omega_0)}\Omega_0/c$. Since Ω_0 is an optical frequency and we assumed that Ω_0 does not approach the stopgap, we have $\Omega_0 R_c/c \ll 1$ and $k_0 R_c \ll 1$ (cf. Fig. 1), which justifies the approximation on $\bar{\mathbf{R}}(\mathbf{k}, \omega)$. We note that also the extension to infinity of the k integral over the lower polariton branch as performed in Appendix B does not affect $\gamma_{\alpha\beta}$, again because the relevant wave number k_0 lies inside the first Brillouin zone. It is an open question how the above approximations affect the real interaction $\Omega_{\alpha\beta}$.

An important question is how our results are limited by the position of the impurity's transition frequency Ω_0 relative to the crystal transition frequency Ω . We explicitly assumed in Sec. IV that Ω_0 does not fall inside the polariton stopgap ranging from $\Omega(1-4\pi\beta/3)^{1/2}$ to $\Omega(1+8\pi\beta/3)^{1/2}$ and we reasoned above already that Ω_0 should also not approach the stopgap from below. Strictly speaking, within our theory the imaginary (self-) interactions $\gamma_{\alpha\beta}$ vanish for Ω_0 inside the stopgap because the δ function then falls outside the region of integration in Eq. (4.14). One should realize, however, that this is entirely due to our approximation on the tensor $\bar{\mathbf{R}}(\mathbf{k}, \omega)$, which coincides with an infinite effective exciton mass approximation, leading to a total absence of polariton states inside the stopgap. In reality, the lower polariton curve together with the transverse exciton curve, bends upward into the stopgap at high wave numbers giving a finite density of states and finite spontaneous decay rates. There is a second, more fundamental reason why our theory does not apply when Ω_0 approaches the crystal's exciton band, namely that it does not account for delocalization of the excitation of an impurity over neighboring crystal atoms. This is a consequence of the Markov approximation, as a result of which the interactions $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ are only obtained to second order in the

polariton-impurity interaction. Delocalization can only be taken into account in a nonperturbative theory. In his calculation of the near-zone dipole-dipole coupling mentioned above,⁶ Agranovich did go beyond second-order perturbation theory in the molecule-exciton coupling, and he therefore obtained extra scaling factors which are important near the exciton band. These extra factors do not simply depend on $\epsilon(\Omega_0)$; the universal scaling with the dielectric function must be expected to break down when delocalization sets in. Obviously, our results are most interesting in the frequency region where delocalization is not important and the dielectric function shows a clear dispersion. A measure for the importance of delocalization is given by $\rho\mu_0\mu/\hbar|\omega_1-\Omega_0|$, ratio of the impurity-lattice coupling and the energy mismatch. Comparing this with Eq. (4.10) for $\epsilon(\omega)$, we observe that the frequency dispersion may still be appreciable while the delocalization is negligible as long as $\mu \gg \mu_0$, i.e., for a host crystal with a relatively large oscillator strength.

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APPENDIX A

In this appendix, we derive Eq. (4.3a) for the coupling coefficient $K_{\mathbf{k}\nu}(\alpha)$ for the four lowest polariton branches. Using Eqs. (3.23), we have, for $\mathbf{G} = 0$,

$$\begin{aligned} & w_{0\lambda\nu}^*(\mathbf{k}) + y_{0\lambda\nu}^*(\mathbf{k}) \\ &= \left[\frac{\omega_k}{\omega} \right]^{1/2} \\ & \times \frac{\omega^2 - \Omega^2 - 2\Omega R_1(\mathbf{k}, \omega)}{\{[\omega^2 - \Omega^2 - 2\Omega R_1(\mathbf{k}, \omega)]^2 + 4\pi\beta\Omega^2\omega_k^2\}^{1/2}} \delta_{\lambda\lambda'} \end{aligned} \quad (\text{A1})$$

and for $\mathbf{G} \neq 0$

$$\begin{aligned} & w_{\mathbf{G}\lambda\nu}^*(\mathbf{k}) + y_{\mathbf{G}\lambda\nu}^*(\mathbf{k}) \\ &= \left[\frac{\pi\beta\Omega^3}{\omega} \right]^{1/2} \left[\frac{2\pi\omega_{\mathbf{k}+\mathbf{G}\rho}}{\hbar} \right]^{1/2} \frac{4\omega_k\omega_{\mathbf{k}+\mathbf{G}}}{\omega^2 - \omega_{\mathbf{k}+\mathbf{G}}^2} \\ & \times \frac{\mu\mathbf{e}_{\mathbf{k}+\mathbf{G}\lambda} \cdot \mathbf{e}_{\mathbf{k}\lambda'}}{\{[\omega^2 - \Omega^2 - 2\Omega R_1(\mathbf{k}, \omega)]^2 + 4\pi\beta\Omega^2\omega_k^2\}^{1/2}} \end{aligned} \quad (\text{A2})$$

Substituting Eqs. (A1) and (A2) into Eq. (4.2b), we find

$$\begin{aligned}
K_{\mathbf{k}\nu}(\alpha) &= \left(\frac{2\pi}{\hbar} \right)^{1/2} \frac{\omega_{\mathbf{k}}}{\sqrt{\omega}} \\
&\times \frac{e^{i\mathbf{k}\cdot\mathbf{r}_\alpha}}{\{[\omega^2 - \Omega^2 - 2\Omega R_\perp(\mathbf{k}, \omega)]^2 + 4\pi\beta\Omega^2\omega_{\mathbf{k}}^2\}^{1/2}} \\
&\times \{[\omega^2 - \Omega^2 - 2\Omega R_\perp(\mathbf{k}, \omega)]\boldsymbol{\mu}_\alpha \cdot \mathbf{e}_{\mathbf{k}\lambda'} \\
&\quad + 2\Omega\boldsymbol{\mu}_\alpha \cdot \vec{\mathbf{R}}(\mathbf{k}, \omega) \cdot \mathbf{e}_{\mathbf{k}\lambda'}\} . \tag{A3}
\end{aligned}$$

The first term in the second set of curly brackets comes from the $\mathbf{G}=\mathbf{0}$ contribution in Eq. (4.2b), while the second term emerges from $\sum_{\mathbf{G}(\neq\mathbf{0})}$. We used explicitly that $\exp(i\mathbf{G}\cdot\mathbf{r}_\alpha)=1$, and the interaction tensor $\vec{\mathbf{R}}(\mathbf{k}, \omega)$ is as defined in Eq. (3.15b). If we neglect the off-diagonal matrix elements of this tensor, as we did in the main text, we may write

$$\boldsymbol{\mu}_\alpha \cdot \vec{\mathbf{R}}(\mathbf{k}, \omega) \cdot \mathbf{e}_{\mathbf{k}\lambda'} = R_\perp(\mathbf{k}, \omega)(\boldsymbol{\mu}_\alpha \cdot \mathbf{e}_{\mathbf{k}\lambda'}) , \tag{A4}$$

since $\mathbf{e}_{\mathbf{k}\lambda'}$ is a transverse polarization vector ($\lambda'=1$ or 2). Equation (4.3a) now follows trivially from Eq. (A3).

APPENDIX B

In this Appendix we derive Eq. (4.9). If we take the limit $V \rightarrow \infty$ of the left-hand side of this equation it transforms to

$$I \equiv \frac{1}{(2\pi)^3} \sum_{\nu} \int_{\text{1BZ}} d\mathbf{k} K_{\mathbf{k}\nu}(\alpha) K_{\mathbf{k}\nu}^*(\beta) e^{-i\omega_{\mathbf{k}\nu}\tau} , \tag{B1}$$

where τ stands for $t-t'$. Next we note that if \mathbf{k} approaches the edge of the first Brillouin zone, the polariton frequency for the branches $\nu=(b=\text{upper}, \lambda')$ (the upper two of the lowest branches) approaches $\omega_{\mathbf{k}}$. This is clear from physical insight; at the zone boundary the exciton

and photon are so well separated in energy that they do not mix. Alternatively, this limiting behavior can be derived more rigorously from the dispersion relation Eq. (3.20) provided that $2\Omega R_\perp(\mathbf{k}, \omega) \ll \omega_{\mathbf{k}}^2$ in the region of interest. This condition is fulfilled in particular within the approximation $\vec{\mathbf{R}}(\mathbf{k}, \omega)=4\pi\beta\Omega/3$, which we will confine ourselves to in the remainder. It now follows from Eq. (4.3a) that at the edge of the first Brillouin zone

$$K_{\mathbf{k}u\lambda'}(\alpha) \rightarrow \left(\frac{2\pi\omega_{\mathbf{k}}}{\hbar} \right)^{1/2} (\boldsymbol{\mu}_\alpha \cdot \mathbf{e}_{\mathbf{k}\lambda'}) e^{i\mathbf{k}\cdot\mathbf{r}_\alpha} , \tag{B2}$$

where the branch label ν has been split into its two sublabels, and u stands for $b=\text{upper}$. In fact, we note that if the definitions (3.20) and (4.3a) for $\omega_{\mathbf{k}u\lambda'}$ and $K_{\mathbf{k}u\lambda'}(\alpha)$ as functions of \mathbf{k} are considered to pertain also outside the first Brillouin zone ($\mathbf{k}+\mathbf{G}'$), these functions are equal to $\omega_{\mathbf{k}\nu}$ and $K_{\mathbf{k}\nu}(\alpha)$ for the higher Brillouin zones as defined in Eqs. (3.11) and (4.3b). Therefore it is possible to combine in Eq. (B1) the integrals for the branches $\nu=(u, \lambda')$ and $\nu=(\mathbf{G}'\neq\mathbf{0}, \lambda')$ to one integral over the entire \mathbf{k} space

$$I = I_1 + I_2 , \tag{B3a}$$

$$I_1 = \frac{1}{(2\pi)^3} \sum_{\lambda'=1}^2 \int d\mathbf{k} K_{\mathbf{k}u\lambda'}(\alpha) K_{\mathbf{k}u\lambda'}^*(\beta) e^{-i\omega_{\mathbf{k}u\lambda'}\tau} , \tag{B3b}$$

$$I_2 = \frac{1}{(2\pi)^3} \sum_{\lambda'=1}^2 \int_{\text{1BZ}} d\mathbf{k} K_{\mathbf{k}l\lambda'}(\alpha) K_{\mathbf{k}l\lambda'}^*(\beta) e^{-i\omega_{\mathbf{k}l\lambda'}\tau} . \tag{B3c}$$

Here it should be understood that in the first integral the definitions of $K_{\mathbf{k}u\lambda'}(\alpha)$ and $\omega_{\mathbf{k}u\lambda'}$ have been extended to \mathbf{k} values outside the first Brillouin zone. The label l in Eq. (B3c) stands for $b=\text{lower}$.

We will first evaluate I_1 . Using Eq. (4.3a) we find ($\nu=u\lambda'$)

$$I_1 = \frac{1}{(2\pi)^3} \sum_{\lambda'=1}^2 \int d\mathbf{k} \frac{2\pi}{\hbar} \frac{\omega_{\mathbf{k}}^2}{\omega_{\mathbf{k}\nu}} \frac{(\omega_{\mathbf{k}\nu}^2 - \Omega^2)^2 (\boldsymbol{\mu}_\alpha \cdot \mathbf{e}_{\mathbf{k}\lambda'}) (\mathbf{e}_{\mathbf{k}\lambda'} \cdot \boldsymbol{\mu}_\beta) e^{i\mathbf{k}\cdot\mathbf{r}_{\alpha\beta} - i\omega_{\mathbf{k}\nu}\tau}}{[\omega_{\mathbf{k}\nu}^2 - \Omega^2(1+8\pi\beta/3)]^2 + 4\pi\beta\Omega^2\omega_{\mathbf{k}}^2} , \tag{B4}$$

with $\mathbf{r}_{\alpha\beta} \equiv \mathbf{r}_\alpha - \mathbf{r}_\beta$. Since the frequency $\omega_{\mathbf{k}\nu}$ in this integral does not depend on the polarization λ' [cf. Eq. (3.20)] and is also independent of the direction $\hat{\mathbf{k}}$ of \mathbf{k} [as a consequence of the approximation $\vec{\mathbf{R}}(\mathbf{k}, \omega)=4\pi\beta\Omega/3$], the sum over λ' and the integration over $\hat{\mathbf{k}}$ can be performed. It follows that

$$\begin{aligned}
I_1 &= \frac{1}{\pi\hbar} \int_0^\infty dk k^2 \frac{\omega_{\mathbf{k}}^2}{\omega_{\mathbf{k}\nu}} \frac{(\omega_{\mathbf{k}\nu}^2 - \Omega^2)^2 \boldsymbol{\mu}_\alpha \cdot \vec{\boldsymbol{\tau}}(kr_{\alpha\beta}) \cdot \boldsymbol{\mu}_\beta}{[\omega_{\mathbf{k}\nu}^2 - \Omega^2(1+8\pi\beta/3)]^2 + 4\pi\beta\Omega^2\omega_{\mathbf{k}}^2} \\
&\quad \times e^{-i\omega_{\mathbf{k}\nu}\tau} , \tag{B5}
\end{aligned}$$

with

$$4\pi\vec{\boldsymbol{\tau}}(kr_{\alpha\beta}) \equiv \int d\hat{\mathbf{k}} (\vec{\mathbf{1}} - \hat{\mathbf{k}}\hat{\mathbf{k}}) e^{i\mathbf{k}\cdot\mathbf{r}_{\alpha\beta}} . \tag{B6}$$

The integral in Eq. (B6) can be worked out to obtain the explicit form of $\vec{\boldsymbol{\tau}}$ given in Eqs. (4.11).³⁶ We now transform the k integration in Eq. (B5) to an integration over the polariton frequency $\omega_{\mathbf{k}\nu} \equiv \omega$. This is done using $\omega_{\mathbf{k}} = kc = \sqrt{\epsilon(\omega)}\omega$, with $\epsilon(\omega)$ the frequency-dependent dielectric function of the atomic lattice given by Eq. (3.22) with $\vec{\mathbf{R}}(k, \omega)=4\pi\beta\Omega/3$:

$$\epsilon(\omega) = 1 + \frac{4\pi\beta\Omega^2}{-\omega^2 + \Omega^2(1-4\pi\beta/3)} . \tag{B7}$$

Straightforward algebra yields, for the integration element,

$$k^2 dk = \epsilon(\omega) \frac{\omega^2}{c^3} \frac{d\omega_{\mathbf{k}}}{d\omega} d\omega = \sqrt{\epsilon(\omega)} \frac{\omega^2}{c^3} \frac{d\omega_{\mathbf{k}}^2}{d\omega} d\omega \tag{B8}$$

[independent of the form of $\epsilon(\omega)$]. Taking the differential of the dispersion relation Eq. (3.20), it is easily shown that

$$\frac{d\omega_k^2}{d\omega^2} = \frac{\Omega^2(1+8\pi\beta/3)-2\omega^2+\omega_k^2}{\Omega^2(1-4\pi\beta/3)-\omega^2}. \quad (\text{B9})$$

Finally, the lower boundary $k=0$ of the integral in Eq. (B5) transforms to a lower boundary at the longitudinal exciton frequency (ω_{\parallel}) as defined in Eq. (3.21b) (see Fig. 1). We thus obtain

$$I_1 = \frac{1}{\pi\hbar} \int_{\omega_{\parallel}}^{\infty} d\omega \left[\frac{\omega}{c} \sqrt{\epsilon(\omega)} \right]^3 \mu_{\alpha} \cdot \vec{\tau} \left[\sqrt{\epsilon(\omega)} \frac{\omega r_{\alpha\beta}}{c} \right] \cdot \mu_{\beta} e^{-i\omega\tau} \times \left[\frac{\Omega^2(1+8\pi\beta/3)-\omega^2+[\epsilon(\omega)-1]\omega^2}{\Omega^2(1-4\pi\beta/3)-\omega^2} \frac{(\omega^2-\Omega^2)^2}{[\omega^2-\Omega^2(1+8\pi\beta/3)]^2+4\pi\beta\epsilon(\omega)\Omega^2\omega^2} \right]. \quad (\text{B10})$$

Using Eq. (B7) it can be shown through tedious but straightforward algebra that the factor in the second set of large parentheses in Eq. (B10) equals

$$\frac{\Omega^2(1+8\pi\beta/3)-\omega^2+[\epsilon(\omega)-1]\omega^2}{\Omega^2(1-4\pi\beta/3)-\omega^2} \frac{(\omega^2-\Omega^2)^2}{[\omega^2-\Omega^2(1+8\pi\beta/3)]^2+4\pi\beta\epsilon(\omega)\Omega^2\omega^2} = \frac{1}{\epsilon(\omega)} \left[\frac{\epsilon(\omega)+2}{3} \right]^2, \quad (\text{B11})$$

so that

$$I_1 = \frac{1}{\pi} \int_{\omega_{\parallel}}^{\infty} d\omega f_{\alpha\beta}(\omega) e^{-i\omega\tau}, \quad (\text{B12})$$

with $f_{\alpha\beta}(\omega)$ as defined in Eq. (4.9b).

Now the term I_2 in Eq. (B3a) is left to be determined. If we extend the integration over all \mathbf{k} space, this term can be treated in exactly the same way as I_1 . The only difference is that for the lowest polariton branch the interval of the final integration ranges from $\omega=0$ to $\omega=\omega_1$, the transverse exciton frequency as defined in Eq. (3.21a) (see Fig. 1). We thus get

$$I_2 = \frac{1}{\pi} \int_0^{\omega_1} d\omega f_{\alpha\beta}(\omega) e^{-i\omega\tau}. \quad (\text{B13})$$

This result together with Eqs. (B3a) and (B12), yields Eq. (4.9a). We note that, since in reality the \mathbf{k} integration in Eq. (B3c) stops at the boundary of the first Brillouin zone, the ω integration will stop slightly below the lower boundary ω_1 of the stopgap.

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¹P. Roussignol, D. Ricard, J. Lukasik, and C. Flytzanis, *J. Opt. Soc. Am. B* **4**, 5 (1987).

²D. S. Chemla and J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic, New York, 1987), Vols. I and II.

³*Topical Meeting on Optical Properties of Materials*, 1988 Technical Digest Series (Optical Society of America, Washington, D. C., 1988), Vol. 9.

⁴J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley, New York, 1970).

⁵R. H. Pantell and H. E. Puthoff, *Fundamentals of Quantum Electronics* (Wiley, New York, 1969).

⁶V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1982).

⁷E. Yablonovitch, T. J. Gmitter, and R. Bhat, *Phys. Rev. Lett.* **61**, 2546 (1988).

⁸S. Haroche and D. Kleppner, *Phys. Today* **42**, (1), 24 (1989).

⁹J. Gersten and A. Nitzan, *J. Chem. Phys.* **75**, 1139 (1981).

¹⁰S. C. Ching, H. M. Lai, and K. Young, *J. Opt. Soc. Am. B* **4**, 1995, (1987); **4**, 2004 (1987).

¹¹E. Yablonovitch, *Phys. Rev. Lett.* **58**, 2059 (1987).

¹²G. Kurizki and A. Z. Genack, *Phys. Rev. Lett.* **61**, 2269 (1988).

¹³(a) G. S. Agarwal, *Quantum Optics* (Springer, Berlin, 1974); (b) R. H. Lehberg, *Phys. Rev. A* **2**, 883 (1970); (c) R. Bonifacio, P. Schwendimann, and F. Haake, *ibid.* **4**, 302 (1971).

¹⁴M. Gross and S. Haroche, *Phys. Rep.* **93**, 301 (1982).

¹⁵E. A. Power and S. Zienau, *Philos. Trans. R. Soc. London* **251**, 427 (1959); D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, New York, 1984).

¹⁶J. J. Hopfield, *Phys. Rev.* **112**, 1555 (1958).

¹⁷V. M. Agranovich, *Zh. Eksp. Teor. Fiz.* **37**, 430 (1959) [Sov.

- Phys.—JETP **37**, 307 (1960)].
- ¹⁸J. Knoester and S. Mukamel, *J. Chem. Phys.* **91**, 989 (1989).
- ¹⁹M. Orrit and P. Kottis, *Adv. Chem. Phys.* **74**, 1 (1988).
- ²⁰S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum, New York, 1967).
- ²¹A. S. Davydov and V. A. Onishchuk, *Phys. Status Solidi* **24**, 373 (1967).
- ²²R. K. Bullough and B. V. Thompson, *J. Phys. C* **3**, 1780 (1970).
- ²³M. R. Philpott, *J. Chem. Phys.* **52**, 5842 (1970).
- ²⁴J. van Kranendonk and J. E. Sipe, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1977), Vol. 15, p. 245.
- ²⁵J. Knoester and S. Mukamel, *Phys. Rev. A* **39**, 1899 (1989).
- ²⁶W. R. Heller and A. Marcus, *Phys. Rev.* **84**, 809 (1951).
- ²⁷J. Knoester and S. Mukamel, *J. Opt. Soc. Am. B* **6**, 643 (1989).
- ²⁸A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).
- ²⁹R. Silbey, *J. Chem. Phys.* **46**, 4029 (1967).
- ³⁰M. R. Philpott and J. W. Lee, *J. Chem. Phys.* **58**, 595 (1973).
- ³¹B. R. A. Nijboer and F. W. de Wette, *Physica* **24**, 422 (1958).
- ³²G. D. Mahan, *J. Chem. Phys.* **43**, 1569 (1965).
- ³³W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).
- ³⁴A. Amirav (private communication).
- ³⁵The factor $3\epsilon/2(\epsilon+1)$ has recently used by Yablonovitch, Gmitter, and Bhat (Ref. 7) in a study of the dependence of the radiative decay rate of small semiconductor particles on the index of refraction of the medium in which they were immersed. ϵ is now the relative dielectric constant $\epsilon_{\text{ext}}/\epsilon_{\text{int}}$ of the medium (ϵ_{ext}) and the semiconductor material (ϵ_{int}). For this situation the factor $3\epsilon/(2\epsilon+1)$ is correct, as there is a real cavity (the particle). The microscopic scaling with ϵ_{int} according to $(\epsilon_{\text{int}}+2)/3$ still exists on top of this, but is not observed since ϵ_{int} is not varied.
- ³⁶E. A. Power, *J. Chem. Phys.* **46**, 4297 (1967).