

Nonlinear optical response in condensed phases: A microscopic theory using the multipolar Hamiltonian

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A general scheme is presented for calculating the nonlinear optical response in condensed phases that provides a unified picture of excitons, polaritons, retardation, and local-field effects in crystals and in disordered systems. A fully microscopic starting point is taken by considering the evolution of the quantized radiation-matter system described by the multipolar ($\mu \cdot \mathbf{D}^{\dagger}$) Hamiltonian. For a molecular system with localized electronic states we derive equations of motion in which the instantaneous intermolecular interactions are explicitly recovered and the interaction with the Maxwell electric field is of the $\mu \cdot \mathbf{E}^{\dagger}$ type. It is shown that with total neglect of retardation, these equations lead to the usual expressions for nonlinear optical susceptibilities in terms of equilibrium correlation functions of the polarization field of the molecular system. A mean-field approximation for these equations of motion yields the commonly used local-field expression. Finally, a procedure is proposed for calculating the optical response that fully accounts for retardation, based on a hierarchy of equations of motion for polaritons.

I. INTRODUCTION

The theoretical calculation of the nonlinear optical response of condensed phases is an important step towards the interpretation of the many experimental studies performed in this field. Often, the response is expressed in a convenient way by means of susceptibilities,¹⁻³ which are the expansion coefficients of the material polarization field in terms of the average Maxwell (internal) electric field. The calculation of the optical signal then follows from using these susceptibilities in conjunction with the Maxwell equations and the appropriate boundary conditions. Traditionally, susceptibilities are considered purely material quantities, given by equilibrium correlation functions of the polarization field of the material system with *instantaneous* Coulomb interactions between its constituents.⁴⁻⁶ This result is usually derived by performing response theory on the material system with respect to the external laser fields and by noticing that the transverse Maxwell field is equal to the external field if retarded interactions are neglected.⁶ However, the picture of the material system with Coulomb interactions being perturbed by the external fields is microscopically not justified. In general, the transverse radiation field must be considered a degree of freedom and the evolution of the coupled radiation-matter system should be studied in the description of optical processes. In contrast to the common belief that susceptibilities are insensitive to retardation, it has recently been shown both experimentally⁷ and theoretically⁸ that in crystals at low temperature the susceptibilities contain damping constants which are given by scattering rates of mixed material-radiation eigenstates (polaritons) on phonons. Many other nonlinear optical experiments on semiconductors,⁹ molecular crystals,¹⁰ ionic crystals,^{11,12} and solutions¹³ are currently interpreted in terms of creation,

propagation, scattering and detection of excitonic or vibronic polaritons. An example is the creation of picosecond phonon-polariton pulses in ammonium chloride and their detection at a different point of the crystal using time- and space-resolved coherent anti-Stokes Raman spectroscopy¹¹ (CARS). The concept of susceptibilities is not used in the phenomenological explanation of these experiments; in fact, the usefulness of susceptibilities in situations of strong radiation-matter coupling should be doubted. On the other hand, there are many experimental situations (see Sec. VI) in which polaritons cannot play a role and the susceptibilities are useful measures of the optical response. The connection between these two regimes is an important problem, which can only be addressed by treating them from a unified starting point.

Even if the role of the radiation field is totally neglected, the actual calculation of susceptibilities in dense systems is not trivial. Namely, the application of response theory requires the knowledge of the eigenstates of the material system with instantaneous intermolecular interactions, which for many systems, in particular for disordered media, cannot be obtained. One therefore often resorts to the local-field approximation.^{3,14} This is a mean-field theory in which one focuses on the response of a single molecule to an effective (local) electric field which contains the effects of the electrostatic interactions with the environment. The susceptibilities are then simply given by the single-molecule hyperpolarizabilities (which are obtained from time-dependent perturbation theory) multiplied by appropriate local-field correction factors.

In this paper, we derive equations of motion which serve as a general starting point for calculating the optical response of an arbitrary molecular system with localized electronic states, and we discuss several practical approximate ways to exploit these equations. We consider

the time evolution of the complete system consisting of the molecules and the radiation field, which allows us to describe retardation effects. As in an earlier publication,¹⁵ we use the multipolar ($\mu \cdot \mathbf{D}^\perp$) Hamiltonian.^{16,17} In contrast to Ref. 15, however, our present approach is technically much less involved and, moreover, the results are valid for arbitrary configurations of multilevel molecules. Advantages of the multipolar Hamiltonian over the often used minimal coupling ($\mathbf{p} \cdot \mathbf{A}$) Hamiltonian^{16,17} are (i) the appearance of the electric displacement field in it rather than the vector potential, so that it is inherently gauge independent and, moreover, the equations of motion obtained from it lend themselves better for numerical propagation (Maxwell-Bloch equations); (ii) the possibility to define, under certain approximations, a local field (see below). The drawback of the multipolar Hamiltonian is the absence of explicit intermolecular interactions in it; these are carried through exchange of photons. The interactions may be recovered by eliminating the radiation field,¹⁸ but this procedure does not make a clear separation between retarded and instantaneous interactions and, furthermore, it is impossible to describe mixed material-radiation eigenmodes after this elimination. The approach that we present in this paper recovers in a straightforward way the instantaneous interactions (Sec. II), and still allows for the treatment of polariton states (Sec. III). It is shown under what conditions susceptibilities can be calculated by using response theory (Sec. IV), and when these susceptibilities can be obtained from a local-field approach (Sec. V). In Sec. VI, we discuss in what situations susceptibilities are no longer expected to be useful and how in that case, too, our equations may be exploited to calculate the optical response. Finally, Sec. VII contains a summary and some concluding remarks.

This paper focuses on conceptual problems in formulating the theory of nonlinear optical response. Our purpose is to show how from a unified and fully microscopic starting point different limiting regimes, some of which have been well explored in the literature, can be reached. To make sure that the main line of reasoning does not get buried in massive algebra, we outline most derivations very briefly or refer to analogous cases in the literature.

II. EQUATIONS OF MOTION

We consider an arbitrary system of multilevel molecules with localized electronic states coupled to the radiation field. In the dipole approximation, the multipolar Hamiltonian for this system reads (a caret denotes an operator)^{16,17}

$$\hat{H} = \sum_m \hat{H}_m + \hat{H}_{\text{rad}} - \int \hat{\mathbf{P}}(\mathbf{r}) \cdot \hat{\mathbf{D}}^\perp(\mathbf{r}) d\mathbf{r} + 2\pi \sum_m \int |\hat{\mathbf{P}}_m^\perp(\mathbf{r})|^2 d\mathbf{r}, \quad (1)$$

where \hat{H}_m is the Hamiltonian of the isolated molecule m and \hat{H}_{rad} is the contribution from the free radiation field. In second quantization, both can be expressed in the usual way in creation and annihilation operators.^{17,19-21} The third term in Eq. (1) gives the interaction between

the radiation and the molecules. $\hat{\mathbf{P}}(\mathbf{r})$ is the polarization field in the medium, which in the dipole approximation may be written as

$$\hat{\mathbf{P}}(\mathbf{r}) = \sum_m \hat{\boldsymbol{\mu}}_m \delta(\mathbf{r} - \mathbf{r}_m). \quad (2)$$

Here $\hat{\boldsymbol{\mu}}_m$ denotes the total dipole operator of molecule m (position \mathbf{r}_m), which can be expressed in terms of the molecular dipole matrix elements and exciton creation and annihilation operators.⁸ $\hat{\mathbf{D}}^\perp(\mathbf{r})$, the transverse part of the electric displacement field at position \mathbf{r} , is related to the Maxwell electric field operator $\hat{\mathbf{E}}(\mathbf{r})$ by

$$\hat{\mathbf{D}}^\perp(\mathbf{r}) = \hat{\mathbf{E}}^\perp(\mathbf{r}) + 4\pi \hat{\mathbf{P}}^\perp(\mathbf{r}). \quad (3)$$

We stress that in the multipolar Hamiltonian, $\hat{\mathbf{D}}^\perp(\mathbf{r})$ is the conjugate momentum of the vector potential $\hat{\mathbf{A}}^\perp(\mathbf{r})$,^{16,17} so that in second quantization it is totally expressed in terms of radiation creation ($\hat{a}_{\mathbf{k}\lambda}^\dagger$) and annihilation ($\hat{a}_{\mathbf{k}\lambda}$) operators only. Explicitly, we have

$$\hat{\mathbf{A}}^\perp(\mathbf{r}) = \sum_{\mathbf{k}, \lambda} \left[\frac{2\pi\hbar c^2}{V\omega_k} \right]^{1/2} (\hat{a}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{a}_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}) \mathbf{e}_{\mathbf{k}\lambda}, \quad (4a)$$

$$\hat{\mathbf{D}}^\perp(\mathbf{r}) = i \sum_{\mathbf{k}, \lambda} \left[\frac{2\pi\hbar\omega_k}{V} \right]^{1/2} (\hat{a}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} - \hat{a}_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}) \mathbf{e}_{\mathbf{k}\lambda}, \quad (4b)$$

with V the quantization volume, $\mathbf{e}_{\mathbf{k}\lambda}$ ($\lambda=1,2$) the transverse unit polarization vectors belonging to the wave vector \mathbf{k} , and $\omega_k \equiv |\mathbf{k}|c$ the vacuum photon dispersion relation. The operators $\hat{a}_{\mathbf{k}\lambda}^\dagger$ and $\hat{a}_{\mathbf{k}\lambda}$ obey the usual Bose commutation relations

$$[\hat{a}_{\mathbf{k}\lambda}, \hat{a}_{\mathbf{k}'\lambda'}^\dagger] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\lambda\lambda'}, \quad [\hat{a}_{\mathbf{k}\lambda}, \hat{a}_{\mathbf{k}'\lambda'}] = 0, \quad (5)$$

and, of course, they commute with all material operators. Finally, the last term in Eq. (1) is a self-energy, in which $\hat{\mathbf{P}}_m^\perp(\mathbf{r})$ is the transverse polarization field caused by molecule m only. For two-level molecules this term is an infinite constant which does not contribute to the evolution, so that it is often omitted completely from the Hamiltonian. For the more realistic case of multilevel molecules, however, this term is not a constant and is essential for the proper description of the Lamb shift.¹⁷ Using the identity $\int \mathbf{a}^\perp(\mathbf{r}) \cdot \mathbf{b}^\perp(\mathbf{r}) d\mathbf{r} = \int \mathbf{a}(\mathbf{r}) \cdot \mathbf{b}^\perp(\mathbf{r}) d\mathbf{r}$ for arbitrary vector fields \mathbf{a} and \mathbf{b} ,²² and Eq. (2), we rewrite

$$2\pi \sum_m \int |\hat{\mathbf{P}}_m^\perp(\mathbf{r})|^2 d\mathbf{r} = 2\pi \sum_m \hat{\boldsymbol{\mu}}_m \cdot \hat{\mathbf{P}}_m^\perp(\mathbf{r}_m). \quad (6)$$

The basis for calculating optical response is the time evolution of the coupled radiation-matter system. From the Hamiltonian Eq. (1) we may derive the Heisenberg equations of motion for arbitrary operators. The equation for the photon annihilation operator reads (all operators taken at time t)

$$\frac{\hbar}{i} \frac{d\hat{a}_{\mathbf{k}\lambda}}{dt} = -\hbar\omega_k \hat{a}_{\mathbf{k}\lambda} - i \left[\frac{2\pi\hbar\omega_k}{V} \right]^{1/2} \hat{\mathbf{P}}(\mathbf{k}) \cdot \mathbf{e}_{\mathbf{k}\lambda}, \quad (7)$$

with $\hat{\mathbf{P}}(\mathbf{k}) \equiv \int d\mathbf{r} \hat{\mathbf{P}}(\mathbf{r}) \exp(-i\mathbf{k}\cdot\mathbf{r})$, the spatial Fourier transform of the polarization field. From Eq. (7) and its

Hermitian conjugate for $\hat{a}_{-\mathbf{k}\lambda}^\dagger$ the Maxwell equations in the electric dipole approximation are easily obtained:

$$\hat{\mathbf{E}}^\perp(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial}{\partial t} \hat{\mathbf{A}}^\perp(\mathbf{r}, t), \quad (8a)$$

$$\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \hat{\mathbf{E}}^\perp(\mathbf{r}, t) = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \hat{\mathbf{P}}^\perp(\mathbf{r}, t). \quad (8b)$$

We do not present the derivation here, as it is very similar to the one given in Ref. (15) (the restriction to a lattice of two-level molecules in that reference is not essential for these equations). Next we consider the Heisenberg equation of motion for an arbitrary material operator \hat{Q} acting in the Hilbert space of the molecules,

$$\begin{aligned} \frac{\hbar}{i} \frac{d\hat{Q}}{dt} = & \sum_m [\hat{H}_m, \hat{Q}] + 2\pi \sum_m [\hat{\mu}_m \cdot \hat{\mathbf{P}}^\perp(\mathbf{r}_m), \hat{Q}] \\ & - \frac{1}{2} \int d\mathbf{r} \{ [\hat{\mathbf{P}}(\mathbf{r}), \hat{Q}] \cdot \hat{\mathbf{D}}^\perp(\mathbf{r}) + \hat{\mathbf{D}}^\perp(\mathbf{r}) \cdot [\hat{\mathbf{P}}(\mathbf{r}), \hat{Q}] \} \end{aligned} \quad (9)$$

(all operators taken at time t). The two contributions in the last term of this equation are equal, because $\hat{\mathbf{D}}^\perp(\mathbf{r})$ commutes with all material operators. The reason for the symmetrization used here will become clear below. After substituting Eqs. (2) and (3) into Eq. (9), we get

$$\begin{aligned} \frac{\hbar}{i} \frac{d\hat{Q}}{dt} = & \sum_m [\hat{H}_m, \hat{Q}] + 2\pi \sum_m [\hat{\mu}_m \cdot \hat{\mathbf{P}}^\perp(\mathbf{r}_m), \hat{Q}] \\ & - 2\pi \sum_m \{ [\hat{\mu}_m, \hat{Q}] \cdot \hat{\mathbf{P}}^\perp(\mathbf{r}_m) + \hat{\mathbf{P}}^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{Q}] \} \\ & - \frac{1}{2} \sum_m \{ [\hat{\mu}_m, \hat{Q}] \cdot \hat{\mathbf{E}}^\perp(\mathbf{r}_m) + \hat{\mathbf{E}}^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{Q}] \}. \end{aligned} \quad (10)$$

The transverse δ dyadic²² may be used to rewrite

$$\hat{\mathbf{P}}^\perp(\mathbf{r}_m) \equiv \int \delta^{\perp}(\mathbf{r}_m - \mathbf{r}) \cdot \hat{\mathbf{P}}(\mathbf{r}) d\mathbf{r}, \quad (11a)$$

with

$$\delta^{\perp}(\mathbf{r}) = \frac{2}{3} \mathbf{1} \delta(\mathbf{r}) - \frac{1}{4\pi} \vec{\mathbf{T}}(\mathbf{r}), \quad (11b)$$

$$\vec{\mathbf{T}}(\mathbf{r}) \equiv (r^2 \mathbf{1} - 3\mathbf{r}\mathbf{r})/r^5. \quad (11c)$$

The unit tensor is denoted by $\mathbf{1}$. We now split the transverse polarization field $\hat{\mathbf{P}}^\perp(\mathbf{r}_m)$ into a contribution from molecule m only and a contribution from all other molecules by substituting Eq. (2) into Eq. (11a). We then find that the second term in Eq. (10) is exactly canceled by the contribution from $\hat{\mathbf{P}}^\perp(\mathbf{r}_m)$ in the third term, whereas the contributions from all other molecules can be cast into the form of the instantaneous dipole-dipole interaction [this is a direct consequence of the symmetrization used in Eq. (9)]. Details of the algebra involved in these steps can be found in the Appendix. Explicitly, we obtain

$$\begin{aligned} \frac{\hbar}{i} \frac{d\hat{Q}}{dt} = & [\hat{H}_0, \hat{Q}] - \frac{1}{2} \sum_m \{ [\hat{\mu}_m, \hat{Q}] \cdot \hat{\mathbf{E}}^\perp(\mathbf{r}_m) \\ & + \hat{\mathbf{E}}^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{Q}] \}, \end{aligned} \quad (12)$$

with

$$\hat{H}_0 = \sum_m \hat{H}_m + \frac{1}{2} \sum'_{m,n} \hat{\mu}_m \cdot \vec{\mathbf{T}}(\mathbf{r}_{mn}) \cdot \hat{\mu}_n, \quad (13)$$

where $\mathbf{r}_{mn} \equiv \mathbf{r}_m - \mathbf{r}_n$ and the prime on the summation excludes the terms with $m = n$. Equation (12) is our basic result. We note that this equation is an *exact* representation of the Heisenberg equation for \hat{Q} . The great merit of writing the equation in this form, is that it clearly separates the contribution from \hat{H}_0 , which is usually considered the unperturbed material Hamiltonian when performing response theory with respect to the electric field.⁴⁻⁶ Furthermore, the interaction with the transverse Maxwell electric field has the familiar $\boldsymbol{\mu} \cdot \mathbf{E}^\perp$ form. In Eq. (12), however, the electric field still appears as an operator and may not be considered an external quantity to which response theory can be applied. Moreover, $\hat{\mathbf{E}}^\perp(\mathbf{r})$ is not a pure radiation operator; in second quantization it should be expressed in both radiation and material creation and annihilation operators by using Eqs. (3), (4b), and the second quantized form of the polarization field. Consequently, the ordering of the operators used in Eq. (12) is important. In the remainder of this paper, we outline several practical ways to make use of the equations of motion derived in this section.

III. DEFINITION OF POLARITONS

Because Eq. (12) is a time-local operator equation, it is possible to define combined matter-radiation excitations from it. This is not the case in, e.g., the superradiant master equation,¹⁸ which is another equation for material operators in which starting from the multipolar Hamiltonian intermolecular interactions are recovered. The reason is that this master equation is obtained by formally integrating the radiation operator equations of motion and performing a Markov approximation, so that it only contains radiation operators at some initial time.

For a rigid lattice of molecules, the calculation of polaritons from Eqs. (7) and (12) is analogous to Hopfield's original derivation,¹⁹ which was carried out within the minimal coupling ($\mathbf{p} \cdot \mathbf{A}$) Hamiltonian.^{16,17} We just outline the general method here, without showing the actual algebra. One works in second quantization for both the radiation field and the material excitations.¹⁹⁻²¹ As usual in the theory of polaritons, the creation and annihilation operators for the material excitations are assumed to obey Bose commutation relations (linearization).^{19-21,23,24} Then, the right-hand side of Eq. (12) for any of these operators is a linear combination of these operators themselves and of the transverse electric field. The latter must be expressed in both radiation and matter creation and annihilation operators as explained above. Combining the thus obtained equations with Eq. (7) and its Hermitian conjugate for $\hat{a}_{-\mathbf{k}\lambda}^\dagger$, we obtain a closed linear set of equations, whose eigenmodes are the polaritons. Formally, it is a detour to make the steps that lead to Eq. (12) in order to obtain this set, since the linearized material equations may equally well be obtained directly from the Hamiltonian Eq. (1). There is, however, an im-

portant advantage to using Eq. (12) as a starting point, which finds its root in the explicit separation of the intermolecular Coulomb interactions in it. To define polaritons, one works in momentum (\mathbf{k}) space. The equations of motion are local in \mathbf{k} modulo reciprocal-lattice vectors (\mathbf{G}) and couple material operators at wave vector \mathbf{k} to radiation operators at $\mathbf{k} + \mathbf{G}$ for all \mathbf{G} . Hopfield¹⁹ argued that the \mathbf{k} components of the transverse electric field outside the first Brillouin zone (umklapp processes) may be neglected. Within this approximation the equations are totally local in \mathbf{k} , which greatly simplifies the eigenvalue calculation (cf., e.g., Ref. 25, where this assumption was not made). It is important to note that in the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian (i) intermolecular interactions are explicitly present and (ii) $\hat{\mathbf{E}}^\perp$ is the conjugate momentum to the vector potential,^{16,17} so that neglecting umklapp contributions in $\hat{\mathbf{E}}^\perp$ is equivalent to neglecting radiation creation and annihilation operators outside the first Brillouin zone. This is not the case in the multipolar Hamiltonian, where the high-wave-vector radiation operators are essential to carry the intermolecular interactions. The most straightforward way to solve for polaritons in the multipolar Hamiltonian is to neglect umklapp contributions in $\hat{\mathbf{D}}^\perp$; then, the derivation of Eq. (12) is not necessary. Alternatively, we can work with Eq. (12) and neglect umklapp contributions in $\hat{\mathbf{E}}^\perp$. Of course, the two approximations are not equivalent and it turns out that the former leads to the incorrect polariton dispersion relation, whereas the latter yields the expected dispersion relation with poles at the transverse exciton frequencies.^{19,20,26} We illustrate this briefly with the case of a lattice of N nonpolar two-level molecules (transition frequency Ω , transition dipole $\boldsymbol{\mu}$). Creation and annihilation operators for an excitation on molecule m are denoted by \hat{B}_m and \hat{B}_m^\dagger ,^{21,26} respectively, and from these, exciton operators are defined by $\hat{B}_\mathbf{k} = \sum_m \hat{B}_m \exp(-i\mathbf{k} \cdot \mathbf{r}_m) / \sqrt{N}$ and by the Hermitian conjugate for $\hat{B}_\mathbf{k}^\dagger$. For simplicity, we only consider polaritons with wave vector $\mathbf{k} \perp \boldsymbol{\mu}$ and polarized parallel to $\boldsymbol{\mu}$. Suppressing the polarization index in the radiation operators, we obtain (\mathbf{k} in the first Brillouin zone)

$$\frac{d\hat{a}_\mathbf{k}}{dt} = -i\omega_k \hat{a}_\mathbf{k} + (\pi\beta\Omega\omega_k)^{1/2} (\hat{B}_\mathbf{k} + \hat{B}_{-\mathbf{k}}^\dagger), \quad (14a)$$

$$\begin{aligned} \frac{d\hat{B}_\mathbf{k}}{dt} = & -i\Omega\hat{B}_\mathbf{k} - (\pi\beta\Omega\omega_k)^{1/2} (\hat{a}_\mathbf{k} - \hat{a}_{-\mathbf{k}}^\dagger) \\ & - i\kappa [J(\mathbf{k}) + 2\pi\beta\Omega] (\hat{B}_\mathbf{k} + \hat{B}_{-\mathbf{k}}^\dagger). \end{aligned} \quad (14b)$$

If umklapp contributions are neglected in $\hat{\mathbf{D}}^\perp$, these equations apply with $\kappa=0$; for neglect of umklapp terms in $\hat{\mathbf{E}}^\perp$, we have $\kappa=1$. The parameter β is a measure of the oscillator strength per unit volume introduced by Hopfield¹⁹ and is defined as

$$\beta = 2\rho\mu^2 / \hbar\Omega, \quad (15)$$

with $\rho \equiv N/V$ the average density of molecules in the lattice. The lattice Fourier transform of the dipole-dipole interaction (for the case $\mathbf{k} \perp \boldsymbol{\mu}$) is denoted $J(\mathbf{k})$ and defined through

$$\hbar J(\mathbf{k}) = \sum_{m \neq 0} \boldsymbol{\mu} \cdot \vec{\mathbf{T}}(\mathbf{r}_m) \cdot \boldsymbol{\mu} e^{-i\mathbf{k} \cdot \mathbf{r}_m}. \quad (16)$$

Together with the equations for $\hat{a}_{-\mathbf{k}}^\dagger$ and $\hat{B}_{-\mathbf{k}}^\dagger$, Eqs. (14a) and (14b) yield polaritons through a simple diagonalization, analogous to the one performed by Hopfield.^{19,27} From the secular equation of this eigenvalue problem, the dispersion relation of the polaritons is obtained as

$$\epsilon(\mathbf{k}, \omega) \equiv \frac{\omega_k^2}{\omega^2} = 1 + \frac{4\pi\beta\Omega^2}{-\omega^2 + \Omega^2 + 2\kappa\Omega J(\mathbf{k}) + (\kappa-1)4\pi\beta\Omega^2}, \quad (17)$$

where ω is the frequency of the polariton with wave vector \mathbf{k} and $\epsilon(\mathbf{k}, \omega)$ is by definition the crystal's transverse dielectric function. Equation (17) shows explicitly that from neglect of umklapp terms in $\hat{\mathbf{E}}^\perp$ ($\kappa=1$), the usual form for $\epsilon(\mathbf{k}, \omega)$ is obtained, with a resonance at the transverse dipolar exciton frequency.^{19,26,27} Neglect of umklapp contributions in $\hat{\mathbf{D}}^\perp$ ($\kappa=0$) does not recover this result. The underlying reason for this is that the instantaneous intermolecular interactions (the $4\pi\hat{\mathbf{P}}^\perp$ contribution to $\hat{\mathbf{D}}^\perp$) are dealt with exactly in the derivation of Eq. (12) and are not affected by the neglect of umklapp terms in $\hat{\mathbf{E}}^\perp$. Inclusion of umklapp processes in $\hat{\mathbf{E}}^\perp$ only introduces small corrections in the polariton dispersion relation, caused by the effect of retardation on the (transverse) exciton frequency.^{21,25,28} Of course, retardation *does* play a crucial role in the dispersion of polaritons. Its primary effect, however, is accounted for by finding the coupled eigenmodes of the Coulomb excitons (eigenmodes of \hat{H}_0 [Eq. (13)]) and the *first* Brillouin zone electric field modes only, and is reflected in the appearance of $\omega_k = kc$ in the dispersion relation Eq. (17). The physical rationale for the unimportance of retardation in the high-wave-number radiation modes is that these are related to short length scales. Therefore, their primary role can be incorporated in the instantaneous interaction in the material Hamiltonian \hat{H}_0 . This observation is not limited to a lattice, but applies to disordered systems as well. This is the basis for the success of the partitioning of $\hat{\mathbf{D}}^\perp$ which lead to Eqs. (12) and (13).

As a further advantage to our scheme, we note that the explicit appearance of the Coulomb interactions in Eq. (13) allows us to incorporate lattice phonons in the standard way,²¹ namely, by expanding the interactions in the deviations of the molecular positions and orientations from their equilibrium values. We then obtain a material Hamiltonian \hat{H}_0 which explicitly contains phonon contributions. By contrast, if we do not separate the polarization contribution to the displacement field as has been done in deriving Eq. (12), the inclusion of phonons is much less straightforward.

IV. CALCULATION OF SUSCEPTIBILITIES

In order to obtain susceptibilities, the expectation value of the polarization field must be expanded in the average Maxwell electric field

$$\langle \hat{\mathbf{P}}(\mathbf{k}, \omega) \rangle = \chi^{(1)}(\mathbf{k}, \omega) \cdot \langle \hat{\mathbf{E}}(\mathbf{k}, \omega) \rangle + \int d\mathbf{k}_1 \int d\omega_1 \int d\mathbf{k}_2 \int d\omega_2 \chi^{(2)}(-\mathbf{k} - \omega; \mathbf{k}_1 \omega_1, \mathbf{k}_2 \omega_2) : \langle \hat{\mathbf{E}}(\mathbf{k}_1, \omega_1) \rangle \langle \hat{\mathbf{E}}(\mathbf{k}_2, \omega_2) \rangle + \dots \quad (18)$$

Here, the n th order susceptibility $\chi^{(n)}$ is a tensor of rank $n+1$, and the space and time Fourier transform for the electric field is defined as

$$\hat{\mathbf{E}}(\mathbf{k}, \omega) = \int_{-\infty}^{+\infty} dt \int d\mathbf{r} \hat{\mathbf{E}}(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r} + i\omega t). \quad (19)$$

The polarization field $\hat{\mathbf{P}}(\mathbf{k}, \omega)$ is defined in an analogous way. If the electric field in Eq. (12) would be an external c number (say \mathbf{E}_0), an expansion in \mathbf{E}_0 could be obtained in the following way. We substitute in Eq. (12) the polarization field for $\hat{\mathbf{Q}}$ and take the expectation value of the equation. This relates $\langle \hat{\mathbf{P}} \rangle$ to \mathbf{E}_0 , but also to the averages of other material operators generated by the commutators (to describe nonlinear optics, we of course no longer use Bose commutators for the material operators). We proceed by calculating the equations of motion for these new averages in the same way, etc. This generates an infinite hierarchy of equations of motion which has to be truncated at some point to be useful (in Ref. 8, e.g., this was done by invoking a factorization approximation). Now assume that expansions in terms of \mathbf{E}_0 exist for all introduced material variables. Substitute these expansions into the generated equations of motion and solve those iteratively order by order (cf. Ref. 8). This yields all expansion coefficients and in particular the susceptibilities. In Eq. (12), however, $\hat{\mathbf{E}}^\perp$ is an operator, so that the equation for $\langle \hat{\mathbf{P}} \rangle$ involves averages of products of material operators and the electric field operator. Therefore, susceptibilities cannot be obtained through the above procedure, unless the *ad hoc* approximation is invoked that the expectation value of such products factorizes into the product of the expectation values of the material operator and the transverse electric field. There is an alternative, more systematic way to view this factorization. To this end, we consider the formal solution to the Maxwell equation, which reads²⁹

$$\hat{\mathbf{E}} = \mathbf{E}_{\text{ext}} + \vec{\mathbf{G}} \cdot \hat{\mathbf{P}}. \quad (20)$$

The Green function $\vec{\mathbf{G}}$ reads in momentum-frequency representation

$$\vec{\mathbf{G}}(\mathbf{k}, \omega) = -4\pi \frac{\mathbf{k}\mathbf{k} - (\omega/c)^2 \mathbf{1}}{k^2 - (\omega/c + i0^+)^2}. \quad (21)$$

\mathbf{E}_{ext} denotes the external field, which is a c number, since it is independent of the state of the system. Subtracting from Eq. (20) its expectation value, we arrive at

$$\hat{\mathbf{E}} = \langle \hat{\mathbf{E}} \rangle + \vec{\mathbf{G}} \cdot (\hat{\mathbf{P}} - \langle \hat{\mathbf{P}} \rangle). \quad (22)$$

In momentum space, the transverse part of this equation is easily found by multiplying with $\mathbf{1} - \mathbf{k}\mathbf{k}/k^2$. We then find that $\hat{\mathbf{E}}^\perp$ equals its expectation value up to a contribution of the order $(\omega/c)^2$. In other words, if we totally neglect retardation ($\omega/c = 0$), Eq. (12) may be written as

$$\frac{\hbar}{i} \frac{d\hat{\mathbf{Q}}}{dt} = [\hat{H}_{\text{eff}}(t), \hat{\mathbf{Q}}], \quad (23a)$$

with the time-dependent Hamiltonian given by

$$\hat{H}_{\text{eff}}(t) = \hat{H}_0 - \sum_m \hat{\mu}_m \cdot \langle \hat{\mathbf{E}}^\perp(\mathbf{r}_m, t) \rangle. \quad (23b)$$

The iteration described above can now be applied to Eq. (23a) to find an expansion like Eq. (18), but in terms of $\langle \hat{\mathbf{E}}^\perp \rangle$. This is easily converted to an expansion in terms of $\langle \hat{\mathbf{E}} \rangle$ by using for every Fourier component $\hat{\mathbf{E}}^\perp(\mathbf{k}, \omega) = (\mathbf{1} - \mathbf{k}\mathbf{k}/k^2) \hat{\mathbf{E}}(\mathbf{k}, \omega)$. We thus conclude that susceptibilities can be defined if retardation is neglected. This is equivalent to ignoring polariton effects since the operator nature of the electric field is neglected. An alternative description of the material evolution is obtained by changing from the Heisenberg picture to the Schrödinger picture and giving the equation of motion for the reduced material density operator $\hat{\rho}^M(t) \equiv \text{Tr}_R \hat{\rho}(t)$, with $\hat{\rho}(t)$ the total density operator and Tr_R the trace over the radiation field. Exploiting the same technique as used in Ref. 30, Eq. (23a) may be converted into the following Liouville equation for $\hat{\rho}^M(t)$:

$$\frac{\hbar}{i} \frac{d\hat{\rho}^M(t)}{dt} = -[\hat{H}_{\text{eff}}(t), \hat{\rho}^M(t)]. \quad (24)$$

This is the most common starting point for the calculation of optical response.¹⁻⁴ Transforming to the interaction picture, the susceptibilities are obtained from Eq. (24) as equilibrium multitime and multiposition correlation functions of the polarization field for the material system described by the Hamiltonian \hat{H}_0 .⁴⁻⁶ From the above it is clear that this common definition of susceptibilities completely ignores retardation. Some retardation effects may, however, still be incorporated into the susceptibilities. First, in low-temperature crystals the effect of polariton-phonon scattering can approximately be accounted for by adjusting the phonon damping rates of the excitonic variables in \hat{H}_0 , as has been shown in Ref. 8. Second, the complete expression Eq. (22) can be substituted into Eq. (12), instead of just the unretarded $\langle \hat{\mathbf{E}}^\perp \rangle$ contribution. Although formally correct, it is not clear how to implement this procedure, because the Green function $\vec{\mathbf{G}}$ is not time local, so that only a hierarchy of equations of motion coupling expectation values of material operators to multitime correlation functions can be generated. At best, the equations may be made time local again by invoking a Markov approximation similar to the one invoked in the usual derivation of the superradiance master equation.¹⁸ In analogy to this literature, dissipative contributions, similar to superradiant interactions and single molecule radiative decay, must then be expected to enter the equations of motion. These dissipative terms are re-

tardation effects (they vanish if the velocity of light is taken to be infinite), which will affect the susceptibilities.

V. LOCAL-FIELD APPROXIMATION

Let us for the moment neglect retardation, so that Eq. (23a) holds and susceptibilities may be calculated by iteratively solving a hierarchy of equations of motion. As pointed out above, we are faced with an infinite hierarchy, so that exact solutions are difficult to obtain. Alternatively, this problem amounts to finding the Green function corresponding to the Hamiltonian \hat{H}_0 for the total material system.³¹ The calculation of the Green function involves the eigenstates of the material Hamiltonian \hat{H}_0 , which for many systems are not known. If the intermolecular interactions are neglected, the susceptibilities are given by single-molecule hyperpolarizabilities. These are relatively easy to obtain if the number of molecular states that one wants to account for is not too large.³² This motivates one to consider mean-field theories. Suppose that in the hierarchy based on Eq. (23a) we make a mean-field approximation by factoring the expectation values of products of operators acting on different molecules. It is easily shown that within this approximation the equation of motion for any operator \hat{Q}_m acting on molecule m only may be replaced by

$$\frac{\hbar}{i} \frac{d\hat{Q}_m}{dt} = [\hat{H}_m, \hat{Q}_m] - [\hat{\mu}_m, \hat{Q}_m] \cdot \mathbf{E}_L(\mathbf{r}_m, t), \quad (25a)$$

with the local field

$$\mathbf{E}_L(\mathbf{r}_m, t) \equiv \langle \hat{\mathbf{E}}^\perp(\mathbf{r}_m, t) \rangle - \left\langle \sum_{n (\neq m)} \vec{\mathbf{T}}(\mathbf{r}_{mn}) \cdot \hat{\mu}_n(t) \right\rangle. \quad (25b)$$

If we now completely ignore spatial correlations, take this expression to momentum space and exploit that the Fourier transform of $\vec{\mathbf{T}}(\mathbf{r})$ is given by $\vec{\mathbf{T}}(\mathbf{k}) = 4\pi(\mathbf{k}\mathbf{k}/k^2 - \vec{\mathbf{I}}/3)$,²² we arrive at the celebrated form for the local field:^{1-3,14}

$$\mathbf{E}_L(\mathbf{r}_m, t) = \langle \hat{\mathbf{E}}(\mathbf{r}_m, t) \rangle + \frac{4\pi}{3} \langle \hat{\mathbf{P}}(\mathbf{r}_m, t) \rangle. \quad (25c)$$

Our derivation clearly shows what approximation needs to be made in order to obtain the local field. The significance of Eqs. (25) is that within the mean-field approximation we may focus on the multilevel Bloch equations³³ for a single molecule in order to find the optical response of the total system. The effects of intermolecular interactions are incorporated in the local field. Susceptibilities expressing the system's polarization in terms of \mathbf{E}_L are then simply given by the single molecule hyperpolarizabilities. It is well known that [using Eq. (25c)] these can be converted into the susceptibilities with respect to $\langle \hat{\mathbf{E}} \rangle$ by multiplying with the appropriate local-field correction factors and by accounting for cascading.^{1-3,14,27,34} We note that the present form for the local field differs from the expression we obtained earlier for the special case of a lattice of two-level molecules [Eqs. (43) and (44) of Ref. 15]. The result in Ref. 15 is more rigorous in the sense that there we accounted for (i) retardation effects and (ii) the lattice structure, which gives rise to finite effective exciton masses (spatial disper-

sion). Spatial dispersion can also be incorporated in the above derivation, by using a hard-sphere cutoff in the integrals over the intermolecular interaction; this is the simplest way of accounting for spatial correlation effects.

In spite of the success and widely spread use of the local-field approximation, it certainly has its limitations. One of these is its incapability to describe exciton transport in four wave mixing experiments. This depends in a crucial way on the form of the spatial dispersion of the third order susceptibility,³⁵ which cannot be recovered by the simple local-field correction factors, even if spatial correlations are incorporated in the local field as described in the previous paragraph.

VI. RETARDATION: BEYOND SUSCEPTIBILITIES

Although, as discussed at the end of Sec. IV, some retardation effects can be incorporated into the susceptibilities, the concept of susceptibilities is one which by definition separates the radiation field and the material system. This is most clearly illustrated by the fact that the resonances of the susceptibilities, by the very nature of their calculation, occur at eigenfrequencies of the material system described by \hat{H}_0 (excitons) only. Ovander²³ used this as an argument against the introduction of susceptibilities. He reasoned that it is the coupled matter-radiation field which responds to the external laser fields, so that any experimental signal should show resonances at eigenfrequencies of this coupled system, i.e., at polariton frequencies. The electric field and the polarization should thus be treated on equal footing, rather than trying to expand one in terms of the other. First, it should be noted that the fact that susceptibilities have poles at the exciton frequencies does not mean that the signal has the same resonances. A careful analysis of the boundary condition problem for the Maxwell equations can introduce polariton effects in the resonances.^{26,36} Second, in many experimental situations susceptibilities are very useful quantities serving as intermediates between the microscopic dynamics and the macroscopic calculation of the signal. At high temperatures or in disordered systems, the coupling of the material excitons to other degrees of freedom (phonons, vacancies, etc.) is stronger than the exciton-radiation coupling, so that polaritons cannot play an important role. Let Γ_{ex} be the exciton damping constant due to other degrees of freedom, which may be found from a single-photon (linear) absorption experiment.^{7,8} From Eqs. (14) it follows that the exciton-radiation coupling is (close to resonance) characterized by $\sqrt{\pi\beta}\Omega$. We thus find that polaritons must play an important role and the usefulness of susceptibilities must be doubted if $\pi\beta \gg (\Gamma_{ex}/\Omega)^2$.^{8,26} Typical situations where this condition is met include low temperature pure crystals. In recent years, several experiments on such systems have been performed. The series of experiments by Small and co-workers on naphthalene crystals⁷ could still be fitted using susceptibilities with exciton resonances, but the width of the resonance had to be identified with the phonon scattering rate of polaritons rather than excitons. The transient-grating (TG) experiments by Fayer and co-workers¹⁰ provide an even clearer example of polariton

effects. TG experiments are traditionally believed to probe diffusion of excitons.³⁷ Starting from the Haken-Strobl model^{37(b),38} of exciton dynamics, a fully microscopic calculation of the grating signal can be given showing how the signal's decay rate depends on the exciton group velocity.^{35,37(b),39} In the experiments on anthracene,¹⁰ however, an unusually high decay rate was observed, which could be explained^{10(b)} by assuming that incoherent propagation of polaritons, which move much faster than excitons, destroys the grating. From a fundamental point of view this seems not surprising, but a fully microscopic calculation of the grating signal incorporating polaritons and showing how the polariton group velocity plays a role has so far not been given. We remark that the observation of diffusive polariton propagation can only be expected in crystals with very high density of oscillator strength, such as anthracene. The reason is that diffusive behavior occurs at high scattering (dephasing) rates of the polaritons, which automatically implies a strong coupling of excitons to other degrees of freedom (because polaritons only scatter through their exciton component). As argued above, in materials with low oscillator strength this coupling easily reduces the significance of polaritons.

The cw analog of the TG is the degenerate four wave mixing (DFWM) experiment. If the polariton dispersion plays a role in the TG signal, the same must be expected for the DFWM signal. In the incoherent limit, within total neglect of retardation, the two signals have been shown³⁵ to be related by a Fourier transform. The DFWM signal is usually identified with $|\chi^{(3)}|^2$, where $\chi^{(3)}$ is the appropriate component of the third-order susceptibility. This quantity, however, only contains exciton resonances; no polariton dispersion (an explicit calculation is given in Ref. 35). As mentioned above, the DFWM signal may still turn out to contain polariton effects when carefully solving the boundary value problem for the Maxwell equations. However, this example is a prototype situation in which a more direct and probably more fruitful approach exists in addressing the response of the coupled material-radiation system to the external laser fields, instead of using susceptibilities.

The first formulation of nonlinear optics entirely based on polaritons was proposed by Ovander.²³ In his approach the total Hamiltonian is expressed in polariton operators and the nonlinear signal is obtained by applying the Fermi golden rule to the anharmonic terms in this Hamiltonian. Drawbacks of this procedure are the complexity of the Hamiltonian in terms of polariton operators and the fact that it uses the Bose approximation for the exciton commutators, which is not consistent with the goal to study nonlinearities.⁸ Recently,⁴⁰ Hanamura presented a theory of phase-conjugate FWM in crystals, in which he considered the perturbation of the crystal's polaritons by the external field. He divides the space into a part occupied by the crystal, where polaritons are the eigenmodes, and the outer space with the external field. Instead of solving the boundary-condition problem connecting the two subspaces, he describes the creation of polaritons on the crystal's surface by adding to the Hamiltonian an interaction term between the external field

and the polaritons [Eq. (7) of Ref. 40]. Although intuitively appealing, this procedure cannot be justified microscopically. Moreover, Hanamura does not explain (or give) the commutation relations which he assumes for the polaritons, so that it is unclear what the (microscopic) origin of the nonlinearities in his theory is.

We propose a procedure to formulate nonlinear optics in terms of polaritons which *does* address the boundary-condition problem, instead of assuming an interaction between the external field and the polaritons. We start from Eqs. (7) and (12) for the radiation and material (exciton) creation and annihilation operators, respectively. The nonlinearities are contained within the commutators $[\hat{\mu}_m, \hat{Q}]$ in Eq. (12); the radiation equations are linear. We split this commutator into a linear part (as if excitons are bosons) and the exact nonlinear rest term. As explained in Sec. III, the linear part combined with the Maxwell equations yields the polaritons as eigenmodes through a simple diagonalization. The external field falling on the sample creates polaritons which may be called "first-order" polaritons. For example, an external field component with frequency ω and wave vector \mathbf{k} creates a polariton with frequency ω and wave vector \mathbf{k}' determined by the sample's dispersion relation and Snell's law. The expectation values of the creation ($\hat{\xi}_{\mathbf{k}}^\dagger$) and annihilation ($\hat{\xi}_{\mathbf{k}}$) operators of the "first-order" polaritons can be found by matching the boundary conditions, and are proportional to the external field. (If a finite effective exciton mass is included, two different wave vectors \mathbf{k}' are possible and the problem of additional boundary conditions has to be addressed.⁴¹⁻⁴³) The nonlinear term in the equations of motion can always be written as a sum of products of polariton creation and annihilation operators at certain wave vectors, and gives rise to the generation of polaritons at sum or difference wave vectors of the "first-order" polaritons. For each of the operator products we may again write an equation of motion, which also contains linear (bosonic) and nonlinear parts. The linear part is simply given by the same operator product, multiplied by sums (or differences) of polariton frequencies. For example, the linear part of the equation of motion for $\hat{\xi}_{\mathbf{k}_1}^\dagger \hat{\xi}_{\mathbf{k}_2}$ reads

$$\frac{d}{dt} \hat{\xi}_{\mathbf{k}_1}^\dagger \hat{\xi}_{\mathbf{k}_2} = i[\omega(\mathbf{k}_1) - \omega(\mathbf{k}_2)] \hat{\xi}_{\mathbf{k}_1}^\dagger \hat{\xi}_{\mathbf{k}_2}, \quad (26)$$

with $\omega(\mathbf{k})$ the polariton dispersion relation. For the nonlinear part, we have to generate a new equation of motion, etc. We thus obtain a hierarchy of equations for products of polariton operators. Eventually, we are interested in the expectation values of higher-order polariton creation and annihilation operators (e.g., $\langle \hat{\xi}_{\mathbf{k}_1 + \mathbf{k}_2}^\dagger \rangle$) in terms of the external field, because the nonlinear polarization $[\langle \hat{P}(\mathbf{k}_1 + \mathbf{k}_2) \rangle]$, and thus the signal, can be expressed in these expectation values. In the present approach, the only connection to the external field amplitudes can be made through the expectation values of the "first-order" polariton operators, which have been matched on the sample's surface. In order to exploit this, we take expectation values of all the generated equations and propose to truncate the hierarchy by factorizing at a

certain level the expectation value of the nonlinear term in the equation into the expectation values of lower-order products, and single polariton operators. In this way a closed set of equations is obtained which may eventually be solved in terms of the expectation values of the "first-order" polariton operators, and thus yields the signal in terms of the external field amplitudes. An important aspect of this procedure is that the linear term at every level of the hierarchy is treated in an exact way and fully accounts for the proper polariton dispersion. Therefore, this method is guaranteed to give signals with resonances at (sums or differences of) polariton frequencies. A specific application to DFWM and TG experiments, illustrating the proposed scheme, will be given elsewhere.

VII. SUMMARY AND CONCLUSIONS

In this paper we discussed the theoretical calculation of nonlinear optical response from a fully microscopic starting point for both the material system and the radiation field. The various procedures and approximations discussed can be depicted in a schematic way as in Fig. 1. The general starting point is the multipolar Hamiltonian. As a step common to all procedures we derive from this Hamiltonian the Maxwell equations for the field operators and an exact equation of motion for arbitrary material operators [Eq. (12)]. This material equation explicitly contains the instantaneous intermolecular Coulomb interactions, which turns out to be very advantageous. We showed that in the case of total neglect of retardation (polariton effects), susceptibilities can be calculated from Eq. (12) in the usual way, namely, as equilibrium correla-

tion functions of the polarization field of the molecular system *with instantaneous Coulomb interactions*.⁴⁻⁶ The optical signal is then calculated by substituting the expansion Eq. (18) into the Maxwell equations. Furthermore, we showed that by applying a mean-field approximation to the material system, these susceptibilities can be obtained from single-molecule polarizabilities through the well-known local-field approach.^{1-3,14} On the other hand, it is clear that for systems in which retardation is important (e.g., low-temperature crystals) an approach which directly addresses the mixed radiation-matter eigenstates (polaritons) is favorable. The problem one has to face in such approaches is that the coupling of the polaritons to the external laser fields occurs at the boundary of the sample and cannot be incorporated in the Hamiltonian. Consequently, a simple response theory is not possible. We proposed a scheme based on a hierarchy of equations of motion for polariton operators, obtained through Eqs. (7) and (12), which is truncated by a factorization approximation in the nonlinear terms. The coupling to the external field is made through the boundary condition. This procedure yields nonlinear signals with resonances determined by the polariton dispersion, and not by the exciton dispersion (as in the susceptibilities).

As discussed in Sec. VI, there are many experimental situations in which polariton effects cannot play a role and susceptibilities are useful measures for the nonlinear response. On the other hand, there are also many current nonlinear optical experiments^{7,9-13} in which polariton properties are probed. It is therefore useful to see how approaches dealing with these different regimes are obtained from a unified starting point.

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APPENDIX

In this Appendix, we expand on the derivation of Eq. (12) in the main text from Eq. (10). We concentrate on the second and third terms in the right-hand side of Eq. (10):

$$I \equiv 2\pi \sum_m [\hat{\mu}_m \cdot \hat{\mathbf{P}}_m^\perp(\mathbf{r}_m), \hat{Q}] - 2\pi \sum_m \{ [\hat{\mu}_m, \hat{Q}] \cdot \hat{\mathbf{P}}^\perp(\mathbf{r}_m) + \hat{\mathbf{P}}^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{Q}] \} \quad (\text{A1})$$

Working out the commutator within the first sum and separating $\hat{\mathbf{P}}^\perp(\mathbf{r}_m)$ in the second sum into contributions from the individual molecules, we obtain

$$I = I_1 + I_2, \quad (\text{A2a})$$

with

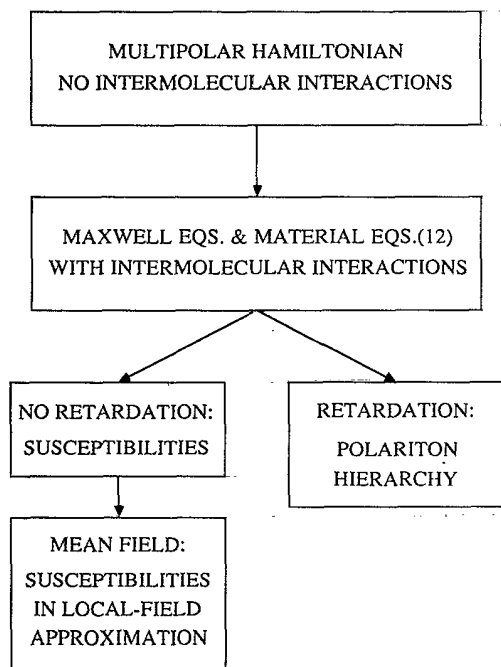


FIG. 1. Diagram illustrating how the different approaches to calculate nonlinear optical response discussed in the text derive from a common root.

$$I_1 = 2\pi \sum_m \{ \hat{\mu}_m \cdot [\hat{\mathbf{P}}_m^\perp(\mathbf{r}_m), \hat{\mathcal{Q}}] + [\hat{\mu}_m, \hat{\mathcal{Q}}] \cdot \hat{\mathbf{P}}^\perp(\mathbf{r}_m) \} \\ - 2\pi \sum_m \{ [\hat{\mu}_m, \hat{\mathcal{Q}}] \cdot \hat{\mathbf{P}}_m^\perp(\mathbf{r}_m) + \hat{\mathbf{P}}_m^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{\mathcal{Q}}] \} \quad (\text{A2b})$$

and

$$I_2 = -2\pi \sum_m \sum_{n (\neq m)} \{ [\hat{\mu}_m, \hat{\mathcal{Q}}] \cdot \hat{\mathbf{P}}_n^\perp(\mathbf{r}_m) \\ + \hat{\mathbf{P}}_n^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{\mathcal{Q}}] \} \quad (\text{A2c})$$

Here, $\hat{\mathbf{P}}_n^\perp(\mathbf{r})$ is the transverse part of the polarization field caused by molecule n only, evaluated at position \mathbf{r} . The total polarization field due to molecule n is given by [cf. Eq. (2)]

$$\hat{\mathbf{P}}_n(\mathbf{r}) = \hat{\mu}_n \delta(\mathbf{r} - \mathbf{r}_n), \quad (\text{A3a})$$

so that with Eq. (11a) we find for its transverse part

$$\hat{\mathbf{P}}_n^\perp(\mathbf{r}) = \hat{\delta}^\perp(\mathbf{r} - \mathbf{r}_n) \cdot \hat{\mu}_n. \quad (\text{A3b})$$

Clearly, the second term within the first sum of I_1 cancels the first term in the second sum. Using Eq. (A3b) and the fact that $\hat{\delta}^\perp$ is a symmetric tensor, the two remaining terms in I_1 ($\hat{\mu}_m \cdot [\hat{\mathbf{P}}_m^\perp(\mathbf{r}_m), \hat{\mathcal{Q}}]$ and $\hat{\mathbf{P}}_m^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{\mathcal{Q}}]$) are also found to cancel each other, so that I_1 vanishes identically. We now turn to the evaluation of I_2 . To this end we substitute Eq. (A3b) into Eq. (A2c) and use the explicit form for the transverse δ dyadic, given in Eq. (11), to obtain

$$I_2 = \frac{1}{2} \sum_m \sum_{n (\neq m)} \{ [\hat{\mu}_m, \hat{\mathcal{Q}}] \cdot \vec{\mathbf{T}}(\mathbf{r}_{mn}) \cdot \hat{\mu}_n \\ + [\vec{\mathbf{T}}(\mathbf{r}_{mn}) \cdot \hat{\mu}_n] \cdot [\hat{\mu}_m, \hat{\mathcal{Q}}] \}, \quad (\text{A4})$$

with $\mathbf{r}_{mn} \equiv \mathbf{r}_m - \mathbf{r}_n$. In the second term of Eq. (A4) we now interchange the dummy labels m and n and we use the properties $T_{ij}(\mathbf{r}_{mn}) = T_{ji}(\mathbf{r}_{mn})$ and $\vec{\mathbf{T}}(-\mathbf{r}) = \vec{\mathbf{T}}(\mathbf{r})$ to arrive at

$$I_2 = \frac{1}{2} \sum_m \sum_{n (\neq m)} [\hat{\mu}_m \cdot \vec{\mathbf{T}}(\mathbf{r}_{mn}) \cdot \hat{\mu}_n, \hat{\mathcal{Q}}]. \quad (\text{A5})$$

Substituting this result into Eq. (10) yields Eq. (12).

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