

Quantum electrodynamics of molecular nanostructures

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We present a microscopic account of the linear and nonlinear optical response of an assembly of molecules with nonoverlapping charge distributions and arbitrary geometry. Our approach requires only the knowledge of single-molecule wave functions. The microscopic polarization is defined by a dipole distribution for each transition; we do not make the dipole approximation and it is then unnecessary to introduce the Ewald summation technique. Equations of motion are derived which provide a quasiparticle (anharmonic oscillator) picture of the optical response. As an application, we calculate both the linear susceptibility $\chi^{(1)}$ and the light scattering signal off a crystal in d dimensions ($d=1, 2$, and 3). We find that retardation does not affect $\chi^{(1)}$, which contains a shift in the exciton frequency compared with the single molecule, but no signature of spontaneous emission. However, the scattered field is retarded and shows cooperative spontaneous emission in reduced dimensionality $d=1$ and 2. The present approach can be applied to ordered nanostructures as well as disordered systems such as liquids and addresses fully the effects of retardation, polaritons, and cooperativity in linear as well as nonlinear optical processes.

I. INTRODUCTION

The study of excitons in restricted geometries, e.g., in molecular multilayers (quantum wells),¹⁻³ chains,⁴⁻⁷ and clusters⁸⁻¹⁰ is currently drawing considerable attention. Of particular interest is the behavior of excitons in finite molecular crystals, which is both a topical and longstanding problem in physics.¹¹⁻¹⁴ The optical response of low temperature crystals is characterized by the formation of polaritons, which are quasiparticles with combined field and matter character. In order to properly describe polaritons in two-dimensional lattices, the electromagnetic field must be fully taken into account. This has been done by using projection operators^{1,12} or by defining creation and annihilation operators for the polaritons.¹⁵⁻¹⁷ The former method is limited to the study of linear response, while the latter is not conducive to the formulation of the response in terms of the susceptibilities of the crystal, defined with respect to the Maxwell electric field. Both approaches lead to the correct dispersion relations for polaritons in infinite crystals, but neither method adequately presents an account of the nonlinear response of polaritons in restricted geometries. An additional point of interest is the correct and systematic incorporation of spontaneous emission into the optical response function. In reduced dimensionality, Cho¹⁸ has shown that the electric susceptibilities should not contain a radiative width. Spano and Mukamel,⁵ on the other hand, incorporated spontaneous emission by working with the external field. In widespread accounts in the literature, the various fields $\hat{E}(\mathbf{r})$, the Maxwell field, its transverse component $\hat{E}^{\perp}(\mathbf{r})$, the local field $\hat{E}_{\text{local}}(\mathbf{r})$ and the external field $\hat{E}_{\text{ex}}(\mathbf{r})$ have all been used phenomenologically to describe optical response.^{19,20}

In this article, we develop a fully microscopic method for the consistent treatment of intermolecular and field interactions in the optical response. We give a unified treatment of nanostructures valid for arbitrary size and confine-

ment, whether smaller than or greater than the optical wavelength—this gives a consistent treatment of retardation (and polariton) effects without double counting of fields (notably the electrostatic intermolecular interactions).

In our approach, we consider real charges and currents directly and do not invoke the electric dipole approximation (EDA). We follow Longuet-Higgins²¹ by working with the molecular charge density and recast it in terms of distributions of dipoles. This affords us several advantages, both conceptually and practically. We are able (i) to treat molecule-molecule interactions and molecule-field interactions with equal footing—both are sets of oscillators and so their interaction is straightforward; (ii) to implement the EDA when treating the interaction of the matter with the field (this poses no problem for the most part, although we make sure to address properly the effects of cooperativity and spontaneous emission), but keep molecule-molecule interactions formulated through interaction of the molecular polarizations (we do not want to invoke the EDA here); (iii) to avoid the complexity associated with the multipolar expansion into quadrupole and higher moments (which even then is only accurate to a certain order), while retaining the option to obtain the EDA result, which is equivalent to the first moment of our results; (iv) to avoid the divergencies associated with short- and long-range limits in the dipole approximation which result in infinite self-energies and shape-dependent dipole sums.^{22,23}

Since we calculate the macroscopic polarization from a microscopic starting point, we directly address the relationship between the macro- and microscopic quantities, which is an important issue in the study of optical materials.²⁴ Our equations allow a connection to be established between quantum chemistry (calculation of eigenstates of molecular systems) and the physics of numerical simulation. For example, a common model in the simulation of optical response (whether linear or nonlinear) of liquids is

to take the molecules as dipolar hard spheres.²⁵ The use of a polarization distribution to model the behavior of charges in liquids will greatly improve the accuracy of such calculations.

Our approach maps condensed phase systems into coupled anharmonic oscillators. We work in real space as opposed to momentum (\mathbf{k}) space and are thus able to gain physical insight into how individual processes affect the optical response, e.g., retarded and electrostatic intermolecular interactions and single molecule Lamb shifts. This quasiparticle approach to optical response uses only single-molecule (or atomic) wave functions as input and thus does not require the solution of a secular equation in order to calculate the eigenstates of the entire assembly. This greatly simplifies the numerical work involved when dealing with large systems. Our oscillator picture in the joint field-matter space also allows both linear and nonlinear optical response to be described using the same equations, thus giving a consistent account of nonlinear susceptibilities. This contrasts previous treatments of retardation in molecular monolayers,^{1,6,12,13} whose nature (projection onto the matter subspace, incorporating field effects through a self-energy) necessarily confined the investigation to a study of linear optical response only.

In the following section, we give the model and Hamiltonian, which has the Power-Zienau (multipolar) form,²⁶ and present a general equation of motion, which we shall use in Sec. III to write oscillator equations for the transition operators associated with the elementary excitations of the assembly of molecules. These equations will be presented in different forms; we write them with respect to the transverse Maxwell field, the external field, and the local electromagnetic field. They constitute the basis for the remainder of the paper, since from them we are able to derive in Secs. IV and V the linear susceptibility of and light scattered from a molecular crystal, assuming periodic boundary conditions. We present our conclusions in Sec. VI.

II. THE MULTIPOLAR HAMILTONIAN FOR MOLECULAR ASSEMBLIES WITH NON-OVERLAPPING CHARGE DISTRIBUTIONS

In this section, we present our model and Hamiltonian. We consider an assembly of neutral, nonoverlapping multilevel molecules. The molecules need not be identical and are taken to be nonpolar, but polarizable with a well defined charge distribution. We denote an operator by a caret, e.g., \hat{O} , and write $\langle \hat{O}(t) \rangle$ or simply $O(t)$ as its expectation value at time t . The multipolar Hamiltonian in the Coulomb gauge^{17,26} is (neglecting magnetic terms)

$$\hat{H}_{\text{mult}} = \hat{H}_{\text{rad}} + \hat{H}_{\text{mol}} - \int d\mathbf{r} \hat{P}(\mathbf{r}) \cdot \hat{D}^\perp(\mathbf{r}) + \hat{V}_{\text{inter}} + 2\pi \int d\mathbf{r} |\hat{P}^\perp(\mathbf{r})|^2. \quad (2.1)$$

The quantized free-field Hamiltonian

$$\hat{H}_{\text{rad}} = \frac{1}{8\pi} \int d\mathbf{r} \{ \hat{D}^{\perp 2}(\mathbf{r}) + [\nabla \times \hat{A}(\mathbf{r})]^2 \} \quad (2.2a)$$

may be expanded in harmonic oscillator modes as

$$\hat{H}_{\text{rad}} = \hbar \sum_{\mathbf{k}\epsilon} \omega_{\mathbf{k}} \left(\hat{a}_{\mathbf{k}\epsilon}^\dagger \hat{a}_{\mathbf{k}\epsilon} + \frac{1}{2} \right). \quad (2.2b)$$

The electric displacement field and vector potential are defined respectively by

$$\hat{D}^\perp(\mathbf{r}) = i \sum_{\mathbf{k}\epsilon} \left(\frac{2\pi\hbar\omega_{\mathbf{k}}}{\mathcal{V}} \right)^{1/2} [\hat{a}_{\mathbf{k}\epsilon} \exp(i\mathbf{k} \cdot \mathbf{r}) - \hat{a}_{\mathbf{k}\epsilon}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{r})] \mathbf{e}_{\mathbf{k}\epsilon}, \quad (2.3a)$$

$$\hat{A}(\mathbf{r}) = \sum_{\mathbf{k}\epsilon} \left(\frac{2\pi\hbar c^2}{\mathcal{V}\omega_{\mathbf{k}}} \right)^{1/2} [\hat{a}_{\mathbf{k}\epsilon} \exp(i\mathbf{k} \cdot \mathbf{r}) + \hat{a}_{\mathbf{k}\epsilon}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{r})] \mathbf{e}_{\mathbf{k}\epsilon}, \quad (2.3b)$$

where $\hat{a}_{\mathbf{k}\epsilon}^\dagger$ and $\hat{a}_{\mathbf{k}\epsilon}$ are the creation and annihilation operators of the photon of field mode $\mathbf{k}\epsilon$, with photon wave vector \mathbf{k} and polarization ϵ . \mathcal{V} is the quantization volume of the field and $\mathbf{e}_{\mathbf{k}\epsilon}$ is the unit vector of polarization of the photon. The Hamiltonian is subject to the field commutation relations

$$[\hat{D}_i^\perp(\mathbf{r}), [\nabla \times \hat{A}(\mathbf{r}')]]_{,j} = 4\pi i \hbar c \epsilon_{ij\ell} \nabla'_\ell \delta(\mathbf{r} - \mathbf{r}'), \quad (2.4a)$$

$$[\hat{a}_{\mathbf{k}\epsilon}, \hat{a}_{\mathbf{k}'\epsilon'}^\dagger] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\epsilon\epsilon'}, \quad (2.4b)$$

where $\epsilon_{ij\ell}$ is the Levi-Civita tensor and $i, j,$ and ℓ denote Cartesian axial components. The molecular Hamiltonian in second quantized form

$$\hat{H}_{\text{mol}} = \hbar \sum_m \sum_{\lambda(m)} \Omega_{m\lambda} \hat{B}_{m\lambda}^\dagger \hat{B}_{m\lambda} \quad (2.5)$$

contains all intramolecular electrostatic interactions and $\Omega_{m\lambda}$ is the transition frequency of the single molecule m from its ground state $|g(m)\rangle$ to level $|\lambda(m)\rangle$. \hat{B} and \hat{B}^\dagger are transition operators defined by

$$\hat{B}_{m\lambda} = |g(m)\rangle \langle \lambda(m)|, \quad \hat{B}_{m\lambda}^\dagger = |\lambda(m)\rangle \langle g(m)| \quad (2.6)$$

subject to the commutation relations

$$[\hat{B}_{m\lambda}, \hat{B}_{m'\lambda'}^\dagger] = (1 - 2\hat{B}_{m\lambda}^\dagger \hat{B}_{m\lambda}) \delta_{mm'} \delta_{\lambda\lambda'}. \quad (2.7)$$

Pauli exclusion is obeyed for excitations on the same molecule, but if \hat{B} and \hat{B}^\dagger operate on different molecules, the excitations behave as bosons.

We denote the transverse and longitudinal parts of any vector field $F(\mathbf{r})$ by $F^\perp(\mathbf{r})$ and $F^\parallel(\mathbf{r})$, respectively,²⁷ with $\nabla \cdot F^\perp(\mathbf{r}) = 0$ and $\nabla \times F^\parallel(\mathbf{r}) = 0$. They are given by

$$F^\perp(\mathbf{r}) = \int d\mathbf{r}' \delta^\perp(\mathbf{r} - \mathbf{r}') F(\mathbf{r}'), \quad (2.8a)$$

$$F^\parallel(\mathbf{r}) = \int d\mathbf{r}' \delta^\parallel(\mathbf{r} - \mathbf{r}') F(\mathbf{r}'), \quad (2.8b)$$

where the components of the δ dyadics are

$$\delta_{\psi}^{\parallel}(\mathbf{r}) = \frac{1}{3} \delta_{\psi} \delta(\mathbf{r}) + \frac{1}{4\pi} T_{\psi}(\mathbf{r}), \quad (2.9a)$$

$$\delta_{\psi}^{\perp}(\mathbf{r}) = \frac{2}{3} \delta_{\psi} \delta(\mathbf{r}) - \frac{1}{4\pi} T_{\psi}(\mathbf{r}), \quad (2.9b)$$

and where we have defined the second rank tensor

$$T(\mathbf{r}) = \frac{\mathbf{1} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}}{r^3}. \quad (2.9c)$$

The Maxwell field $\hat{E}(\mathbf{r})$ is related to the electric displacement field by the relation

$$\hat{D}(\mathbf{r}) = \hat{E}(\mathbf{r}) + 4\pi\hat{P}(\mathbf{r}), \quad (2.10)$$

which holds since we are considering neutral molecules only and hence $\hat{E}^{\parallel}(\mathbf{r}) = -4\pi\hat{P}^{\parallel}(\mathbf{r})$. Note that $\hat{D}(\mathbf{r})$ and not $\hat{E}(\mathbf{r})$ is the pure field variable in this Hamiltonian. The total electric polarization operator is made up of contributions from all molecules and is given by²⁸

$$\hat{P}(\mathbf{r}) = \sum_m \hat{\mathcal{P}}_m(\mathbf{r}) \quad (2.11a)$$

with

$$\hat{\mathcal{P}}_m(\mathbf{r}) = -e \sum_{\alpha} (\hat{\mathbf{q}}_{\alpha} - \mathbf{R}_m) \int_0^1 d\xi \delta(\mathbf{r} - \mathbf{R} - \xi(\hat{\mathbf{q}}_{\alpha} - \mathbf{R}_m)), \quad (2.11b)$$

where $\hat{\mathbf{q}}_{\alpha}$ is the position operator of electron α belonging to molecule m , which has center of mass (or charge) \mathbf{R}_m . The ξ integration is a number integration which ensures the correct coefficients of the multipolar expansion of the polarization operator. We next expand the polarization in the molecular basis set. The electric polarization of a single molecule is a sum of contributions from all levels. Thus

$$\begin{aligned} \hat{\mathcal{P}}_m(\mathbf{r}) = & \sum_{\lambda(m)} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) (\hat{B}_{m\lambda} + \hat{B}_{m\lambda}^{\dagger}) \\ & + \sum_{\lambda'(m)} \tilde{\rho}(\lambda, \lambda'; \mathbf{r} - \mathbf{R}_m) (\hat{B}_{m\lambda}^{\dagger} \hat{B}_{m\lambda'} + \hat{B}_{m\lambda'}^{\dagger} \hat{B}_{m\lambda}), \end{aligned} \quad (2.12a)$$

where

$$\rho(\lambda; \mathbf{r} - \mathbf{R}_m) \equiv \langle \lambda(m) | \hat{\mathcal{P}}_m(\mathbf{r}) | g(m) \rangle, \quad (2.12b)$$

$$\tilde{\rho}(\lambda, \lambda'; \mathbf{r} - \mathbf{R}_m) \equiv \langle \lambda(m) | \hat{\mathcal{P}}_m(\mathbf{r}) | \lambda'(m) \rangle, \quad (2.12c)$$

are the polarization densities associated with the transitions $|\lambda\rangle \leftarrow |g\rangle$ and $|\lambda\rangle \leftarrow |\lambda'\rangle$. These are obtained from the matrix elements of the polarization operator, provided we know the wave functions of the molecular levels. For molecules with nonoverlapping charge distributions, we have

$$\int d\mathbf{r} \rho(\lambda(m); \mathbf{r} - \mathbf{R}_m) \rho(\lambda'(m'); \mathbf{r} - \mathbf{R}_{m'}) = 0 \quad (2.13)$$

for all λ, λ' , and the electrostatic interaction is

$$\begin{aligned} \hat{V}_{\text{inter}} = & - \sum_{m < m'} \int d\mathbf{r} \hat{\mathcal{P}}_m^{\perp}(\mathbf{r}) \cdot \hat{\mathcal{P}}_{m'}^{\perp}(\mathbf{r}) \\ = & \sum_{m < m'} \int d\mathbf{r} \hat{\mathcal{P}}_m^{\parallel}(\mathbf{r}) \cdot \hat{\mathcal{P}}_{m'}^{\parallel}(\mathbf{r}). \end{aligned} \quad (2.14)$$

Although the total polarization field of a single molecule is localized to the region of its charges, satisfying Eq. (2.13), its transverse and longitudinal parts are finite everywhere as can be seen from Eqs. (2.8) and (2.9) (this is true for any vector field).

The intermolecular potential energy is simply the interaction of the charge distributions associated with each molecule, namely,

$$\hat{V}_{\text{inter}} = \sum_{m < m'} \int d\mathbf{r} \int d\mathbf{r}' \frac{\hat{\rho}(m; \mathbf{r}) \hat{\rho}(m'; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.15a)$$

where we have defined the molecular charge distribution as

$$\hat{\rho}(m; \mathbf{r}) = -\nabla \cdot \hat{\mathcal{P}}_m(\mathbf{r}). \quad (2.15b)$$

This approach is close to that of Longuet-Higgins,²¹ who calculated the intermolecular forces between nonoverlapping polyatomic molecules, which he pointed out are simply the interactions between charge distributions. Longuet-Higgins termed such interactions long-range forces in the sense that electron exchange is neglected (we do not stipulate the magnitude of the separation between the polarization distributions—either the London²⁹ or Casimir-Polder³⁰ dispersion interaction may apply). We do not consider pure electrostatic or charge-induced polarization interactions since we are considering neutral molecules. However, Eq. (2.15) does describe the complete dispersion interaction. Since the polarization is the key quantity in the optical response it may be convenient to recast the interactions in terms of the polarization density (rather than the charge density). To this end, we integrate Eq. (2.15a) by parts or rewrite Eq. (2.14) with the use of Eqs. (2.8) and (2.9). We obtain

$$\begin{aligned} \hat{V}_{\text{inter}} = & \sum_{m < m'} \int d\mathbf{r} \int d\mathbf{r}' \hat{\mathcal{P}}_m(\mathbf{r}) \\ & \cdot T(\mathbf{r} - \mathbf{r}') \cdot \hat{\mathcal{P}}_{m'}(\mathbf{r}'). \end{aligned} \quad (2.16)$$

The form of Eq. (2.16) is important as it allows us to work with the total polarization field and not the transverse field. The final term of the Hamiltonian is the modulus square of the transverse part of the electric polarization $\hat{P}(\mathbf{r})$. Since it does not depend on the electromagnetic field, this term merely gives rise to an energy shift, which is often neglected.^{1,31} We do not make this approximation, since in the following derivation it is eliminated identically.

The present approach is based on the derivation of equations of motion in the Heisenberg picture. We first derive from our Hamiltonian an equation of motion for an arbitrary operator which we shall use in later sections in conjunction with the form of electric polarization and electrostatic interaction which we have already defined. Standard practice^{17,32} is to construct an equation of motion in terms of the transverse Maxwell field using the electric dipole form $\mu \cdot T(\mathbf{R}_m - \mathbf{R}_{m'}) \cdot \mu$ of the intermolecular po-

tential energy. This procedure then allows us to expand the polarization in powers of this transverse field and hence obtain the susceptibilities. Here we naturally extend this procedure to account for the complete charge distributions as opposed to point dipoles. We substitute for the displacement field equation (2.10) in the Hamiltonian equation (2.1), which we then use to form the Heisenberg equation of motion for an arbitrary operator \hat{Q} , which itself may be a matter operator, field operator, or both. We obtain

$$\begin{aligned} \frac{\hbar}{i} \frac{\partial \hat{Q}}{\partial t} = & [\hat{H}_{\text{mol}} + \hat{H}_{\text{rad}} + \hat{V}_{\text{inter}}, \hat{Q}] - \frac{1}{2} \int d\mathbf{r} \{ [\hat{P}(\mathbf{r}), \hat{Q}] \\ & \cdot \hat{E}^{\perp}(\mathbf{r}) + \hat{E}^{\parallel}(\mathbf{r}) \cdot [\hat{P}(\mathbf{r}), \hat{Q}] \} \\ & - \frac{1}{2} \int d\mathbf{r} \{ [\hat{D}^{\perp}(\mathbf{r}), \hat{Q}] \cdot \hat{P}(\mathbf{r}) + \hat{P}(\mathbf{r}) \\ & \cdot [\hat{D}^{\perp}(\mathbf{r}), \hat{Q}] \}, \end{aligned} \quad (2.17)$$

in which all operators are taken at time t . Equation (2.17) is exact.

Writing the Heisenberg equation of motion for the displacement field using Eqs. (2.2a) and (2.4a) directly gives the Maxwell equation in real space

$$\frac{1}{c} \frac{\partial \hat{D}(\mathbf{r})}{\partial t} = \nabla \times \nabla \times \hat{A}(\mathbf{r}). \quad (2.18a)$$

Also, since the displacement field is entirely transverse, we have

$$\nabla \cdot \hat{D}(\mathbf{r}) = 0. \quad (2.18b)$$

The other Maxwell equations

$$\frac{1}{c} \frac{\partial [\nabla \times \hat{A}(\mathbf{r})]}{\partial t} = \nabla \times \hat{E}(\mathbf{r}), \quad (2.18c)$$

$$\nabla \cdot [\nabla \times \hat{A}(\mathbf{r})] = 0, \quad (2.18d)$$

are automatically satisfied by the choice of Coulomb gauge $\nabla \cdot \hat{A}(\mathbf{r}) = 0$. Combining Eqs. (2.18a) and (2.18c) and using Eq. (2.7) leads to the Maxwell wave equation

$$\nabla \times \nabla \times \hat{E}(\mathbf{r}, t) + \frac{1}{c^2} \frac{d^2}{dt^2} \hat{E}(\mathbf{r}, t) = \frac{4\pi d^2}{c^2 dt^2} \hat{P}(\mathbf{r}; t). \quad (2.19)$$

The general solution³³ of Eq. (2.19)

$$\begin{aligned} \hat{E}(\mathbf{r}, t) = & \hat{E}_{\text{ext}}(\mathbf{r}, t) + \int_{-\infty}^t dt' \int_{\epsilon(\mathbf{r})}^V d\mathbf{r}' \mathcal{G}(\mathbf{r} - \mathbf{r}', t - t') \\ & \times \hat{P}(\mathbf{r}', t') - \frac{4\pi}{3} \hat{P}(\mathbf{r}; t) \end{aligned} \quad (2.20a)$$

with the Green's function

$$\mathcal{G}(\mathbf{r} - \mathbf{r}'; t - t') = \int d\omega \mathcal{G}(\mathbf{r} - \mathbf{r}'; \omega) \exp(-i\omega |t - t'|), \quad (2.20b)$$

$$\mathcal{G}(\mathbf{r} - \mathbf{r}'; \omega) = \left(\nabla \nabla + \frac{\omega^2}{c^2} \mathbf{1} \right) \frac{\exp(i\omega |\mathbf{r} - \mathbf{r}'|/c)}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.20c)$$

Here $\hat{E}_{\text{ext}}(\mathbf{r}, t)$ is an external field coming from sources not considered explicitly. The electric field given by Eq.

(2.20a) is defined at all points \mathbf{r} . Within the extent of each charge distribution, the contribution to the field is given by the polarization (the final term). The region of integration in Eq. (2.20a) thus excludes the particular polarization to which \mathbf{r} belongs and hence the second term on the right-hand side gives the field due to all the other molecules. In a later section, we shall calculate the light scattered off a crystal with such polarization. Clearly \mathbf{r} will lie outside the region of the polarizations and we may neglect the final term. The scattered field is the inhomogeneous part of the solution to Eq. (2.20a) superposed with the incident field. Provided we can relate $\hat{E}^{\perp}(\mathbf{r})$ to the full Maxwell field, then using Eq. (2.20a) we will be able to write an equation of motion in which the internal field has been eliminated completely and we require only the external field. Now we may partition the full electric field into its transverse and longitudinal components, each defined at all points \mathbf{r} , such that

$$\hat{E}^{\perp}(\mathbf{r}, t) = \hat{E}(\mathbf{r}, t) - \hat{E}^{\parallel}(\mathbf{r}, t), \quad (2.21a)$$

where the longitudinal part is given by

$$\hat{E}^{\parallel}(\mathbf{r}, t) = -\frac{4\pi}{3} \hat{P}(\mathbf{r}; t) - \int d\mathbf{r}' T(\mathbf{r} - \mathbf{r}') \cdot \hat{P}(\mathbf{r}'; t), \quad (2.21b)$$

which follows using Eq. (2.9a). In Eq. (2.21b), the longitudinal field at the point \mathbf{r} has contributions from the local electric polarization and the electrostatic field due to the remaining dipoles outside the region of polarization containing \mathbf{r} .

Thus we may relate the polarization to either the external or the transverse electric field. This will allow us to calculate both the susceptibility to all orders and the field radiated by a lattice upon which an external field is incident.

III. REAL SPACE TREATMENT OF THE OPTICAL RESPONSE OF MOLECULAR ASSEMBLIES

We now show how the optical response of a finite assembly of multilevel molecules may be formulated with respect to the transverse, external, and local fields. For simplicity, we assume each molecule has a hydrogen-like level scheme with four levels satisfying the selection rules of an s - p transition in hydrogen. For this model, the polarization matrix element for the $|2p_z\rangle \leftarrow |1s\rangle$ transition of a hydrogen atom at the origin is²⁸

$$\begin{aligned} \rho(2p_z; \mathbf{r}) = & -\frac{e\hat{\mathbf{r}} \cos \theta}{\sqrt{32\pi r^2}} \left(\frac{2}{3} \right)^4 \left[6 + 6 \left(\frac{3r}{2a_0} \right) + 3 \left(\frac{3r}{2a_0} \right)^2 \right. \\ & \left. + \left(\frac{3r}{2a_0} \right)^3 \right] \exp(-3r/2a_0), \end{aligned} \quad (3.1a)$$

$$\tilde{\rho}(2p_\alpha, 2p_\beta; \mathbf{r}) = 0, \quad (3.1b)$$

where e is the electronic charge, a_0 is the Bohr radius, and α and β can be x , y , or z . For \hat{Q} , we take the transition operator $\hat{B}_m(t)$ and construct its Heisenberg equation of motion using Eqs. (2.17) and (2.7). We obtain

$$\begin{aligned} \frac{\hbar}{i} \frac{d}{dt} \hat{B}_{m\lambda}(t) = & -\hbar\Omega_{m\lambda} \hat{B}_{m\lambda}(t) + \frac{1}{2} \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \\ & \times [\hat{E}^\perp(\mathbf{r}; t), 1 - \hat{W}_{m\lambda}(t)]_+ \\ & - \frac{1}{2} \sum_{m'} \sum_{\lambda'} J(m\lambda, m'\lambda') \\ & \times [\hat{P}_{m'\lambda'}(t), 1 - \hat{W}_{m\lambda}(t)]_+ \end{aligned} \quad (3.2a)$$

with

$$\hat{P}_{m\lambda} = \hat{B}_{m\lambda} + \hat{B}_{m\lambda}^\dagger, \quad (3.2b)$$

$$\begin{aligned} J(m\lambda, m'\lambda') = & \int d\mathbf{r} \int d\mathbf{r}' \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \cdot T(\mathbf{r} - \mathbf{r}') \\ & \cdot \rho(\lambda'; \mathbf{r}' - \mathbf{R}_{m'}), \end{aligned} \quad (3.2c)$$

and where we have introduced the exciton population operator¹⁵

$$\hat{W}_{m\lambda}(t) \equiv 2\hat{B}_{m\lambda}^\dagger(t) \hat{B}_{m\lambda}(t). \quad (3.2d)$$

In Eq. (3.2), the time dependence of the operators is written explicitly. The prime on the sum indicates that the $m'=m$ term is to be excluded from the summation. To obtain this expression, we have implemented Eq. (2.13). The quantity $J(m\lambda, m'\lambda')$, defined by Eq. (3.2c), may be calculated for each (m, m') if we wish to determine the optical response of a finite assembly of molecules in real space.

$$\begin{aligned} \frac{d^2}{dt^2} \hat{P}_{m\lambda}(t) = & -\Omega_{m\lambda}^2 \hat{P}_{m\lambda}(t) + (\Omega_{m\lambda}/\hbar) \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \cdot [\hat{E}_{\text{ext}}(\mathbf{r}; t), 1 - \hat{W}_{m\lambda}(t)]_+ \\ & + (\Omega_{m\lambda}/\hbar) \sum_{m'} \sum_{\lambda'} \int_{-\infty}^t dt' \\ & \times \Phi(t-t'; m\lambda, m'\lambda') [\hat{P}_{m'\lambda'}(t'), 1 - \hat{W}_{m\lambda}(t)]_+ \\ & + (\Omega_{m\lambda}/\hbar) \sum_{\lambda'} \int_{-\infty}^t dt' (\Phi(t-t'; m\lambda, m\lambda') \\ & + \delta_{t,t'} J(m\lambda, m\lambda')) [\hat{P}_{m\lambda'}(t'), 1 - \hat{W}_{m\lambda}(t)]_+, \end{aligned} \quad (3.4a)$$

where we have defined the retarded Green's function

$$\begin{aligned} \Phi(t-t'; m\lambda, m'\lambda') = & \int d\mathbf{r} \int d\mathbf{r}' \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \\ & \cdot \mathcal{G}(\mathbf{r} - \mathbf{r}'; t - t') \cdot \rho(\lambda'; \mathbf{r}' - \mathbf{R}_{m'}). \end{aligned} \quad (3.4b)$$

Compare this equation with Eq. (3.3). Now, of course, the equation of motion is nonlocal in time and thus does contain retarded interactions, which is natural since we have eliminated the field degrees of freedom; the field signature is represented by the Green's function contained within Φ . The final term will be shown to lead to the single molecule Lamb shift and radiative width. In Sec. IV, we shall show that from Eq. (3.4) we may obtain the field scattered from a finite crystal. This field will depend on retardation effects and will show cooperative radiative decay in reduced dimensions.

Equation (3.2) is the basis for the calculation of the linear and nonlinear responses of our assembly of molecules. In order to solve Eq. (3.2), we also require an equation of motion for the population operator $\hat{W}_{m\lambda}(t)$, which is coupled to $\hat{B}_m(t)$. We thus generate a hierarchy of equations of motion for variables which are products of higher numbers of \hat{B} operators. We may combine Eq. (3.2) with its Hermitian conjugate equation of motion for $\hat{B}_m^\dagger(t)$. We obtain the second order equation

$$\begin{aligned} \frac{d^2}{dt^2} \hat{P}_{m\lambda}(t) = & -\Omega_{m\lambda}^2 \hat{P}_{m\lambda}(t) + (\Omega_{m\lambda}/\hbar) \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \\ & \times [\hat{E}^\perp(\mathbf{r}; t), 1 - \hat{W}_{m\lambda}(t)]_+ \\ & - (\Omega_{m\lambda}/\hbar) \sum_{m'} \sum_{\lambda'} J(m\lambda, m'\lambda') \\ & \times [\hat{P}_{m'\lambda'}(t), 1 - \hat{W}_{m\lambda}(t)]_+. \end{aligned} \quad (3.3)$$

We see that each molecular transition may be viewed as a separate anharmonic oscillator. Equation (3.3) has immediate significance. The tensor $T(\mathbf{r} - \mathbf{r}')$ accounts only for electrostatic interactions between the molecular charge distributions and so all terms are time local and all retardation is included within $\hat{E}^\perp(\mathbf{r}; t)$. The linear susceptibility, which we shall define with respect to the transverse electric field, will thus be nonretarded.

Alternatively, Eqs. (2.21) and (2.20a) relate the transverse Maxwell field to the externally incident field, allowing us to write this result as

We may also define a local field and write

$$\begin{aligned} \frac{d^2}{dt^2} \hat{P}_{m\lambda}(t) = & -\Omega_{m\lambda}^2 \hat{P}_{m\lambda}(t) + (\Omega_{m\lambda}/\hbar) \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \\ & \times [\hat{E}_{\text{local}}(\mathbf{r}; t), 1 - \hat{W}_{m\lambda}(t)]_+, \end{aligned} \quad (3.5a)$$

where

$$\begin{aligned} \hat{E}_{\text{local}}(\mathbf{r}; t) \equiv & \hat{E}^\perp(\mathbf{r}; t) - \sum_{m'} \sum_{\lambda'} \int d\mathbf{r}' T(\mathbf{r} - \mathbf{r}') \\ & \cdot \rho(\lambda'; \mathbf{r}' - \mathbf{R}_{m'}) \hat{P}_{m'\lambda'}(t). \end{aligned} \quad (3.5b)$$

Thus the local field at a point \mathbf{r} is defined as the transverse Maxwell field at that point plus the static field of the polarization distributions outside the distribution to which \mathbf{r} belongs.

Equations (3.3)–(3.5) allow alternate approaches to the calculation of optical response and the outcome of any

such calculation will vary consequently, once approximations are made. It is customary to define the electric susceptibilities of a material as the coefficients of powers of the transverse Maxwell field in a series expansion of the macroscopic electric polarization. Equation (3.3) is the starting point for such a derivation. On the other hand, it is often more convenient to deal only with external sources, in which case, we choose Eq. (3.4). The two approaches are equivalent in the sense that the same information is contained within the respective equations. In Eq. (3.4), the internal field is contained as a memory within the retarded interactions. Similarly, all retardation and electrostatic interaction is included in the definition of the local field, which is the reason that the dielectric function calculated with respect to this field, as opposed to the transverse field, contains a different exciton frequency.¹⁷ We work with equations of motion rather than with an effective Hamiltonian since the result is more transparent and amenable to classical approximations.

IV. LINEAR RESPONSE OF INFINITE NANOSTRUCTURES OF TWO-LEVEL MOLECULES

The equations presented above are written in real space; they do not assume a periodic structure for the molecular crystal. This assumption will be made now in order to solve the equations for simple model systems. We consider a crystal which has arbitrary dimension d and lattice spacing a . We shall take Eq. (3.3), write it in reciprocal space, and use the resulting equation to obtain the linear susceptibility of the crystal. We then present explicit results for a crystal of two-level molecules. The generalization to the four-level sp model is given in Sec. V.

First we linearize Eq. (3.3). This amounts to making the Bose approximation for the commutation relations, defined in Eq. (2.7), to define

$$[\hat{B}_{m\lambda}, \hat{B}_{m'\lambda'}^\dagger] = \delta_{mm'} \delta_{\lambda\lambda'} \tag{4.1}$$

and thus discard all nonlinear effects, which were carried by the products of B operators.¹⁷ We also assume that all molecules are identical, so that we may drop the m label from the exciton frequency Ω , which of course is identical for each level.

We define the continuous and discrete Fourier transforms as

$$F(\mathbf{k}) = \int_V d\mathbf{r} F(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}), \tag{4.2a}$$

$$F(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d\mathbf{k} F(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}), \tag{4.2b}$$

and

$$F_{\mathbf{K}\lambda} = \sum_m F_{m\lambda} \exp(-i\mathbf{K} \cdot \mathbf{R}_m), \tag{4.2c}$$

$$F_{m\lambda} = \frac{1}{N^d} \sum_{\mathbf{K}} \sum_{\mathbf{G}} F_{\mathbf{K}+\mathbf{G},\lambda} \exp[i(\mathbf{K}+\mathbf{G}) \cdot \mathbf{R}_m], \tag{4.2d}$$

respectively, where N^d is the number of molecules in the crystal. \mathbf{R}_m is the vector of the center of mass of molecule m and it is considered to be fixed. \mathbf{K} is a wave vector with dimension d and it is restricted to the first Brillouin zone; higher Brillouin zones are represented by the wave vector \mathbf{G} . For example, we shall use Eq. (4.2b) to write the polarization density Eq. (2.12b) in \mathbf{k} space and Eq. (4.2c) to transform the transition operators defined by Eq. (3.2b).

In the following derivation, we restrict the exciton wave vector to the first Brillouin zone (we neglect Umklapp processes); the complete expressions are derived in Appendix B. Using Eq. (4.2c), we take Eq. (3.3) and make a discrete transform to reciprocal space. In the frequency domain, we obtain

$$\begin{aligned} (-\omega^2 + \Omega^2) \hat{P}_{\mathbf{K}\lambda}(\omega) &= 2(\Omega/\hbar) \sum_m \exp(-i\mathbf{K} \cdot \mathbf{R}_m) \\ &\times \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \hat{E}^{\perp}(\mathbf{r}; \omega) \\ &- 2(\Omega/\hbar) \sum_{\lambda'} J_d(\lambda, \lambda'; \mathbf{K}) \hat{P}_{\mathbf{K}\lambda'}(\omega), \end{aligned} \tag{4.3a}$$

in which we have defined

$$J_d(\lambda, \lambda'; \mathbf{K}) = \sum_{m-m'} \int d\mathbf{r} \int d\mathbf{r}' \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \cdot T(\mathbf{r} - \mathbf{r}') \cdot \rho(\lambda'; \mathbf{r}' - \mathbf{R}_{m'}) \exp[-i\mathbf{K} \cdot (\mathbf{R}_m - \mathbf{R}_{m'})] \tag{4.3b}$$

$$= (2\pi)^{d-3} a^{-d} \int d\mathbf{q}^{3-d} \rho(\lambda; -\mathbf{q} - \mathbf{K}) \cdot T(\mathbf{q} + \mathbf{K}) \cdot \rho(\lambda'; \mathbf{q} + \mathbf{K}). \tag{4.3c}$$

For example, if $d=3$, Eq. (4.3c) is

$$J_3(\lambda, \lambda'; \mathbf{K}) = (1/a^3) \rho(\lambda; -\mathbf{K}) \cdot T(\mathbf{K}) \cdot \rho(\lambda'; \mathbf{K}). \tag{4.3d}$$

There are two important points to note in the derivation of Eq. (4.3). Firstly, we do not evaluate $J(m\lambda, m'\lambda')$ Eq.

(3.2c) in real space before making the transformation; to do so is equivalent to making the dipole approximation and leads to an incorrect result. It is essential to keep the polarization distributions and Fourier transform them individually according to Eq. (4.2b), as hinted by the form of Eq. (4.3b). This point is discussed more fully in Appendix

C, where Eq. (4.3) is derived explicitly. Second, the \mathbf{q} integration arises from the Fourier transform Eq. (4.3b) for \mathbf{K} confined to a chain or monolayer. The polarization will include an integration over the out of chain/plane part of \mathbf{k} , the wave vector associated with the continuous transforms, representing a coupling to a two- or one-dimensional continuum, respectively; (3-d) indicates the dimension of the continuum vector \mathbf{q} which we are required to integrate over.

Note that Eq. (4.3) is diagonal in \mathbf{K} space. Since $J(\lambda, \lambda'; \mathbf{K})$ is independent of the field frequency, it will be taken into the definition of the exciton frequency shortly. We have assumed periodicity of the polarization in order to obtain this result (in a similar way to the periodic Gaussian distribution used by Ewald;³⁴ in our approach, however, the distributions follow naturally from the formalism). It is important to note that Eq. (4.3) holds regardless of the dimensionality of the crystal. It is only when we specify the crystal geometry that effects due to dimension enter in the different forms of J .

In order to obtain the polarization from our equations, we shall return to real space. We define the polarization in this model

$$\hat{\mathcal{P}}_{m\lambda}(\mathbf{r}; \omega) = \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \hat{P}_{m\lambda}(\omega) \quad (4.4a)$$

to be given by the Fourier transform

$$\hat{\mathcal{P}}_{m\lambda}(\mathbf{r}; \omega) = \frac{1}{(2\pi)^3} \int d\mathbf{k} \frac{1}{N^d} \sum_{\mathbf{K}} \hat{\mathcal{P}}_{\mathbf{K}\lambda}(\mathbf{k}; \omega) \times \exp(i\mathbf{K} \cdot \mathbf{R}_m) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (4.4b)$$

where \mathbf{K} is a discrete wave vector and \mathbf{k} is continuous, according to Eq. (4.2). In this section, we specialize to a lattice of two-level molecules simply to illustrate our method; there is then no λ' sum in Eq. (4.3) and we may drop the λ label. The Fourier transform inverse to Eq. (4.4b) is

$$\hat{\mathcal{P}}_{\mathbf{K}}(\mathbf{k}; \omega) = \sum_{\mathbf{K}'} \delta_{\mathbf{K}', \mathbf{K} + \mathbf{k}^{\parallel}} \rho(\mathbf{k}) \hat{P}_{\mathbf{K}'}(\omega), \quad (4.4c)$$

$$\chi^{(1)}(\mathbf{K}; \omega) = \frac{2(\Omega/\hbar a^d)(2\pi)^{d-3} \mu \mu}{-\omega^2 + \Omega^2 + 2(\Omega/\hbar a^d)(2\pi)^{d-3} \int d\mathbf{q}^{3-d} \mu \cdot T(\mathbf{q} + \mathbf{K}) \cdot \mu}. \quad (4.6)$$

Note that for the monolayer in the dipole approximation, Eq. (4.5a) (with $\mathbf{k}=0$) may be written equivalently in a form with the transverse field $\hat{E}^{\perp}(z=0, \mathbf{K}; \omega)$ replacing the \mathbf{q} integration. The susceptibility in this case is given by Eq. (4.6) with $d=2$.

An important conclusion to be made from Eqs. (4.5) and (4.6) is that the susceptibility is real for this model, whether $d=1, 2$, or 3 . This follows since there is an absence of radiative decay in the denominators. The integration in the denominator (for $d=1$ and 2) introduces a shift in the exciton frequency compared with the 3D case and therefore predicts a shift in the resonance energy of the

where a continuous transform was performed on the vector \mathbf{r} and a discrete transform on the lattice points \mathbf{R}_m . Definitions Eqs. (4.4) reflect the periodicity of the charge distributions while acknowledging their three-dimensional nature. Note that the two wave vectors \mathbf{K} and \mathbf{k} are coupled due to the momentum conservation $\delta_{\mathbf{K}', \mathbf{K} + \mathbf{k}^{\parallel}}$,¹² where \mathbf{k}^{\parallel} denotes the part of \mathbf{k} in the dimension of \mathbf{K} . Effects of reduced dimensionality enter when \mathbf{K} is not three dimensional. For one- and two-dimensional crystals, \mathbf{K} is a wave vector confined to a chain or monolayer and \mathbf{k} is a three-dimensional wave vector. Momentum conservation is then restricted to the chain or plane.

We obtain $\hat{P}_{\mathbf{K}'}(\omega)$ directly from Eqs. (4.3). Then, using Eq. (4.4), we obtain the polarization for a d -dimensional crystal ($d=3$ for a bulk crystal, 2 for a monolayer, and 1 for a linear chain)

$$\hat{\mathcal{P}}_{\mathbf{K}}(\mathbf{k}; \omega) = \int d\mathbf{q}^{3-d} \chi^{(1)}(\mathbf{q}, \mathbf{K}, \mathbf{k}^{\parallel}; \omega) \times \hat{E}^{\perp}(\mathbf{q} + \mathbf{K} + \mathbf{k}^{\parallel}; \omega), \quad (4.5a)$$

where the linear susceptibility is given by

$$\chi^{(1)}(\mathbf{q}, \mathbf{K}, \mathbf{k}^{\parallel}; \omega) = \frac{2(\Omega/\hbar a^d)(2\pi)^{d-3} \rho(-\mathbf{q} - \mathbf{K} - \mathbf{k}^{\parallel}) \rho(\mathbf{k})}{-\omega^2 + \Omega^2 + 2(\Omega/\hbar) J_d(\mathbf{K} + \mathbf{k}^{\parallel})}. \quad (4.5b)$$

Equation (4.5b) is the general, nondipole form of the well-known linear susceptibility for a crystal lattice; it is unusual in that it is a function of both \mathbf{K} and \mathbf{k} . Its unusual form results directly from the use of the polarization distribution as opposed to point dipoles.

The dipole approximation in this case is made by taking $\rho(\lambda; \mathbf{k}) = \mu_{\lambda}$, where μ_{λ} is the transition dipole moment in the case of point dipoles—the polarization (2.12) is no longer a function of the continuous variable \mathbf{r} and in reciprocal space we lose all \mathbf{k} dependence. We put $\mathbf{k}=0$ in Eq. (4.5) and obtain

crystal. Equation (4.5) in the dipole approximation corresponds to the definition

$$\hat{\mathcal{P}}_{\mathbf{K}}(\omega) = \mu \hat{P}_{\mathbf{K}}(\omega) = \mu (\hat{B}_{\mathbf{K}} + \hat{B}_{-\mathbf{K}}^{\dagger})(\omega) \quad (4.7)$$

for the polarization of a crystal of two-level molecules. In the 3D case, there is no integration in Eq. (4.6), which then takes the well-known form¹⁵ for a lattice of two-level molecules. For example, the exciton frequency is then

$$\Omega_{\mathbf{K}}^2 \equiv \Omega [\Omega + (2/\hbar a^3) \mu \cdot T(\mathbf{K}) \cdot \mu]. \quad (4.8)$$

In addition to our conclusions here, we point out that higher-order susceptibilities, e.g., $\chi^{(3)}$ will be real, since

they will also be defined with respect to the transverse field. This point agrees with the conclusion of Cho,¹⁸ who formulated a theory using a classical approximation for the field and vector potential within the minimal-coupling Hamiltonian. We have generalized this result and presented an analytic expression for the susceptibility.

We now use Eq. (3.4) to calculate the response with respect to the external field \hat{E}_{ext} . We shall address here the issue of cooperative spontaneous emission. Observe that this equation contains the retarded Green's function. The calculation is similar to the above derivation and we note likewise that the quantity Φ defined by Eq. (3.4b) should not be evaluated in real space (this is equivalent to making the dipole approximation), but in reciprocal space. Following linearization of Eq. (3.4), we obtain terms which are convolutions in time. In the frequency domain, we obtain

$$\begin{aligned}
 (-\omega^2 + \Omega_\lambda^2) \hat{P}_{\mathbf{K}\lambda}(\omega) &= 2(\Omega_\lambda/\hbar) \sum_m \exp(-i\mathbf{K} \cdot \mathbf{R}_m) \\
 &\times \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \hat{E}_{\text{ext}}(\mathbf{r}; \omega) \\
 &+ 2(\Omega_\lambda/\hbar) \sum_{\lambda'} \Phi(\lambda, \lambda'; \mathbf{K}; \omega) \hat{P}_{\mathbf{K}\lambda'}(\omega)
 \end{aligned}
 \tag{4.9a}$$

with

$$\begin{aligned}
 \Phi_d(\lambda, \lambda'; \mathbf{K}; \omega) &= \sum_{m-m'} \int d\mathbf{r} \int d\mathbf{r}' \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \\
 &\times \mathcal{G}(\mathbf{r} - \mathbf{r}'; \omega) \cdot \rho(\lambda'; \mathbf{r}' - \mathbf{R}_{m'}) \\
 &\times \exp[-i\mathbf{K} \cdot (\mathbf{R}_m - \mathbf{R}_{m'})]
 \end{aligned}
 \tag{4.9b}$$

$$\begin{aligned}
 &= (2\pi)^{d-3} a^{-d} \int d\mathbf{q}^{3-d} \rho(\lambda; -\mathbf{q} - \mathbf{K}) \\
 &\cdot \mathcal{G}(\mathbf{q} + \mathbf{K}; \omega) \cdot \rho(\lambda'; \mathbf{q} + \mathbf{K}).
 \end{aligned}
 \tag{4.9c}$$

In the derivation of this result, we have used the definition that the $J(m\lambda, m\lambda')$ part of the final term of Eq. (3.4a) is zero (see Appendix C). The $\Phi(\omega; m\lambda, m\lambda')$ term was added to the third term on the right-hand side of Eq. (3.4a) in order to generate the complete m sum. In \mathbf{k} space, the Green's function is²⁰

$$\mathcal{G}(\mathbf{k}; \omega) = 4\pi \frac{\omega^2/c^2 - \mathbf{k}\mathbf{k}}{\omega^2/c^2 - k^2}.
 \tag{4.11}$$

We may obtain the scattered field off a semi-infinite crystal by taking \mathbf{K} to be a 3D wave vector. The scattered field at \mathbf{r} is obtained from the Fourier transform

$$E(\mathbf{r}; \omega) = \left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k} \exp(i\mathbf{k} \cdot \mathbf{r}) E(\mathbf{k}; \omega)
 \tag{4.12a}$$

with

$$\begin{aligned}
 E(\mathbf{k}; \omega) &= E_{\text{ext}}(\mathbf{k}, \omega) + \sum_m \sum_\lambda \int d\mathbf{r} \int d\mathbf{r}' \exp(-i\mathbf{k} \cdot \mathbf{r}) \\
 &\times \mathcal{G}(\mathbf{r} - \mathbf{r}'; \omega) \mathcal{P}_{m\lambda}(\mathbf{r}'; \omega)
 \end{aligned}
 \tag{4.12b}$$

$$\begin{aligned}
 &= E_{\text{ext}}(\mathbf{k}, \omega) + \sum_{\mathbf{K}} \sum_\lambda \rho(\lambda; \mathbf{k}) \mathcal{G}(\mathbf{k}; \omega) \delta_{\mathbf{K}, \mathbf{k}} \hat{P}_{\mathbf{K}\lambda}(\omega).
 \end{aligned}
 \tag{4.13}$$

We thus obtain $E(\mathbf{k}, \omega)$ from this equation and Eq. (4.9), in an analogous way to the above derivation of the polarization. For our lattice of two-level molecules, the λ' sum in Eq. (4.9) gives a single term and we thus obtain

$$E(\mathbf{k}; \omega) = E_{\text{ext}}(\mathbf{k}, \omega) + \frac{2(\Omega/\hbar a^d) (2\pi)^{d-3} \rho(\mathbf{k}) \mathcal{G}(\mathbf{k}, \omega) \int d\mathbf{q}^{3-d} \rho(-\mathbf{q} - \mathbf{k}^\parallel) E_{\text{ext}}(\mathbf{q} + \mathbf{k}^\parallel, \omega)}{-\omega^2 + \Omega^2 - 2(\Omega/\hbar) \Phi_d(\mathbf{k}^\parallel; \omega)}.
 \tag{4.14}$$

Equation (4.14) is the form of the equations without invoking the dipole approximation. Earlier we stated that it was important to keep the nondipole form of the equation until this point. The reason for this is now apparent, since the non-point-dipole nature of the polarization ensures that Eq. (4.14) contains the \mathbf{q} integration in the denominator and ultimately the cooperative spontaneous emission is introduced by performing this integration. If we make the EDA for the ρ 's at this point, the integrand in the denominator agrees with the result of Orrit and Kottis.¹ Their derivation started with the dipole approximation and required the use of the Ewald summation technique. In our direct derivation, we did not need to introduce the polarization distributions simply to obtain Eq. (4.14), since they were a feature from the outset.

We now turn to the consideration of how spontaneous emission enters into the form of the scattered field. We choose to make the dipole approximation now and write Eq. (4.14) as

$$E(\mathbf{k}; \omega) = E_{\text{ext}}(\mathbf{k}; \omega) + \frac{2(\Omega/\hbar a^d) (2\pi)^{d-3} \mu\mu \mathcal{G}(\mathbf{k}; \omega) \int d\mathbf{q}^{3-d} E_{\text{ext}}(\mathbf{q} + \mathbf{k}^\parallel; \omega)}{-\omega^2 + \Omega^2 - 2(\Omega/\hbar a^d) (2\pi)^{d-3} \int d\mathbf{q}^{3-d} \mu \cdot \mathcal{G}(\mathbf{q} + \mathbf{k}^\parallel; \omega) \cdot \mu}
 \tag{4.15}$$

with $|\mathbf{q} + \mathbf{k}^\parallel| = (q^2 + k^\parallel{}^2)^{1/2}$ in the denominator of the Green's function (4.11). The entire polariton dynamics of the crystal are contained within this equation. If $k^\parallel < (\omega/c)$, the 1D (or 2D) polariton state is radiatively stable; if $k^\parallel > (\omega/c)$, the integral gives rise to an imaginary part and corresponds to a polariton state which is radiatively

unstable, since the exciton will have energy greater than the threshold of the photon continuum ($\mathbf{q}=0$), into which it will emit. Thus from Eq. (4.15) we may obtain the well-known polariton dispersion curves for finite (one- or two-dimensional) crystals.^{13,14} We will not repeat this analysis here. We will just show how cooperative spontaneous emis-

sion effects arise. Performing the \mathbf{q} integration, choosing $\mathbf{k}^{\parallel}=0$, and taking the Markovian limit (i.e., $\omega \rightarrow \Omega$) gives for the denominator of the second term of Eq. (4.15)

$$-\omega^2 + \Omega^2 - 8\pi(\Omega/\hbar a^3)\mu^2, \quad d=3, \quad (4.16a)$$

$$-\omega^2 + \Omega^2 + 3\pi i(\Omega/\hbar)\gamma(\Omega)\left(\frac{\tilde{\lambda}}{a}\right)^2, \quad d=2, \quad (4.16b)$$

$$-\omega^2 + \Omega^2 + (3\pi i/2)(\Omega/\hbar)\gamma(\Omega)\left(\frac{\tilde{\lambda}}{a}\right), \quad d=1, \quad (4.16c)$$

in the case of a 3D crystal, monolayer, and a one-dimensional lattice respectively, where the single molecule radiative width is

$$\gamma(\omega) = \frac{4\omega^3}{3c^3}\mu^2. \quad (4.16d)$$

We have defined the wavelength $\tilde{\lambda}=c/\Omega$. First it is well known that an infinite bulk crystal is radiatively stable. Equation (4.15) for a bulk crystal of two-level molecules possesses no radiative width, since there is no integration and $\mathcal{G}(\mathbf{k};\omega)$ is real. The cooperative effects therefore arise only for the one- and two-dimensional systems; we observe an additional width proportional to $(\tilde{\lambda}/a)^d$ times the single

molecule width with $d=1$ and 2. The linewidth is therefore greater for the monolayer than the chain even though it is coupled to a continuum which is less dense. This is also well known; the effective oscillator strength is larger because of the greater number of dipole-dipole interactions for a dipole in a plane compared with a dipole in a chain. This analysis is consistent with our comments of Sec. III, namely that these effects arise following the elimination of the internal field in favor of the external field. This is very different from the results of the first part of this section, where all retardation effects are present in the transverse field.

V. LINEAR SUSCEPTIBILITIES OF AND LIGHT SCATTERING BY PERIODIC NANOSTRUCTURES OF *sp* MOLECULES

In this section, we extend the two-level calculation and derive the polarization and scattered field for a lattice of four-level hydrogen-like molecules (*sp* molecules). We first derive the 3D result. The transition operators in the oscillator equations (4.3) and (4.9) are now coupled; Eq. (4.3) written in full, with $\lambda=x, y$, and z in short and $\beta=2\Omega/\hbar$, is

$$\begin{bmatrix} -\omega^2 + \Omega^2 + \beta J(x,x;\mathbf{K}) & \beta J(x,y;\mathbf{K}) & \beta J(x,z;\mathbf{K}) \\ \beta J(y,x;\mathbf{K}) & -\omega^2 + \Omega^2 + \beta J(y,y;\mathbf{K}) & \beta J(y,z;\mathbf{K}) \\ \beta J(z,x;\mathbf{K}) & \beta J(z,y;\mathbf{K}) & -\omega^2 + \Omega^2 + \beta J(z,z;\mathbf{K}) \end{bmatrix} \begin{bmatrix} \hat{P}_{\mathbf{K},x}(\omega) \\ \hat{P}_{\mathbf{K},y}(\omega) \\ \hat{P}_{\mathbf{K},z}(\omega) \end{bmatrix} = \frac{\beta}{a^3} \begin{bmatrix} \rho(x;-\mathbf{K}) \\ \rho(y;-\mathbf{K}) \\ \rho(z;-\mathbf{K}) \end{bmatrix} \hat{E}^{\perp}(\mathbf{K},\omega). \quad (5.1a)$$

In matrix form, with $\mathcal{B}(\mathbf{K},\omega)$ and $R(\mathbf{K})$ defining column vectors for the transition operators and matrix elements, respectively, this equation reads

$$\Theta(\mathbf{K})\mathcal{B}(\mathbf{K};\omega) = (\beta/a^3)R(-\mathbf{K})E(\mathbf{K},\omega). \quad (5.1b)$$

We invert Eq. (5.1b) and substitute into Eq. (4.4). Applying the momentum conservation gives

$$\hat{\mathcal{P}}_{\mathbf{K}}(\mathbf{k};\omega) = \sum_{\lambda} \hat{\mathcal{P}}_{\mathbf{K}\lambda}(\mathbf{k};\omega) = \chi^{(1)}(\mathbf{K},\mathbf{k};\omega) \hat{E}^{\perp}(\mathbf{K}+\mathbf{k};\omega) \quad (5.2a)$$

with

$$\chi^{(1)}(\mathbf{K},\mathbf{k};\omega) = (\beta/a^3)R(\mathbf{k})^T \Theta(\mathbf{K}+\mathbf{k})^{-1} R(-\mathbf{K}-\mathbf{k}). \quad (5.2b)$$

In Eq. (5.2b), $\Theta(\mathbf{K}+\mathbf{k})^{-1}$ is then the inverse of a $\lambda \times \lambda$ matrix of the coefficients of the coupled equations for $\hat{P}_{\mathbf{K}+\mathbf{k},\lambda}(\omega)$, T denotes the transpose of the column vector, and $(1/a^3)$ is the molecular density in the crystal. In Sec. IV, we discussed the meaning of these wave vectors and commented on the form of the linear susceptibility for the lattice of two-level molecules in the dipole approximation.

Under these conditions (setting $\mathbf{k}=0$ and considering only one excited level), Eq. (5.2b) reduces to Eq. (4.6) written for $d=3$, with the susceptibility a function of \mathbf{K} only.

For a 1D or 2D crystal, we follow the arguments of Sec. IV to obtain the coupling of the exciton to the out-of-plane/chain continuum. The polarization is then

$$\hat{\mathcal{P}}_{\mathbf{K}}(\mathbf{k};\omega) = \tilde{\beta} \int d\mathbf{q}^{3-d} R(\mathbf{k})^T \Theta(\mathbf{K}+\mathbf{k}^{\parallel})^{-1} \times R(-\mathbf{q}-\mathbf{K}-\mathbf{k}^{\parallel}) \hat{E}^{\perp}(\mathbf{q}+\mathbf{K}+\mathbf{k}^{\parallel};\omega), \quad (5.3)$$

where, e.g., the diagonal element of the matrix $\Theta(\mathbf{K}+\mathbf{k}^{\parallel})$ is

$$-\omega^2 + \Omega^2 + \beta J_d(\lambda,\lambda;\mathbf{K}+\mathbf{k}^{\parallel}) \quad (5.4a)$$

and

$$\tilde{\beta} = (2\Omega/\hbar a^d) (2\pi)^{d-3}. \quad (5.4b)$$

We now derive the field scattered by the lattice of *sp* molecules. The coupled equations (4.9) may be written as

$$\Theta'(\mathbf{K})\mathcal{B}(\mathbf{K};\omega) = (\beta/a^3)R(-\mathbf{K})E_{\text{ext}}(\mathbf{K};\omega), \quad (5.5)$$

where $\Theta'(\mathbf{K})$ is a matrix of coefficients similar to $\Theta(\mathbf{K})$, with the quantities J replaced by the corresponding quantity Φ . Compared with $\Theta(\mathbf{K})$, its diagonal elements are

$$-\omega^2 + \Omega^2 + \beta\Phi_3(\lambda, \lambda; \mathbf{K}; \omega). \quad (5.6)$$

The scattered field is therefore obtained by the straightforward inversion of a 3×3 matrix as in Eq. (5.2). We substitute for $\hat{P}_{\mathbf{K}\lambda}(\omega)$ following the inversion of Eq. (5.5) and obtain

$$E(\mathbf{k}, \omega) = E_{\text{ext}}(\mathbf{k}, \omega) + (\beta/a^3) \mathcal{G}(\mathbf{k}; \omega) R(\mathbf{k})^T \Theta'(\mathbf{k})^{-1} \times R(-\mathbf{k}) E_{\text{ext}}(\mathbf{k}, \omega). \quad (5.7)$$

This is the Fourier component of the scattered field for a semi-infinite crystal. If the exciton wave vector \mathbf{K} is confined to a chain or monolayer, the result is modified in direct analogy to the changes induced in $\chi^{(1)}$. For a d -dimensional crystal, Eq. (5.7) becomes

$$E(\mathbf{k}, \omega) = E_{\text{ext}}(\mathbf{k}, \omega) + \tilde{\beta} \int d\mathbf{q}^{3-d} \mathcal{G}(\mathbf{k}; \omega) R(\mathbf{k})^T \times \Theta'(\mathbf{k})^{-1} R(-\mathbf{q}-\mathbf{k}) E_{\text{ext}}(\mathbf{q}+\mathbf{k}, \omega). \quad (5.8)$$

The off-diagonal element of $\Theta'(\mathbf{k})$, e.g., is

$$\beta\Phi_d(\lambda, \lambda'; \mathbf{k}^{\parallel}; \omega). \quad (5.9)$$

Equations (5.3) and (5.8) are the polarization and scattered field analogs, for a lattice of sp molecules, of the results (4.5) and (4.14) for the lattice of two-level molecules. The physics of the optical response is well described by both sets of results.

VI. CONCLUSIONS

We have calculated both the linear susceptibility of a molecular crystal of reduced dimensionality and the field scattered by this crystal. We have demonstrated the appropriate choice of field for such calculations; working with $\hat{E}^1(\mathbf{r}; \omega)$ by design gives us an unretarded description of the susceptibilities, with retardation entering only through the solution of the Maxwell wave equation. If we work with the external field, on the other hand, there are no field degrees of freedom, since they have been eliminated in favor of a polarization which has a memory of retarded interactions. Bedeaux and Bloembergen²⁴ first proposed a susceptibility which is nonretarded. Their conclusion is correct, although they did not address the point of retardation directly. A further point of note here is the choice of working gauge. We chose the Coulomb gauge for convenience, since we wished the Hamiltonian to include an explicit Coulomb potential term. However, Maxwell's equations, the electric polarization, and the vectors of the transverse and total Maxwell fields, with which we work, are each gauge invariant; all of the results presented here are thus valid in any gauge.

In the derivations of Secs. IV and V, we chose to work with equations of motion for the transition operators $\hat{P}_{m\lambda}$ rather than for the full polarization operator; in so doing, we are not invoking the EDA, yet we are assuming the

advantages of its use, since we may still make the discrete transform to reciprocal space. Our approach has overcome the problems (divergences, etc.) associated with the EDA. First, when dealing with short-range interactions in the EDA, a self-energy is introduced by the exclusion of a region, e.g., sphere around the point of singularity of the problem. In long-range problems, the nonconvergence of dipole sums^{1,23} is usually overcome by the neat, yet artificial trick of the Ewald summation procedure in which the point dipoles are treated in part of the derivation as Gaussian dipole distributions before returning to the EDA. Ewald's method elegantly captures the physics of the problem, yet the point dipole is singular. Instead of introducing and curing this singularity, we obtain the correct result directly, without the requirement for such devices, and perform the dipole approximation, only for convenience, on our final result, which concurs with previous studies of cooperative spontaneous emission in confined geometries. Equation (4.16) may also be obtained from the superradiant master equation of Lehmburg³¹ written in reciprocal space.

Our results agree with the nonlocal susceptibility proposed by Cho.¹⁸ However, the present approach has two advantages (i) we work with single-molecule and not the global crystal states. Thus matrix inversion, required in order to calculate the scattered field as we have done here, would be much simpler ($N \times L$ by $N \times L$ as opposed to L^N by L^N in his method for a lattice of N L -level molecules) should we have formulated our approach in his way; (ii) his formulation assumes a classical approximation for the field, necessary in order to express the nonlocal susceptibility in terms of a correlation function of the unretarded polarization operators. Since we are solving the linear optics, however, there is no requirement to take the classical approximation, as the equations are not affected by this; (iii) we do not invoke the EDA; (iv) the generalization to nonlinear optics is straightforward. Only when we address the higher-order susceptibilities must we consider the appropriate factorization approximation for the product of matter and \hat{E} -field operators.

It is possible to extend this model by the inclusion of phonons (we may incorporate translational motion in the Hamiltonian to do this). We then must include the field at the outset in order to describe the damping of polaritons by the phonons.¹⁷ The calculation of optical response can thus no longer be separated into the two-step procedure of the calculation of $\chi^{(1)}$ and the solution of the Maxwell wave equation.

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APPENDIX A: EQUATIONS OF MOTION IN TERMS OF THE FULL MAXWELL FIELD

The equation of motion (2.17) presented in Sec. II describes the time evolution of an operator relative to the transverse Maxwell field. It is possible to restructure this equation so that it is expressed relative to the full Maxwell field $\hat{E}(\mathbf{r})$ by defining

$$\hat{V}_{\text{inter}} = \frac{1}{8\pi} \int d\mathbf{r} \hat{E}^{\parallel}(\mathbf{r}) \cdot \hat{E}^{\parallel}(\mathbf{r}) - 2\pi \sum_m \int d\mathbf{r} |\hat{\mathcal{P}}_m^{\parallel}(\mathbf{r})|^2, \quad (\text{A1})$$

with

$$\begin{aligned} & -2\pi \sum_m \int d\mathbf{r} |\hat{\mathcal{P}}_m^{\parallel}(\mathbf{r})|^2 \\ & = -\frac{2\pi}{3} \sum_m \int d\mathbf{r} \hat{\mathcal{P}}_m(\mathbf{r}) \cdot \hat{\mathcal{P}}_m(\mathbf{r}) \\ & \quad - \frac{1}{2} \sum_m \int d\mathbf{r} \int d\mathbf{r}' \hat{\mathcal{P}}_m(\mathbf{r}) T(\mathbf{r}-\mathbf{r}') \cdot \hat{\mathcal{P}}_m(\mathbf{r}'). \end{aligned} \quad (\text{A2})$$

Equation (A1) follows since the longitudinal electric field is defined everywhere. To define \hat{V}_{inter} , we must therefore subtract the longitudinal self-interactions of the polarization from the longitudinal electric field product, which represents the total electrostatic interaction. Thus, for an arbitrary operator \hat{Q} , the Heisenberg equation of motion is

$$\begin{aligned} \frac{\hbar}{i} \frac{\partial \hat{Q}}{\partial t} = & (\hat{H}_{\text{mol}} + \hat{H}_{\text{rad}}, \hat{Q}) - \frac{1}{2} \int d\mathbf{r} \{ [\hat{P}(\mathbf{r}), \hat{Q}] \cdot \hat{E}(\mathbf{r}) + \hat{E}(\mathbf{r}) \cdot [\hat{P}(\mathbf{r}), \hat{Q}] \} - 2\pi \sum_m \int d\mathbf{r} \{ [\hat{\mathcal{P}}_m^{\parallel}(\mathbf{r}), \hat{Q}] \cdot \hat{\mathcal{P}}_m^{\parallel}(\mathbf{r}) \\ & + \hat{\mathcal{P}}_m^{\parallel}(\mathbf{r}) \cdot [\hat{\mathcal{P}}_m^{\parallel}(\mathbf{r}), \hat{Q}] \} - \frac{1}{2} \int d\mathbf{r} \{ [\hat{D}^{\perp}(\mathbf{r}), \hat{Q}] \cdot \hat{P}(\mathbf{r}) + \hat{P}(\mathbf{r}) \cdot [\hat{D}^{\perp}(\mathbf{r}), \hat{Q}] \}, \end{aligned} \quad (\text{A3})$$

in which all operators are taken at time t . Note that this form of the equation of motion does not contain explicit intermolecular interactions, in contrast to Eq. (2.17). These have been removed using Eq. (A1); the commutator of the first term on the right-hand side of Eq. (A1) with \hat{Q} may then be combined with the second term of Eq. (2.17) to give the above equation of motion. We treat the third term on the right-hand side using Eq. (A2). For example, our oscillator equation now reads

$$\begin{aligned} \frac{d^2}{dt^2} \hat{P}_{m\lambda}(t) = & -\Omega_{m\lambda}^2 \hat{P}_{m\lambda}(t) + (\Omega_{m\lambda}/\hbar) \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \cdot [\hat{E}(\mathbf{r}; t), 1 - 2\hat{W}_{m\lambda}(t)]_+ + (\Omega_{m\lambda}/\hbar) \sum_{\lambda'} J(m\lambda, m\lambda') \\ & \times [\hat{P}_{m\lambda'}(t), 1 - \hat{W}_{m\lambda'}(t)]_+ + (4\pi\Omega_{m\lambda}/3\hbar) \sum_{\lambda'} \int d\mathbf{r} \rho(\lambda; \mathbf{r} - \mathbf{R}_m) \rho(\lambda'; \mathbf{r} - \mathbf{R}_m) [\hat{P}_{m\lambda'}(t), 1 - \hat{W}_{m\lambda'}(t)]_+, \end{aligned} \quad (\text{A4})$$

where the time dependence of the operators is denoted in the same manner as in Sec. III. The final two terms are self-interactions of the molecule m . Equation (A4) is useful if we want to work with the total Maxwell field. However, note that $\hat{E}(\mathbf{r}; \omega)$ must contain all retardation and intermolecular interactions. Thus if we were to define the susceptibility with respect to this field, the exciton frequency would not contain these interactions. This shows the advantage of using the transverse Maxwell field, as given by Sec. IV. The results of Sec. III may likewise be obtained from Eq. (A4), with the use of Eqs. (2.20a) and (2.21).

APPENDIX B: INCLUSION OF UMKLAPP PROCESSES

In Secs. IV and V, we neglected the conservation of momentum which coupled the exciton wave vector \mathbf{K}' to wave vectors outside the first Brillouin zone (Umklapp processes). In addition to the use of the transform equation (4.2d), we must make use of the relationships

$$\sum_m \exp[i(\mathbf{K}' - \mathbf{K} - \mathbf{k}) \cdot \mathbf{R}_m] = N^3 \sum_{\mathbf{G}} \delta_{\mathbf{G}, \mathbf{K}' - \mathbf{K} - \mathbf{k}} \quad (\text{B1})$$

for the 3D case, or

$$\sum_m \exp[i(\mathbf{K}' - \mathbf{K} - \mathbf{k}) \cdot \mathbf{R}_m] = N^d \sum_{\mathbf{G}} \delta_{\mathbf{G}, \mathbf{K}' - \mathbf{K} - \mathbf{k}^{\parallel}} \quad (\text{B2})$$

if \mathbf{K} and \mathbf{K}' are vectors in one or two dimensions, while performing the transform to reciprocal space. The polarization in real space [Eq. (4.4b)] should read

$$\begin{aligned} \mathcal{P}_{m\lambda}(\mathbf{r}; \omega) = & \frac{1}{(2\pi)^3} \int d\mathbf{k} \frac{1}{N^d} \\ & \times \sum_{\mathbf{K}} \sum_{\mathbf{G}} \hat{\mathcal{P}}_{\mathbf{K} + \mathbf{G}, \lambda}(\mathbf{k}; \omega) \\ & \times \exp[i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{R}_m] \exp[i\mathbf{k} \cdot \mathbf{r}] \end{aligned} \quad (\text{B3})$$

and have a corresponding inverse transform

$$\hat{\mathcal{P}}_{\mathbf{K}\lambda}(\mathbf{k};\omega) = \sum_{\mathbf{G}} \sum_{\mathbf{K}'} \sum_{\mathbf{G}'} \rho(\lambda; \mathbf{k}; \mathbf{K}') \hat{P}_{\mathbf{K}'+\mathbf{G}',\lambda}(\omega) \times \delta_{\mathbf{K}'+\mathbf{G}',\mathbf{G}+\mathbf{K}+\mathbf{k}} \quad (\text{B4})$$

We calculate the quantity $\hat{P}_{\mathbf{K}'+\mathbf{G}',\lambda}(\omega)$, substitute it into Eq. (B4), and implement the momentum conservation. The form of the equations is best illustrated for the lattice of two-level molecules. We obtain

$$\hat{P}_{\mathbf{K}'+\mathbf{G}'}(\omega) = \frac{\tilde{\beta} \sum_{\mathbf{G}''} \int d\mathbf{q}^{3-d} \rho(-\mathbf{q}-\mathbf{K}'-\mathbf{G}'-\mathbf{G}'') \hat{E}^{\perp}(\mathbf{q}+\mathbf{K}'+\mathbf{G}'+\mathbf{G}'';\omega)}{-\omega^2 + \Omega^2 + \beta J_d(\mathbf{K}'+\mathbf{G}')} \quad (\text{B5})$$

where the quantity defined in Eq. (4.3c) is given by

$$J_d(\lambda, \lambda'; \mathbf{K}) = (2\pi)^{d-3} a^{-d} \sum_{\mathbf{G}''} \int d\mathbf{q}^{3-d} \rho(\lambda; -\mathbf{q}-\mathbf{K}-\mathbf{G}'') \cdot T(\mathbf{q}+\mathbf{K}+\mathbf{G}'') \cdot \rho(\lambda', \mathbf{q}+\mathbf{K}+\mathbf{G}'') \quad (\text{B6})$$

after neglecting the \mathbf{G}'' sum. The polarization in reciprocal space is then

$$\hat{\mathcal{P}}_{\mathbf{K}\lambda}(\mathbf{k};\omega) = \tilde{\beta} \sum_{\mathbf{G}} \frac{\sum_{\mathbf{G}''} \int d\mathbf{q}^{3-d} \rho(\mathbf{k}) \rho(-\mathbf{q}-\mathbf{K}-\mathbf{G}-\mathbf{G}''-\mathbf{k}^{\parallel}) \hat{E}^{\perp}(\mathbf{q}+\mathbf{K}+\mathbf{G}+\mathbf{G}''+\mathbf{k}^{\parallel};\omega)}{-\omega^2 + \Omega^2 + \beta J_d(\mathbf{K}+\mathbf{G}+\mathbf{k}^{\parallel})} \quad (\text{B7})$$

The scattered field including Umklapp processes is derived in a similar way and is

$$\hat{E}(\mathbf{k};\omega) = \hat{E}_{\text{ext}}(\mathbf{k};\omega) + \tilde{\beta} \rho(\mathbf{k}) \mathcal{G}(\mathbf{k};\omega) \sum_{\mathbf{G}} \frac{\sum_{\mathbf{G}''} \int d\mathbf{q}^{3-d} \rho(-\mathbf{q}-\mathbf{G}-\mathbf{G}''-\mathbf{k}^{\parallel}) \hat{E}_{\text{ext}}(\mathbf{q}+\mathbf{G}+\mathbf{G}''+\mathbf{k}^{\parallel};\omega)}{-\omega^2 + \Omega^2 + \beta \Phi_d(\mathbf{G}+\mathbf{k}^{\parallel})} \quad (\text{B8})$$

Since the contributions from Umklapp processes are expected to be very small for $\mathbf{G} \neq 0, 1, 2, 3$ we neglect the \mathbf{G} summations.

APPENDIX C: CALCULATION OF $J_d(\lambda, \lambda'; \mathbf{K})$

In the derivation of Eq. (4.3), we stressed that the electrostatic interaction between spatially extended charge distributions (3.2c) should not be evaluated in real space. Before expanding on this statement, we first derive the quantity $J_d(\lambda, \lambda'; \mathbf{K})$ [Eq. (4.3c)], which is used throughout Secs. IV and V. We are interested in the discrete transform of Eq. (3.3). In particular, the transform of the final term is, neglecting higher Brillouin zones,

$$\sum_m \sum_{m'} \exp(-i\mathbf{K} \cdot \mathbf{R}_m) \int d\mathbf{r} \int d\mathbf{r}' \rho(\lambda; \mathbf{r}-\mathbf{R}_m) \cdot T(\mathbf{r}-\mathbf{r}') \cdot \rho(\lambda'; \mathbf{r}'-\mathbf{R}_{m'}) \hat{P}_{m'\lambda'}(\omega), \quad (\text{C1})$$

where we have omitted the prefactor and λ' sum as they are not part of the derivation. In Eq. (C1), the $m'=m$ term is excluded from the sum. We define the quantity $J(m\lambda, m\lambda')$ to be zero. We then have complete sums and are able to write Eq. (C1) as

$$\sum_{m-m'} \exp[-i\mathbf{K} \cdot (\mathbf{R}_m - \mathbf{R}_{m'})] \int d\mathbf{r} \int d\mathbf{r}' \rho(\lambda; \mathbf{r}-\mathbf{R}_m) \times T(\mathbf{r}-\mathbf{r}') \cdot \rho(\lambda'; \mathbf{r}'-\mathbf{R}_{m'}) \sum_{m'} \hat{P}_{m'\lambda'}(\omega) \times \exp(-i\mathbf{K} \cdot \mathbf{R}_{m'}) \quad (\text{C2})$$

We now use Eq. (4.2b) to transform both polarization functions and $T(\mathbf{r}-\mathbf{r}')$ to \mathbf{k} space and Eq. (4.2c) to perform the m' sum. Equation (C2) becomes

$$(1/2\pi)^{-9} \sum_{m-m'} \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{k}_1 \int d\mathbf{k}_2 \int d\mathbf{k}_3 \rho(\lambda; \mathbf{k}_1) \times T(\mathbf{k}_2) \cdot \rho(\lambda'; \mathbf{k}_3) \hat{P}_{\mathbf{K}\lambda'}(\omega) \exp[-i(\mathbf{K}+\mathbf{k}_1) \cdot \mathbf{R}_m] \times \exp[i(\mathbf{K}-\mathbf{k}_3) \cdot \mathbf{R}_{m'}] \exp[i(\mathbf{k}_1+\mathbf{k}_2) \cdot \mathbf{r}] \times \exp[i(\mathbf{k}_3-\mathbf{k}_2) \cdot \mathbf{r}'] \quad (\text{C3})$$

After integration over \mathbf{r} and \mathbf{r}' , and some algebra, we obtain (dropping the subscript 1 on \mathbf{k}_1)

$$(2\pi)^{d-3} a^{-d} \sum_{\mathbf{k}_{\parallel}^d} \int d\mathbf{k}_1^{3-d} \rho(\lambda; -\mathbf{k}) \cdot T(\mathbf{k}) \cdot \rho(\lambda'; \mathbf{k}) \hat{P}_{\mathbf{K}\lambda'}(\omega) \delta_{\mathbf{K}, \mathbf{k}_{\parallel}} \quad (\text{C4})$$

where we have divided \mathbf{k} into a continuous part \mathbf{k}_{\parallel}^d , which we shortly redefine as \mathbf{q} , and a discrete part \mathbf{k}_{\parallel}^d which has the dimension of \mathbf{K} . Of course, for the 3D case, Eq. (C4) does not contain a sum. From Eq. (C4), we obtain the quantity

$$(2\pi)^{d-3} a^{-d} \int d\mathbf{q}^{3-d} \rho(\lambda; -\mathbf{q}-\mathbf{K}) \cdot T(\mathbf{q}+\mathbf{K}) \cdot \rho(\lambda'; \mathbf{q}+\mathbf{K}) \hat{P}_{\mathbf{K}\lambda'}(\omega) \equiv J_d(\lambda, \lambda'; \mathbf{K}) \hat{P}_{\mathbf{K}\lambda'}(\omega) \quad (\text{C5})$$

The derivation of $\Phi_d(\lambda, \lambda'; \mathbf{K}; \omega)$ [Eq. (4.9c)] follows identically. It is only following Eq. (B3) that we are assured of obtaining the \mathbf{q} integration, which leads to the cooperative effects discussed in Sec. IV. The evaluation of $J(m\lambda, m'\lambda')$ in real space is equivalent to making the dipole approximation; we would obtain a quantity dependent only on \mathbf{R}_m and $\mathbf{R}_{m'}$ and the subsequent transform to \mathbf{K} space would

miss the pertinent physics. The correct derivation of the optical response is obtained only if the polarization densities are transformed to \mathbf{k} space and the appropriate momentum conservation is applied. The EDA may be invoked only at the end of the calculation.

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