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Nonlinear optics using the multipolar Hamiltonian: The Bloch-Maxwell equations and local fields

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A systematic method for calculating nonlinear-optical susceptibilities in condensed phases, which incorporates intermolecular forces and spontaneous emission in a consistent way, is developed, using the multipolar ($\boldsymbol{\mu}\cdot\mathbf{D}$) Hamiltonian. Reduced equations of motion that couple the electromagnetic field and material variables are derived for a crystal of point dipoles. The Bloch equations in the local-field approximation, which were derived previously using macroscopic considerations, are obtained as a limiting case of the present microscopic theory. It is shown that correlations among the molecules and the radiation field are not treated rigorously in the local-field approximation, whereas they can be incorporated in a systematic way using the present formalism. An expression for the dielectric function $\epsilon(\mathbf{k},\omega)$ is obtained, which is different from Hopfield's exciton-polariton model. Our result does agree, however, with Hopfield's expression, which is based on the minimal-coupling ($\mathbf{p}\cdot\mathbf{A}$) Hamiltonian, in the long-wavelength and small-frequency limit ($k,\omega\rightarrow 0$), provided spontaneous emission is neglected.

I. INTRODUCTION

The systematic calculation of nonlinear-optical susceptibilities in condensed phases is a fundamental open problem in nonlinear optics.[1-3] The interpretation of nonlinear-optical measurements in terms of molecular properties and intermolecular forces requires the development of suitable theoretical methods. The linear-optical properties of a medium are given by its frequency- and wave-vector-dependent dielectric function $\epsilon(\mathbf{k},\omega)$. Numerous models and methods were developed to calculate $\epsilon(\mathbf{k},\omega)$.[4,19] Less rigorous and often phenomenological models are generally used in the calculation of nonlinear-optical processes.[1-3,20-27] In this paper we focus on the nonlinear optics of atomic or molecular systems with localized electronic states and multipolar intermolecular forces. A commonly used method for calculating the optical response of such systems starts by adding a term $-\boldsymbol{\mu}\cdot\mathbf{E}_{\text{ex}}(\mathbf{r},t)$ to the material Hamiltonian with instantaneous Coulomb forces.[1-3,11,16] This term represents the interaction with an external classical field. The density matrix of the system is then calculated using perturbation theory in $\mathbf{E}_{\text{ex}}(\mathbf{r},t)$, resulting in an expansion of the polarization. In this way, it is possible to use linear- and nonlinear-response theory to relate the molecular susceptibilities to appropriate multitime correlation functions of the dipole operator (response functions).[22,28,29] At low molecular density, the Maxwell (average) field $\mathbf{E}(\mathbf{r},t)$ equals $\mathbf{E}_{\text{ex}}(\mathbf{r},t)$, so that the macroscopic susceptibilities, which are the coefficients in the expansion of the polarization in terms of $\mathbf{E}$, are given by the molecular susceptibilities times the density. For realistic condensed phase systems with intermolecular forces, however, we need to relate $\mathbf{E}$ to $\mathbf{E}_{\text{ex}}$ in order to obtain the macroscopic susceptibilities. This goal may be accomplished using an exact macroscopic integral relation between $\mathbf{E}$ and $\mathbf{E}_{\text{ex}}$ (Refs. 9 and 20) [see Eq. (73)]. There are several problems with this procedure. First, the molecular polarizabilities and the relation between $\mathbf{E}$ and $\mathbf{E}_{\text{ex}}$ both depend on the shape and geometry of the sample, so that the calculation has to be done for a specific geometry.[17,18] It is believed that the susceptibilities are intrinsic material properties, which are shape independent. Nevertheless, their calculation with this procedure requires the calculation of shape-dependent quantities, and the shape dependence is canceled only at the final stage of the calculation. In addition, the approach is not fully microscopic, and retarded interactions are not properly taken into account. An alternative approach is based on the local-field approximation.[20,22,30] The idea is to incorporate intermolecular forces in a local field $\mathbf{E}_L$ and solve the time evolution of a single molecule in this field. The Lorentz relation[4] between $\mathbf{E}_L$ and $\mathbf{E}$ [see Eq. (75)] can then be used to obtain the desired susceptibilities. Again, intermolecular forces are not systematically included, and it is not clear how to improve upon these results.

In this paper we develop a systematic microscopic basis for the calculation of nonlinear-response functions and susceptibilities using the multipolar Hamiltonian, in which the radiation-matter interaction is given by $\boldsymbol{\mu}\cdot\mathbf{D}$, $\boldsymbol{\mu}$ being the dipole operator and $\mathbf{D}$ the electric displacement. This Hamiltonian can be obtained by a canonical transformation[31-33] from the more fundamental minimal-coupling ($\mathbf{p}\cdot\mathbf{A}$) Hamiltonian, in which the radiation-matter interaction is of the form $\mathbf{p}\cdot\mathbf{A}+\mathbf{A}^2$ ($\mathbf{p}$ being the electronic momentum and $\mathbf{A}$ the vector potential). On a formal level both Hamiltonians are equivalent, and it has been shown that when intermolecular forces are neglected the nonlinear-optical susceptibilities predicted by both Hamiltonians are identical.[2] Intermolecular forces enter both Hamiltonians, however, in a profoundly different fashion, and therefore they may yield different predictions for optical observables once approximations are made.[31-39]

The Hamiltonian and the microscopic model (a lattice of identical polarizable absorbers) are presented in Sec. II. In Sec. III, we construct a time-dependent projection operator,[22,40–43] which may be used to derive reduced equations of motion for material and radiation fields. These equations are formally exact and enable us in practice to incorporate intermolecular correlations as well as correlations between the matter and the radiation field in an approximate but systematic way. The reduced equations of motion are derived in Sec. IV. We show that the macroscopic Maxwell equations always hold, regardless of the approximations made to derive the equations for the material variables. The latter are obtained to second order in the dipole (which is the coupling constant), and spontaneous emission is properly included. The Bloch-Maxwell equations in the local-field approximation may be obtained from our reduced equations of motion after further approximations have been made. This is shown in Sec. V. Within this approximation, each molecule interacts with a local field $\mathbf{E}_L$, which contains the effects of the retarded dipole interactions with the other molecules. A precise definition of $\mathbf{E}_L$ is given. The important point of the present derivation of the Bloch equations is that it is a first term in a systematic expansion and that it shows limitations of the local-field concept arising from the incomplete treatment of correlations. In Sec. VI, we calculate the frequency- and wave-vector-dependent dielectric function $\varepsilon(\mathbf{k},\omega)$ for our model. In Sec. VII we repeat the derivation of the reduced equations of motion using the minimal-coupling Hamiltonian. The equations of motion obtained for the material variables are different from those derived in Sec. IV, and the resulting dielectric function $\varepsilon(\mathbf{k},\omega)$, which was first derived by Hopfield, is found to be different from that obtained in Sec. VI, using the $\boldsymbol{\mu}\cdot\mathbf{D}$ Hamiltonian. Finally, we discuss our results in Sec. VIII.

II. MICROSCOPIC MODEL AND HAMILTONIAN

We consider a lattice of arbitrary structure with sites occupied by identical molecules. We shall be interested in transitions between two electronic states of these molecules that are well separated from other electronic levels, so that each molecule may be described as a two-level system with transition energy $\hbar\Omega$. The molecules have no diagonal dipole matrix elements (nonpolar), but they are polarizable, and the transition dipole matrix element between the two states will be denoted $\boldsymbol{\mu}$. We further assume that this vector has the same orientation in the lattice for all molecules. Higher-order multipole moments will be neglected, so that we basically consider a lattice of point dipoles.

To describe the electromagnetic field, we work in the Coulomb gauge $\nabla\cdot\mathbf{A}=0$, $\mathbf{A}$ representing the vector potential, which in a natural way separates transverse ($\perp$) and longitudinal ($\parallel$) field components.[44] We confine ourselves in this paper to the linear and nonlinear response to transverse-electric fields (no excess charge). As explained in the Introduction, we start from the multipolar Hamiltonian, which in its dipole approximation (exact for point dipoles) reads[33]

$$\hat{H}=\hat{H}_0+\hat{H}_{\text{int}}\ , \tag{1}$$

with

$$\hat{H}_0=\hbar\Omega\sum_m \hat{B}_m^\dagger\hat{B}_m+\hbar\sum_{\mathbf{k}\lambda}\omega_k\hat{a}_{\mathbf{k}\lambda}^\dagger\hat{a}_{\mathbf{k}\lambda}\ , \tag{2}$$

and

$$\hat{H}_{\text{int}}=-\sum_m\hat{\boldsymbol{\mu}}_m\cdot\hat{\mathbf{D}}^\perp(\mathbf{r}_m)\ . \tag{3}$$

Throughout this paper, an operator is indicated by a caret, e.g., $\hat{O}$. Its expectation value at time t is written $\langle\hat{O}(t)\rangle$ or simply $O(t)$. $\hat{H}_0$ is the total unperturbed Hamiltonian of isolated molecules and radiation. $\hat{B}_m$ ($\hat{B}_m^\dagger$) is the destruction (creation) operator for an excitation on molecule m, obeying the anticommutation relations[11]

$$[\hat{B}_m^\dagger,\hat{B}_n]_+\equiv\hat{B}_m^\dagger\hat{B}_n+\hat{B}_n\hat{B}_m^\dagger=\delta_{m,n}+2\mathbf{B}_m^\dagger\hat{B}_n(1-\delta_{m,n})\ . \tag{4}$$

$\hat{a}_{\mathbf{k}\lambda}$ ($\hat{a}_{\mathbf{k}\lambda}^\dagger$) denotes the destruction (creation) operator of a photon of wave vector $\mathbf{k}$ and polarization λ, where the usual commutation relations apply,

$$[\hat{a}_{\mathbf{k}\lambda},\hat{a}_{\mathbf{k}'\lambda'}^\dagger]=\delta_{\mathbf{k},\mathbf{k}'}\delta_{\lambda,\lambda'}\ ,$$
$$[\hat{a}_{\mathbf{k}\lambda},\hat{a}_{\mathbf{k}'\lambda'}]=0\ ,$$
$$[\hat{a}_{\mathbf{k}\lambda}^\dagger,\hat{a}_{\mathbf{k}'\lambda'}^\dagger]=0\ .$$

Finally, $\omega_k=kc$ is the vacuum dispersion. $\hat{H}_{\text{int}}$ is the interaction Hamiltonian between matter and the electromagnetic field. $\hat{\boldsymbol{\mu}}_m$ denotes the dipole operator of the mth molecule, which in terms of the basic molecular operators reads

$$\hat{\boldsymbol{\mu}}_m=\boldsymbol{\mu}(\hat{B}_m+\hat{B}_m^\dagger)\ , \tag{5}$$

since the molecules are assumed to be polarizable but nonpolar. The position of molecule m is given by $\mathbf{r}_m$ and $\hat{\mathbf{D}}^\perp(\mathbf{r})$ is the transverse component of the electric displacement field

$$\hat{\mathbf{D}}(\mathbf{r})=\hat{\mathbf{E}}(\mathbf{r})+4\pi\hat{\mathbf{P}}(\mathbf{r})\ , \tag{6}$$

with $\hat{\mathbf{E}}$ and $\hat{\mathbf{P}}$ the electric field and polarization field, respectively. In the multipolar Hamiltonian, $\hat{\mathbf{D}}^\perp(\mathbf{r})$ is the conjugate momentum to the vector potential $\hat{\mathbf{A}}^\perp(\mathbf{r})$ $[=\hat{\mathbf{A}}(\mathbf{r})]$,[32,33] and these fields read in second quantization

$$\hat{\mathbf{A}}^\perp(\mathbf{r})=\sum_{\mathbf{k},\lambda}\left[\frac{2\pi\hbar c^2}{V\omega_k}\right]^{1/2}(\hat{a}_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}}+\hat{a}_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}})\mathbf{e}_{\mathbf{k}\lambda}\ , \tag{7a}$$

$$\hat{\mathbf{D}}^\perp(\mathbf{r})=i\sum_{\mathbf{k},\lambda}\left[\frac{2\pi\hbar\omega_k}{V}\right]^{1/2}(\hat{a}_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}}-\hat{a}_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}})\mathbf{e}_{\mathbf{k}\lambda}\ , \tag{7b}$$

with V the volume of the normalization box, and $\mathbf{e}_{\mathbf{k}\lambda}$ the unit polarization vector of mode $\mathbf{k}\lambda$. We take $\mathbf{e}_{\mathbf{k}\lambda}$ real and use the convention $\mathbf{e}_{-\mathbf{k}\lambda}=\mathbf{e}_{\mathbf{k}\lambda}$. It is important to note that the multipolar Hamiltonian does not contain any explicit intermolecular interactions; all interactions are mediated through the radiation field, by emission and absorption of transverse photons.

Our main goal in this paper is to derive coupled equations of motion for the expectation values of the electromagnetic fields [Eq. (7)] and the molecular operators $\hat{B}_m$, $\hat{B}_m^\dagger$, $\hat{B}_m^\dagger\hat{B}_m$ (for all m). These equations should enable us to calculate electric susceptibilities from a purely microscopic starting point. The three molecular operators, mentioned above, form, together with the identity $\hat{I}$, a complete set in the Hilbert space of the mth molecule, since we treat the molecules as two-level systems. Of course, linear combinations of these operators that are better suited for our purposes can be taken instead. At low density, the material equations of motion should reduce to the optical Bloch equations for an isolated molecule.[3] We further expect the radiation fields to satisfy the macroscopic Maxwell equations.

For future use, we define the following Hermitian material densities:

$$\hat{\mathbf{P}}(\mathbf{r})=\sum_m \boldsymbol{\mu}(\hat{B}_m+\hat{B}_m^\dagger)\delta(\mathbf{r}-\mathbf{r}_m)\ , \tag{8a}$$

$$\hat{\mathbf{V}}(\mathbf{r})=i\sum_m \boldsymbol{\mu}(\hat{B}_m-\hat{B}_m^\dagger)\delta(\mathbf{r}-\mathbf{r}_m)\ , \tag{8b}$$

$$\hat{W}(\mathbf{r})=\sum_m \hat{W}_m\delta(\mathbf{r}-\mathbf{r}_m)\equiv\sum_m(\hat{B}_m^\dagger\hat{B}_m-\hat{B}_m\hat{B}_m^\dagger)\delta(\mathbf{r}-\mathbf{r}_m)\ . \tag{8c}$$

$\hat{\mathbf{P}}$ is the polarization density, as mentioned earlier, and $\hat{W}$ denotes the inversion density, measuring the difference in populations between excited and ground states. It is also useful to define the nondynamical material field

$$\rho(\mathbf{r})=\sum_m \delta(\mathbf{r}-\mathbf{r}_m)\ , \tag{9}$$

which is the ordinary molecular number density.

Throughout this paper, we use the following spatial and temporal Fourier transforms:

$$f(\mathbf{k})=\int_V d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{r})\ , \tag{10a}$$

$$f(\mathbf{r})=\frac{1}{V}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{k})\ , \tag{10b}$$

and

$$h(\omega)=\int_{-\infty}^{+\infty}dt\, e^{i\omega t}h(t)\ , \tag{11a}$$

$$h(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega\, e^{-i\omega t}h(\omega)\ . \tag{11b}$$

The k representation of the polarization field thus reads

$$\hat{\mathbf{P}}(\mathbf{k})=\sum_m \boldsymbol{\mu}(\hat{B}_m+\hat{B}_m^\dagger)e^{-i\mathbf{k}\cdot\mathbf{r}_m}\ , \tag{12}$$

and analogous forms hold for the other material fields. Of course, any density

$$C(\mathbf{r})=\sum_m C_m\delta(\mathbf{r}-\mathbf{r}_m)\ ,$$

with C_m some molecular variable, has a periodic Fourier transform $C(\mathbf{k}+2\pi\mathbf{G})=C(\mathbf{k})$, where $\mathbf{G}$ is a vector on the reciprocal lattice. One may write the inverse Fourier transform to C_m, rather than to $C(\mathbf{r})$, as

$$C_m=\frac{1}{N}\sum_{\substack{k\\ 1\ \mathrm{BZ}}} C(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}_m}\ , \tag{13}$$

where N is the number of lattice sites, and, in contrast to Eq. (10b), the sum now extends over the first Brillouin zone only.

III. PROJECTION OPERATORS AND THE FORMAL REDUCTION SCHEME

A natural way to obtain equations for the expectation values of radiation field and matter operators is provided by taking the expectation values of the Heisenberg equations of motion for these operators. This procedure, however, will never give in a rigorous way a closed set of equations for a finite number of expectation values. The reason is that the time derivatives of the material operators contain products of material and radiation field operators. These products are new operators for which, in turn, the Heisenberg equations must be derived, which would again yield new products, etc. This procedure will thus yield an infinite hierarchy of coupled equations, as is common in statistical mechanics.[45] An approximate way out of this is to factorize the expectation value of a product into the product of expectation values. This would be an exact procedure if for all times the system's total density operator was a direct product of a radiation and a matter density operator. Although this may indeed by the case for some initial moment, interactions obviously correlate the radiation and matter evolution, thus making crude factorization an *ad hoc* approximation. The basic idea of factorization is appealing, however, and leads one to consider projection-operator techniques,[40–43,46] which give the factorization as a lowest-order result, but also prescribe an in principle exact procedure to incorporate corrections due to interactions.

In order to define a projection operator, it is useful to first point out the relevant operators, whose expectation values we want to describe exactly. In our case, these are the single molecule operators ($\hat{B}_m$, $\hat{B}_m^\dagger$, $\hat{B}_m^\dagger\hat{B}_m$, and $\hat{I}$) and the creation and annihilation operators $\hat{a}_{\mathbf{k}\lambda}$ and $\hat{a}_{\mathbf{k}\lambda}^\dagger$ for a certain discrete set of *special modes* $\mathbf{k}\lambda$ only. The dynamics of nonlinear-optical experiments is often adequately described using a few modes of the radiation field which obey the macroscopic Maxwell equations.[3] These modes will constitute the special modes. It turns out that, for our purpose, a time-dependent projection, based on the ideas of Lax[41] and Willis and Picard,[42] and in fact very similar to the projection introduced by the latter, is the most useful. We define the operator $P(t)$ (not to be confused with the vector $\mathbf{P}$, which is the polarization) by

$$P(t)=\sum_m \left[\left[\prod_{n\neq m} \hat{\rho}_n(t) \right] \left[\prod_{\mathbf{k}\lambda}{}' \hat{\rho}_{\mathbf{k}\lambda}(t) \right] (|0\rangle\langle 0|)_{\mathrm{ns}} \mathrm{Tr}^m \right] + \sum_{\mathbf{k}\lambda}{}' \left[\left[\prod_m \hat{\rho}_m(t) \right] \left[\prod_{\mathbf{k}'\lambda'\neq\mathbf{k}\lambda}{}' \hat{\rho}_{\mathbf{k}'\lambda'}(t) \right] (|0\rangle\langle 0|)_{\mathrm{ns}} \mathrm{Tr}^{\mathbf{k}\lambda} \right]$$
$$-(N+N_s-1) \left[\left[\prod_m \hat{\rho}_m(t) \right] \left[\prod_{\mathbf{k}\lambda}{}' \hat{\rho}_{\mathbf{k}\lambda}(t) \right] (|0\rangle\langle 0|)_{\mathrm{ns}} \mathrm{Tr} \right] , \tag{14}$$

where Tr denotes the total trace and Tr^m ($\mathrm{Tr}^{\mathbf{k}\lambda}$) takes the total trace, except over the degrees of freedom of the molecule m (mode $\mathbf{k}\lambda$). A prime on a summation (multiplication) indicates that the summation (multiplication) involved only runs over special modes. Further,

$$\hat{\rho}_m(t)=\mathrm{Tr}^m \hat{\rho}(t) \tag{15a}$$

and

$$\hat{\rho}_{\mathbf{k}\lambda}(t)=\mathrm{Tr}^{\mathbf{k}\lambda} \hat{\rho}(t) , \tag{15b}$$

where $\hat{\rho}(t)$ is the total density operator of the system. Clearly, $\hat{\rho}_m(t)$ and $\hat{\rho}_{\mathbf{k}\lambda}(t)$ are operators in the state space of m and $\mathbf{k}\lambda$ only. Finally, $(|0\rangle\langle 0|)_{\mathrm{ns}}$ represents the vacuum density operator for all nonspecial modes, and N and N_s denote the number of molecules and special modes, respectively. All products in Eq. (14) are, of course, to be understood as direct products.

$P(t)$ can act on any operator for which the trace exists. Although Eq. (14) gives the impression that $P(t)$ is very complicated, it has some simple and appealing properties, which we give without proof. The derivations are either elementary, albeit somewhat tedious, or can be found in close analogy to those given in Ref. 42.

(i) When the projection operator acts on the density matrix of the system, we get

$$P(t)\hat{\rho}(t)= \left[\prod_m \hat{\rho}_m(t) \right] \left[\prod_{\mathbf{k}\lambda}{}' \hat{\rho}_{\mathbf{k}\lambda}(t) \right] (|0\rangle\langle 0|)_{\mathrm{ns}}$$
$$\equiv \hat{\sigma}(t) . \tag{16}$$

$P(t)$ thus projects the total density operator $\hat{\rho}(t)$ onto a product of single-molecule and single-radiation mode operators. The nonspecial modes are projected on the vacuum. Using Eqs. (15), it is easily checked that $\hat{\sigma}(t)$ is normalized if $\hat{\rho}(t)$ is, i.e., $\mathrm{Tr}[\hat{\sigma}(t)]=1$.

(ii) $P(t_1)P(t_2)=P(t_1)$, which, as a special case, yields $[P(t)]^2=P(t)$, so that $P(t)$ is indeed a projection.

(iii) We have

$$\frac{d}{dt}[P(t)\hat{\rho}(t)]=P(t)\frac{d}{dt}\hat{\rho}(t) . \tag{17}$$

(iv) $\hat{\sigma}$ gives the exact expectation values of any operator $\hat{A}$ that only acts in the state space of a single molecule or a single special mode:

$$\mathrm{Tr}[\hat{\sigma}(t)\hat{A}]=\mathrm{Tr}[\hat{\rho}(t)\hat{A}] . \tag{18a}$$

In fact, an even more general relation is valid,

$$\mathrm{Tr}[\hat{A}P(t)\hat{B}]=\mathrm{Tr}(\hat{A}\hat{B}) , \tag{18b}$$

with $\hat{A}$ as before, and $\hat{B}$ an arbitrary operator. Equation (18a) is a special case of Eq. (18b) with $\hat{B}=\hat{\rho}(t)$.

(v) The expectation value of a product of two or more operators, as in (iv), that act on different molecules and (or) different special modes, is factorized by $\hat{\sigma}(t)$ into the product of the exact expectation values of these operators.

Thus, although $\hat{\sigma}(t)$ is a much simpler density operator than $\hat{\rho}(t)$, we can still obtain the exact expectation values of the relevant operators from it. The complexity of $\hat{\sigma}(t)$ is reflected in its time evolution, which can be determined by starting from the Liouville equation for $\hat{\rho}(t)$,

$$\frac{d\hat{\rho}(t)}{dt}=-iL\hat{\rho}(t) , \tag{19}$$

with $\hbar L\hat{C}=[\hat{H},\hat{C}]$ the Liouville operator associated with the total Hamiltonian, $\hat{C}$ being an arbitrary operator. Acting on Eq. (19) with $P(t)$ and $Q(t)\equiv 1-P(t)$, and using the properties of the projection, one eventually derives an exact reduced equation of motion for $\hat{\sigma}(t)$, which, assuming that at some initial time t_0 (taken to be $-\infty$ in practice) $\hat{\sigma}(t_0)=\hat{\rho}(t_0)$, reads

$$\frac{d}{dt}\hat{\sigma}(t)= -iP(t)L\hat{\sigma}(t)$$
$$-\int_{t_0}^{t} dt' P(t)L_{\mathrm{int}}G(t,t')Q(t')L_{\mathrm{int}}\hat{\sigma}(t') . \tag{20}$$

Here

$$G(t,t')=\exp_+ \left\{ -i\int_{t'}^{t} ds[L_0+Q(s)L_{\mathrm{int}}] \right\} , \tag{21}$$

with $\hbar L_0\hat{C}=[\hat{H}_0,\hat{C}]$ and $\hbar L_{\mathrm{int}}\hat{C}=[\hat{H}_{\mathrm{int}},\hat{C}]$. Although the derivation of Eq. (20) is rather standard in projection-operator techniques, we point out some of the essential steps in Appendix A. It should be stressed that property (iii) is of great importance here; for time-dependent projections, which do not obey Eq. (17), it is impossible to obtain a closed equation of motion for $\hat{\sigma}(t)$ alone.

From Eq. (20) one easily derives exact equations of motion for the expectation values of all operators acting on a single molecule or on a special mode. Let $\hat{A}$ denote such an operator. Multiplying Eq. (20) from the left by it, and taking a total trace, one finds, using Eqs. (18),

$$\frac{d}{dt}\langle \hat{A}(t)\rangle = -i\langle\langle \hat{A}^\dagger|L|\hat{\sigma}(t)\rangle\rangle - \int_{t_0}^{t} dt' \langle\langle \hat{A}^\dagger|L_{\mathrm{int}}G(t,t')Q(t')L_{\mathrm{int}}|\hat{\sigma}(t')\rangle\rangle . \tag{22}$$

In this equation, we use Liouville-space notation, whereby an ordinary operator $\hat{A}$ is written as a ket$|\hat{A}\rangle\rangle$, and $\langle\langle\hat{A}|\hat{B}\rangle\rangle\equiv\mathrm{Tr}(\hat{A}^\dagger B)$ is the scalar product. $\langle\langle\hat{A}|L|\hat{B}\rangle\rangle\equiv\mathrm{Tr}(\hat{A}^\dagger L\hat{B})$ is a Liouville-space "matrix element."[47]

The first term to the right-hand side of Eq. (22) will be called the mean-field term, because it describes the behavior of the system as if the individual molecules and radiation modes evolve in an uncorrelated way, only interacting with each other's averages, i.e., as if $\hat{\rho}(t)=\hat{\sigma}(t)$ at all times. Evaluation of this term is completely equivalent to taking the expectation value of the Heisenberg equation of motion and factorizing any expectation value of a product of operators into the product of expectation values. This may be verified most easily by using the fact that L is Hermitian in Liouville space:

$$\langle\langle \hat{A}^{\dagger}|L|\hat{\sigma}(t)\rangle\rangle=\langle\langle L\hat{A}^{\dagger}|\sigma(t)\rangle\rangle \ ,$$

and by changing from the Schrödinger to the Heisenberg picture.

The second term in Eq. (22) will be called the kernel (term); it gives the exact correction due to correlated evolution. If $L_{\text{int}}\hat{A}$ is a linear combination of single-molecule and (or) single special mode operators, it is easily shown [using Eqs. (A5) and (18b)] that this term rigorously equals zero. In other words, the mean-field term then provides the exact equation of motion for $\langle \hat{A}(t)\rangle$. This is equivalent to the fact that the Heisenberg equation of motion for $\hat{A}(t)$ in that case would not contain any operator products that would have to be factorized. In general, however, the kernel term is very complicated, and it is impossible to evaluate it without approximations, since all the problems of correlated dynamics are hidden in it. The natural way to proceed is to expand $G(t,t')$ perturbatively in the interaction,

$$G(t,t')=G_0(t,t')-i\int_{t_0}^{t}dt_1 G_0(t,t_1)Q(t_1)L_{\text{int}}G_0(t_1,t') + \cdots \ , \tag{23}$$

with $G_0(t,t')=\exp[-iL_0(t-t')]$, the unperturbed propagator. The first term in this expansion describes the contribution if no interactions take place between t' and t, in the second term one interaction occurs at time t_1, etc. Alternatively, a density (cluster) expansion of $G(t,t')$ may be developed.[45] To calculate the kernel term, we have to parametrize $\hat{\sigma}(t)$ in terms of the expectation values of the single-molecule and single special mode operators. Formally, this can always be done, because of the factorized form of $\hat{\sigma}(t)$ [cf. Eq. (16)]. If we then evaluate Eq. (22) for all single-molecule and single special mode operators, we obtain a closed set of equations for their expectation values. In practice, the molecular part of $\hat{\sigma}(t)$ can be uniquely parametrized, since there are only four independent single-molecule operators. We thus have

$$\hat{\rho}_m(t)=\tfrac{1}{2}[1-\langle \hat{W}_m(t)\rangle]\hat{B}_m\hat{B}_m^{\dagger}+\langle \hat{B}_m^{\dagger}(t)\rangle\hat{B}_m + \langle \hat{B}_m(t)\rangle\hat{B}_m^{\dagger}+\tfrac{1}{2}[1+\langle \hat{W}_m(t)\rangle]\hat{B}_m^{\dagger}\hat{B}_m \ . \tag{24}$$

This form contains three parameters, namely, the complex expectation value $\langle \hat{B}_m(t)\rangle$ [$\langle \hat{B}_m^{\dagger}(t)\rangle=\langle B_m(t)\rangle^{*}$, $*$ denoting complex conjugation], and $\langle \hat{W}_m(t)\rangle$, the real expectation value of the molecular inversion. A fourth parameter is already used to guarantee the normalization of $\hat{\rho}_m(t)$, i.e., the expectation value of $\hat{I}$. It is an elementary exercise to show that Eq. (24) indeed yields the proper expectation values of all operators in the state space of molecule m. It is not possible to treat the special modes in a similar manner, because the number of independent operators acting in the state space of even one single mode is infinite. The more rigorous way out of this is to extend the projection in such a way that it projects every $\hat{\rho}_{\mathbf{k}\lambda}(t)$ onto a specific form that is physically acceptable and that is described by only a small number of parameters, e.g., a coherent-state density operator, in which case one complex parameter suffices, namely, the expectation value of $\hat{a}_{\mathbf{k}\lambda}$.[48] We will not go into the detail of such an extension, because in the present paper we will take the kernel term of Eq. (22) only to zeroth order in the special mode amplitude. This is equivalent to taking $\hat{\rho}_{\mathbf{k}\lambda}$ in this term to be $(|0\rangle\langle 0|)_{\mathbf{k}\lambda}$, the vacuum of mode $\mathbf{k}\lambda$. This is not the same as neglecting the special modes altogether in this term, as will be shown in the coming sections.

To conclude this section, we comment on some general aspects of the reduced equations of motion [Eq. (20) or (22)]. In their derivation, we assumed that at the initial time $t_0=-\infty$, $\hat{\sigma}(t_0)=\hat{\rho}(t_0)$. This is justified if, first of all, the macroscopic electromagnetic fields are turned on adiabatically in the infinite past, so that initially there are no correlations between the radiation field and the material system. If, furthermore, we confine ourselves to low temperatures, all molecules will be in the ground state at $t=t_0$, so that the material density operator is a product of the ground-state density operators of the individual molecules. Given the initial condition $\hat{\sigma}(t_0)=\hat{\rho}(t_0)$, reduced equations of motion in the form of Eqs. (20) and (22) can always be derived, irrespective of the specific choice of relevant variables. The first term in the equations always describes the evolution of these variables in a mean-field model, whereas the second (kernel) term accounts in an exact way for the dynamic correlations. The practical use of the reduced equations of motion does, however, largely depend on the choice of the relevant set. For an appropriate choice, the corrections given by the kernel term are small or are predominantly contained within the first few terms of the perturbation series [Eq. (22) with Eq. (23)]. A general procedure is to incorporate in the relevant set all those variables that vary on a macroscopic time scale; all other variables are included in the complementary (Q) space. If a clear separation of time scales exists, the kernel term describes relaxation of the macroscopic variables to their equilibrium value.[40(b)] Often, however, intuition has to be used in selecting the relevant variables, and a check on the suitability of a chosen set can only be performed by (i) investigating how extension of the set by more variables affects the results, (ii) studying the behavior of the perturbation series for the selected set, or (iii) comparing limiting cases of the obtained results to other theories, which will be done in Secs. IV and V.

IV. REDUCED EQUATIONS OF MOTION FOR THE MOLECULAR AND FIELD VARIABLES

In this section, we use the formalism developed in Sec. III to obtain explicit reduced equations of motion for our relevant molecular and field variables. To derive the equations for the special modes of the electromagnetic field, we take $\hat{A}=\hat{a}_{\mathbf{k}\lambda}$ in Eq. (22), $\mathbf{k}\lambda$ being in the special set. [$\hat{A}=\hat{a}^{\dagger}_{\mathbf{k}\lambda}$ would give the same information, because $\langle \hat{a}^{\dagger}_{\mathbf{k}\lambda}(t)\rangle=\langle \hat{a}_{\mathbf{k}\lambda}(t)\rangle^{*}$.] For given $\mathbf{k}$, we include both polarizations in the special set and also $-\mathbf{k}$ with its polarizations. From Eqs. (3), (5), and (7b), it is found that

$$L_{\mathrm{int}}\hat{a}_{\mathbf{k}\lambda}=\frac{-i}{\hbar}\sum_{m} C_{\mathbf{k}\lambda}(\hat{B}_m+\hat{B}^{\dagger}_m)e^{-i\mathbf{k}\cdot\mathbf{r}_m} , \tag{25}$$

with

$$C_{\mathbf{k}\lambda}=(\boldsymbol{\mu}\cdot\mathbf{e}_{\mathbf{k}\lambda})\left[\frac{2\pi\hbar\omega_k}{V}\right]^{1/2} . \tag{26}$$

Thus $L_{\mathrm{int}}\hat{a}_{\mathbf{k}\lambda}$ is a sum over single-molecule operators, so that the mean-field term of Eq. (22) provides the exact equation of motion for $\langle \hat{a}_{\mathbf{k}\lambda}(t)\rangle$. We get

$$\frac{d}{dt}\langle \hat{a}_{k\lambda}(t)\rangle = -i\omega_k\langle \hat{a}_{\mathbf{k}\lambda}(t)\rangle + \frac{1}{\hbar}C_{\mathbf{k}\lambda}\sum_{m}\langle(\hat{B}_m+\hat{B}^{\dagger}_m)(t)\rangle e^{-i\mathbf{k}\cdot\mathbf{r}_m} , \tag{27}$$

where $\mathbf{k}\lambda$ denotes one of the special modes. From Eq. (27) we obtain for the Fourier components of the expectation values of the vector potential and displacement

$$\frac{\partial}{\partial t}\mathbf{A}^{\perp}(\mathbf{k},t)=-c\mathbf{D}^{\perp}(\mathbf{k},t)+4\pi c\mathbf{P}^{\perp}(\mathbf{k},t) , \tag{28a}$$

$$\frac{\partial}{\partial t}\mathbf{D}^{\perp}(\mathbf{k},t)=\frac{\omega_k^2}{c}\mathbf{A}^{\perp}(\mathbf{k},t) . \tag{28b}$$

$\mathbf{P}^{\perp}$ is the transverse part of the polarization field, which follows from Eq. (12),

$$\begin{aligned}\hat{\mathbf{P}}^{\perp}(\mathbf{k},t)&=\sum_{\lambda}(\boldsymbol{\mu}\cdot\mathbf{e}_{\mathbf{k}\lambda})\mathbf{e}_{\mathbf{k}\lambda}\sum_{m}\langle(\hat{B}_m+\hat{B}^{\dagger}_m)(t)\rangle e^{-i\mathbf{k}\cdot\mathbf{r}_m}\\ &=(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\sum_{m}\boldsymbol{\mu}\langle(\hat{B}_m+\hat{B}^{\dagger}_m)(t)\rangle e^{-i\mathbf{k}\cdot\mathbf{r}_m} ,\end{aligned} \tag{29}$$

where $\hat{\mathbf{k}}$ is the unit vector in the $\mathbf{k}$ direction, and the sum rule for polarization vectors, $\sum_{\lambda}e_{\mathbf{k}\lambda}\mathbf{e}_{\mathbf{k}\lambda}=\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}}$, has been used ($\mathbf{kk}$ denotes the tensor with ijth component k_ik_j).

We will now show that Eqs. (28) are equivalent to the Maxwell equations. Splitting the latter into longitudinal and transverse parts,[6,7] we get as the only nontrivial equations for our system (in $\mathbf{k}$ representation)

$$\mathbf{E}^{\perp}(\mathbf{k},t)=-\frac{1}{c}\frac{\partial}{\partial t}\mathbf{A}^{\perp}(\mathbf{k},t) , \tag{30a}$$

$$-k^2\mathbf{A}^{\perp}(\mathbf{k},t)-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A}^{\perp}(\mathbf{k},t)=-\frac{4\pi}{c}\mathbf{j}^{\perp}(\mathbf{k},t), \tag{30b}$$

$$\mathbf{E}^{\parallel}(\mathbf{k},t)=-4\pi\mathbf{P}^{\parallel}(\mathbf{k},t) . \tag{30c}$$

Here $\mathbf{j}$ is the current density, and the last equation merely states that there are no monopoles (excess charges) in the system ($\nabla\cdot\mathbf{D}=0$). Equation (30a) is equivalent to Eq. (28a) [cf. Eq. (6)]. To show that Eq. (30b) is satisfied, one eliminates $\mathbf{D}^{\perp}(\mathbf{k},t)$ from Eqs. (28) and uses $\mathbf{j}(\mathbf{r},t)=\partial\mathbf{P}(\mathbf{r},t)/\partial t$, which holds for systems without magnetization.[33] Finally, Eq. (30c) is not part of our radiation equations of motion, which only govern the transverse-electromagnetic fields, but is explicitly valid in our system. $\mathbf{E}^{\parallel}(\mathbf{r},t)$ is the instantaneous Coulomb field generated by the point dipoles, which is, using the static dipole field, easily written explicitly in terms of the expectation values of the molecular dipole operators. Through Eq. (5), $\mathbf{E}^{\parallel}(\mathbf{r},t)$ is then expressed in $\langle \hat{B}_m(t)\rangle$ and $\langle \hat{B}^{\dagger}_m(t)\rangle$. The same can be done for $\mathbf{P}^{\parallel}(\mathbf{r},t)$, using the expectation value of Eq. (8a) and the longitudinal δ function in $\mathbf{r}$ representation.[33,44] Comparison of the two results shows that Eq. (30c) holds, irrespective of the time evolutions of $\langle \hat{B}_m(t)\rangle$ and $\langle \hat{B}^{\dagger}_m(t)\rangle$.

We finally stress that, in view of the exactness of the mean-field term, we do not need the projection and the definition of special modes to recover the Maxwell equation. In fact, Eqs. (28) are even found to hold at every $\mathbf{k}$ for the operators $\hat{\mathbf{A}}^{\perp}$, $\hat{\mathbf{D}}^{\perp}$, and $\hat{\mathbf{P}}^{\perp}$ in the Heisenberg picture, by evaluating their equations of motion. This proves that the multipolar Hamiltonian, even after making the point-dipole approximation, is not incompatible with the validity of Maxwell's equations. This conclusion is different from earlier results.[38]

We proceed by using Eq. (22) to evaluate the equations of motion for the material variables, for which we will take the expectation values of the Hermitian operators $\hat{B}_m+\hat{B}^{\dagger}_m$, $i(\hat{B}_m-\hat{B}^{\dagger}_m)$, and $\hat{W}_m$. It is easily shown that

$$L_{\mathrm{int}}(\hat{B}_m+\hat{B}^{\dagger}_m)=0 ,$$

so that for the first operator, again, the mean-field term is exact. For the two remaining operators, however, L_{int} generates products of single-molecule and single special mode operators, which means that the kernel term in Eq. (22) *does* contribute. We evaluate this term to second order in the interaction, i.e., we only take the first right-hand side term of the perturbation expansion Eq. (23), and to zeroth order in the special mode amplitudes, as explained in Sec. III. The mean-field term is calculated without approximations. The actual calculation of the second-order kernel term is a tedious but straightforward algebraic exercise, of which we do not present any details. Instead, we give a short description of the processes that contribute to it. All these processes contain two interactions with the radiation field. In the first interaction between a molecule and a radiation mode $\mathbf{k}\lambda$, a photon coherence ($|0\rangle\langle\mathbf{k}\lambda|$ or $|\mathbf{k}\lambda\rangle\langle 0|$) is created. In the second interaction, taking place either with the same (self-interaction) or with another molecule, this coherence is changed into a population ($|0\rangle\langle 0|$ or $|\mathbf{k}\lambda\rangle\langle\mathbf{k}\lambda|$). Loosely speaking, many of these processes consist of emission of a photon by a molecule and absorption of it by another, although this is an incomplete description. We stress that in our calculation all possible second-order processes are taken into account, which means that we do not apply a rotating-wave approximation. Also, no Markovian approximation is made. Eventually we find as reduced equations of motion for the material variables

$$\frac{d}{dt}\langle(\hat{B}_m+\hat{B}_m^\dagger)(t)\rangle=-\Omega\langle i(\hat{B}_m-\hat{B}_m^\dagger)(t)\rangle-\Gamma\langle(\hat{B}_m+\hat{B}_m^\dagger)(t)\rangle\ , \tag{31a}$$

$$\begin{aligned}\frac{d}{dt}\langle i(\hat{B}_m-\hat{B}_m^\dagger)(t)\rangle=\ &\Omega\langle(\hat{B}_m+\hat{B}_m^\dagger)(t)\rangle+\frac{2}{\hbar}\boldsymbol{\mu}\cdot\langle\hat{\mathbf{D}}_s^\perp(\mathbf{r}_m,t)\rangle\langle\hat{W}_m(t)\rangle-\Gamma\langle i(\hat{B}_m-\hat{B}_m^\dagger)(t)\rangle\\&+\frac{2}{\hbar}\boldsymbol{\mu}\cdot\int_{t_0}^{t}dt'\left[\sum_{n\neq m}\mathbf{M}(\mathbf{r}_{mn},t-t')\cdot\boldsymbol{\mu}\langle(\hat{B}_n+\hat{B}_n^\dagger)(t')\rangle\langle\hat{W}_m(t')\rangle\right]\\&-\int_{t_0}^{t}dt'K_1(t-t')\langle i(\hat{B}_m-\hat{B}_m^\dagger)(t')\rangle\ ,\end{aligned} \tag{31b}$$

$$\begin{aligned}\frac{d}{dt}\langle\hat{W}_m(t)\rangle=\ &-\frac{2}{\hbar}\boldsymbol{\mu}\cdot\langle\hat{\mathbf{D}}_s^\perp(\mathbf{r}_m,t)\rangle\langle i(\hat{B}_m-\hat{B}_m^\dagger)(t)\rangle\\&-\frac{2}{\hbar}\boldsymbol{\mu}\cdot\int_{t_0}^{t}dt'\left[\sum_{n\neq m}\mathbf{M}(\mathbf{r}_{mn},t-t')\cdot\boldsymbol{\mu}\langle(\hat{B}_n+\hat{B}_n^\dagger)(t')\rangle i[\langle\hat{B}_m(t')\rangle e^{-i\Omega(t-t')}-\langle\hat{B}_m^\dagger(t')\rangle e^{i\Omega(t-t')}]\right]\\&-\int_{t_0}^{t}dt'\{K_2(t-t')\tfrac{1}{2}[1+\langle\hat{W}_m(t')\rangle]-K_3(t-t')\tfrac{1}{2}[1-\langle\hat{W}_m(t')\rangle]\}\ .\end{aligned} \tag{31c}$$

All terms containing time integrals emerge from the kernel term of Eq. (22), and they contain the effects of intermolecular forces as well as superradiance. Previous derivations of the superradiance master equation were made in the absence of the Maxwell field and the present derivation generalizes these earlier works.[49] Γ accounts in a phenomenological way for pure dephasing (T_2 processes).[50] The remaining contributions come from the mean-field term. The field $\hat{\mathbf{D}}_s(\mathbf{r})$ is the displacement field made up by special modes only, i.e., Eq. (7b) with its summation running over special $\mathbf{k}$ values only. The vector $\mathbf{r}_{mn}$ stands for $\mathbf{r}_m-\mathbf{r}_n$, and the tensor $\mathbf{M}$ is defined by

$$\mathbf{M}(\mathbf{r},t)=\frac{2\pi i}{V}\sum_{\mathbf{k}}{}^{*}\,kc(1-\hat{\mathbf{k}}\hat{\mathbf{k}})(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)}-e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)}) \tag{32}$$

for $t>0$, and $\mathbf{M}(\mathbf{r},t)=0$ otherwise. Special modes are excluded from the $\mathbf{k}$ summation, as is indicated by the asterisk. $\mathbf{M}(\mathbf{r},t)$ represents the effective interaction between two molecules at separation $\mathbf{r}$, mediated by nonspecial photon modes in processes as described above. The exclusion of the special photon modes from $\mathbf{M}$ is a direct consequence of the complementary projection $Q(t')$ in the kernel term and the special role these modes still play in the projection [cf. Eq. (14)], even though $\hat{\rho}_{\mathbf{k}\lambda}(t)$ is replaced by $(|0\rangle\langle 0|)_{\mathbf{k}\lambda}$ in the evaluation of the kernel. Without this exclusion, there will be an overcounting of the contribution of the special modes. $K_1(t)$, $K_2(t)$, and $K_3(t)$ in Eqs. (31) are due to the radiative self-interactions. They cause radiative decay and energy shifts; apparently the variable $\langle(\hat{B}_m+\hat{B}_m^\dagger)(t)\rangle$ is not directly affected by such processes, which should not be surprising, since the mean-field term for this operator is exact. Explicitly, we have

$$K_1(t)=\frac{4\pi}{\hbar V}\boldsymbol{\mu}\cdot\left[\sum_{\mathbf{k}}\omega_k(1-\hat{\mathbf{k}}\hat{\mathbf{k}})(e^{i\omega_k t}+e^{-i\omega_k t})\right]\cdot\boldsymbol{\mu}\ . \tag{33}$$

$K_2(t)$ and $K_3(t)$ are given by the same expression, except that ω_k in the time exponentials is replaced by $\omega_k-\Omega$ for $K_2(t)$ and by $\omega_k+\Omega$ for $K_3(t)$. Again, Eq. (33) only holds for $t\geq 0$, for $t<0$ the function equals zero. Strictly speaking, a different summand should be used for special $\mathbf{k}$ values, but their contribution to $K_1(t)$ is negligible in the final results if the normalization volume is taken large enough. A more detailed discussion of $\mathbf{M}(\mathbf{r},t)$ and $K_1(t)$ ($i=1,2,3$) is given in Sec. V.

Equations (31) are, in fact, valid for any configuration of the molecules, and even for arbitrary orientations of the individual dipoles by just placing the proper dipoles in the right-hand sides of Eqs. (31): $\mathbf{M}$ should then be sandwiched between $\boldsymbol{\mu}_m$ and $\boldsymbol{\mu}_n$, and all other dipoles should read $\boldsymbol{\mu}_m$.

In concluding this section, let us consider the case of very dilute samples of absorbers. Let ρ denote the average number density N/V. Then in the limit $\rho\to 0$, the intermolecular interactions $\mathbf{M}$ may be neglected in Eqs. (31). Multiplying these equations by $\delta(\mathbf{r}-\mathbf{r}_m)$ and summation over m yields equations for the densities $\langle\hat{\mathbf{P}}(\mathbf{r},t)\rangle$, $\langle\hat{\mathbf{V}}(\mathbf{r},t)\rangle$, and $\langle\hat{W}(\mathbf{r},t)\rangle$ [cf. Eqs. (8)], in which to first order in ρ, $\langle\hat{\mathbf{D}}_s^\perp(\mathbf{r},t)\rangle$ may be replaced by $\langle\hat{\mathbf{E}}_s^\perp(\mathbf{r},t)\rangle$. We then get in combination with Eqs. (28) the usual Bloch-Maxwell equations:[3,50]

$$\frac{\partial}{\partial t}\langle\hat{\mathbf{P}}(\mathbf{r},t)\rangle=-\Omega\langle\hat{\mathbf{V}}(\mathbf{r},t)\rangle-\Gamma\langle\hat{\mathbf{P}}(\mathbf{r},t)\rangle\ , \tag{34a}$$

$$\frac{\partial}{\partial t}\langle\hat{\mathbf{V}}(\hat{\mathbf{r}},t)\rangle=\Omega\langle\hat{\mathbf{P}}(\mathbf{r},t)\rangle+\frac{2}{\hbar}\boldsymbol{\mu}\boldsymbol{\mu}\cdot\langle\hat{\mathbf{E}}_s^\perp(\mathbf{r},t)\rangle\langle\hat{W}(\mathbf{r},t)\rangle-\Gamma\langle\hat{\mathbf{V}}(\mathbf{r},t)\rangle-\int_{t_0}^{t}dt'K_1(t-r')\langle\hat{\mathbf{V}}(\mathbf{r},t')\rangle\ , \tag{34b}$$

$$\frac{\partial}{\partial t}\langle\hat{W}(\mathbf{r},t)\rangle=-\frac{2}{\hbar}\langle\hat{\mathbf{E}}_s^\perp(\mathbf{r},t)\rangle\langle\hat{\mathbf{V}}(\mathbf{r},t)\rangle-\int_{t_0}^{t}dt'\{K_2(t-t')\tfrac{1}{2}[1+\langle\hat{W}(\mathbf{r},t')\rangle]-K_3(t-t')\tfrac{1}{2}[1-\langle\hat{W}(\mathbf{r},t')\rangle]\}\ , \tag{34c}$$

$$\nabla^2\langle\hat{\mathbf{E}}_s^\perp(\mathbf{r},t)\rangle-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\langle\hat{E}_s^\perp(\mathbf{r},t)\rangle=\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\langle\hat{\mathbf{P}}^\perp(\mathbf{r},t)\rangle\ . \tag{34d}$$

It is common in the Bloch equations to make a Markovian approximation for the lifetime (T_1 process), thus replacing the integral terms in Eqs. (34) by a simple decay.

V. BLOCH-MAXWELL EQUATIONS IN THE LOCAL-FIELD APPROXIMATION

We now show that up to second order in the dipole strength, Eqs. (31) reduce to the Bloch equations for isolated molecules interacting with a local field.[22] To this end, we approximate $\langle \hat{W}_m(t') \rangle$ in Eq. (31b) by $\langle \hat{W}_m(t) \rangle$,

$$\langle \hat{B}_m(t') \rangle \exp[-i\Omega(t-t')]$$

in Eq. (31c) by $\langle \hat{B}_m(t) \rangle$, and

$$\langle \hat{B}_m^\dagger(t') \rangle \exp[i\Omega(t-t')]$$

by $\langle \hat{B}_m^\dagger(t) \rangle$. This is correct to zeroth order in the dipole, because $d\hat{\sigma}(t)/dt = -iL_0\hat{\sigma}(t)$ up to that order [cf. Eq. (20)]. Therefore errors due to these replacements only show up beyond the second-order calculation that we restricted ourselves to. Using these approximations, one again obtains Eqs. (31), but now the terms containing **M** should be omitted, and $\langle \hat{\mathbf{D}}_s^\perp(\mathbf{r}_m,t) \rangle$ is replaced by the local field

$$\mathbf{E}_L(\mathbf{r}_m,t) = \langle \hat{\mathbf{D}}_s^\perp(\mathbf{r}_m,t) \rangle + \int_{t_0}^{t} dt' \left[\sum_{n\neq m} \mathbf{M}(\mathbf{r}_{mn},t-t') \cdot \boldsymbol{\mu} \langle (\hat{B}_n + \hat{B}_n^\dagger)(t') \rangle \right] . \tag{35}$$

We thus define the local field as that field which takes the place of the external electric field in the Bloch equations for an isolated molecule.[3,49,50] As far as we know, this is the first time that a local field in nonlinear optics for systems with interacting molecules is defined from microscopic principles. Clearly, one cannot expect any local-field formulation to hold rigorously in higher order of the dipole interaction.

We now turn to the interpretation of $\mathbf{M}(\mathbf{r},t)$ in more detail. It is easier to concentrate on the temporal Fourier transform $\mathbf{M}(\mathbf{r},\omega)$, and this is also natural in view of the time convolution in Eq. (35). As is shown in Appendix B,

$$\mathbf{M}(\mathbf{r},\omega) = \mathbf{F}(\mathbf{r},\omega) - \mathbf{H}(\mathbf{r},\omega) , \tag{36}$$

with

$$\begin{aligned}\mathbf{F}(\mathbf{r},\omega) &= \{[3-3i\tilde{\omega}r-(\tilde{\omega}r)^2]\hat{\mathbf{r}}\hat{\mathbf{r}}-[1-i\tilde{\omega}r-(\tilde{\omega}r)^2]\mathbf{1}\}\frac{e^{i\tilde{\omega}r}}{r^3} \\ &= (\nabla\nabla+\tilde{\omega}^2\mathbf{1})\frac{e^{i\tilde{\omega}r}}{r}+\frac{4\pi}{3}\delta(\mathbf{r})\mathbf{1}\end{aligned} \tag{37}$$

and

$$\mathbf{H}(\mathbf{r},\omega) = \lim_{\epsilon\to 0} \frac{4\pi}{V} \sum_{\mathbf{k}}{}' \frac{k^2\mathbf{1}-\mathbf{kk}}{k^2-(\tilde{\omega}+i\epsilon)^2} e^{i\mathbf{k}\cdot\mathbf{r}} . \tag{38}$$

$\hat{\mathbf{r}}$ is the unit vector in the r direction, and $\tilde{\omega} \equiv \omega/c$. From Eq. (37), it is clear that $\mathbf{F}(\mathbf{r},\omega)$ is the retarded dipole field tensor,[9] and we conclude that the projection method in lowest-order perturbation calculation already gives us the complete retarded dipole-dipole interactions as effective coupling between the molecules. This is not surprising in view of the processes that contribute to **M** (see Sec. IV). As we note, however, **M** is not completely identical to the dipole field tensor, the difference, **H**, being caused by the exclusion of the special modes in Eq. (32). In order to obtain Eq. (37), the **k** summation has been converted to an integration, which is, strictly speaking, only correct for $V \to \infty$. If we would take this limit in the expression for **H**, its contribution would vanish. It should be noted, however, that **M** always occurs inside a lattice summation [cf. Eqs. (31)], so that in the simultaneous limit $V \to \infty$ and $N \to \infty$, **H** may still give a finite contribution. We, therefore, do not discard **H**.[51]

In order to define susceptibilities, it is more useful to have the Bloch equations in $(\mathbf{k},\omega)$ representation. The Bloch equations for the individual molecules with the local field Eq. (35) are easily rewritten as equations in continuous **r** space by multiplying by $\delta(\mathbf{r}-\mathbf{r}_m)$ and summation over m. After Fourier transformation one then obtains

$$-i\omega\langle \hat{\mathbf{P}}(\mathbf{k},\omega) \rangle = -\Omega\langle \hat{\mathbf{V}}(\mathbf{k},\omega) \rangle - \Gamma\langle \hat{\mathbf{P}}(\mathbf{k},\omega) \rangle , \tag{39a}$$

$$-i\omega\langle \hat{\mathbf{V}}(\mathbf{k},\omega) \rangle = \Omega\langle \hat{\mathbf{P}}(\mathbf{k},\omega) \rangle - [\Gamma+K_1(\omega)]\langle \hat{\mathbf{V}}(\mathbf{k},\omega) \rangle + \frac{2}{\hbar}\boldsymbol{\mu}\boldsymbol{\mu}\cdot\frac{1}{2\pi V}\sum_{\substack{k' \\ 1\,\mathrm{BZ}}} \int d\omega' \mathbf{E}_L(\mathbf{k}',\omega')\langle \hat{W}(\mathbf{k}-\mathbf{k}',\omega-\omega') \rangle , \tag{39b}$$

$$\begin{aligned}-i\omega\langle \hat{W}(\mathbf{k},\omega) \rangle = {} & -\tfrac{1}{2}K_2(\omega)[2\pi\rho(\mathbf{k})\delta(\omega)+\langle \hat{W}(\mathbf{k},\omega) \rangle]+\tfrac{1}{2}K_3(\omega)[2\pi\rho(\mathbf{k})\delta(\omega)-\langle \hat{W}(\mathbf{k},\omega) \rangle] \\ & -\frac{2}{\hbar}\frac{1}{2\pi V}\sum_{\substack{k' \\ 1\,\mathrm{BZ}}} \int d\omega' \mathbf{E}_L(\mathbf{k}',\omega')\langle \hat{\mathbf{V}}(\mathbf{k}-\mathbf{k}',\omega-\omega') \rangle .\end{aligned} \tag{39c}$$

Here the $(\mathbf{k},\omega)$ representation of the local field is given by

$$\mathbf{E}_L(\mathbf{k},\omega) = \langle \hat{\mathbf{D}}_s^\perp(\mathbf{k},\omega) \rangle + \mathbf{M}_0(\mathbf{k},\omega)\langle \hat{\mathbf{P}}(\mathbf{k},\omega) \rangle , \tag{40}$$

with

$$\begin{aligned}\mathbf{M}_0(\mathbf{k},\omega) &= \frac{1}{\rho}\sum_{m\neq 0}\mathbf{M}(\mathbf{r}_m,\omega)e^{-i\mathbf{k}\cdot\mathbf{r}_m} \\ &= \mathbf{F}_l(\mathbf{k},\omega) - 4\pi \lim_{\epsilon\to 0^+} \frac{k^2\mathbf{1}-\mathbf{kk}}{k^2-(\tilde{\omega}+i\epsilon)^2} .\end{aligned} \tag{41}$$

$\mathbf{F}_l(\mathbf{k},\omega)$ is the lattice Fourier transform of the dipole field tensor

$$\mathbf{F}_l(\mathbf{k},\omega)=\frac{1}{\rho}\sum_{m\neq 0}\mathbf{F}(\mathbf{r}_m,\omega)e^{-i\mathbf{k}\cdot\mathbf{r}_m}\ , \tag{42}$$

which cannot be evaluated analytically. The second term in Eq. (41) is the Fourier transform of $\mathbf{H}(\mathbf{r}_m,\omega)$ and is only present for special $\mathbf{k}$ values. Since, in practice, these are the only modes for which the Bloch equations need to be solved, we do not indicate this restriction explicitly in Eq. (41). We note that this term demonstrates the importance of the exclusion of the special modes from the summation in Eq. (32). We have assumed that all special modes lie within the first Brillouin zone, which is correct for optical processes. This assumption has also been used to rule out components of $\langle\hat{\mathbf{D}}_s^{\perp}(\mathbf{k},\omega)\rangle$ (which is the continuous space Fourier transform of $\langle\hat{\mathbf{D}}_s^{\perp}\rangle$) outside the first Brillouin zone.[52]

Splitting $\langle\hat{\mathbf{D}}_s^{\perp}\rangle$ in Eq. (40) into $\langle\hat{\mathbf{E}}_s^{\perp}\rangle$ and $4\pi\langle\hat{\mathbf{P}}_s^{\perp}\rangle$ and after some rearrangements, we recast the local field for special $\mathbf{k}$ values in the form

$$\mathbf{E}_L(\mathbf{k},\omega)=\langle\hat{\mathbf{E}}^{\perp}(\mathbf{k},\omega)\rangle+\frac{4\pi}{3}\boldsymbol{\eta}(\mathbf{k},\omega)\cdot\langle\mathbf{P}(\mathbf{k},\omega)\rangle\ , \tag{43}$$

with

$$\boldsymbol{\eta}(\mathbf{k},\omega)=1-3\hat{\mathbf{k}}\hat{\mathbf{k}}+\frac{3}{4\pi}[\mathbf{F}_l(\mathbf{k},\omega)-\mathbf{F}_c(\mathbf{k},\omega)]\ . \tag{44}$$

Here $\mathbf{F}_c(\mathbf{k},\omega)$ is defined as the continuous space Fourier transform of the dipole field tensor

$$\mathbf{F}_c(\mathbf{k},\omega)=\int d\mathbf{r}\,\mathbf{F}(\mathbf{r},\omega)e^{-i\mathbf{k}\cdot\mathbf{r}}\ , \tag{45}$$

and we have used Eq. (B8). The fact that $\boldsymbol{\eta}(\mathbf{k},\omega)$ contains the difference of the discrete and continuous Fourier transform of the same field makes it more suitable for a numerical calculation, as convergence problems at large distance disappear. In fact, it can be shown that for a simple cubic lattice with lattice spacing a in the limit $k\to 0$ ($ka\ll 1$), *and* $\omega\to 0$ ($\tilde{\omega}a\ll 1$), $\mathbf{F}_l=\mathbf{F}_c$, so that

$$\boldsymbol{\eta}(\mathbf{k},\omega)=1-3\hat{\mathbf{k}}\hat{\mathbf{k}}\quad(k,\omega\to 0)\ . \tag{46}$$

In Eq. (43), we express the local field in terms of $\mathbf{E}^{\perp}$ and $\mathbf{P}$, because $\mathbf{E}^{\perp}$ is the radiation field with respect to which we will define susceptibilities. In principle, one may equally well write

$$\mathbf{E}_L=\mathbf{E}+(4\pi/3)\boldsymbol{\eta}'\cdot\mathbf{P}\ ,$$

and then $\boldsymbol{\eta}'$ would be given by Eq. (44) without the $\hat{\mathbf{k}}\hat{\mathbf{k}}$ term. Thus, in the limit $k,\omega\to 0$, we exactly find the Lorentz local field $\mathbf{E}+(4\pi/3)\mathbf{P}$.

We will now discuss the self-interaction kernels $K_i(\omega)$ ($i=1,2,3$). Starting from Eq. (33), converting the summation to an integration and performing the angular integrations for $\mathbf{k}$, one obtains

$$K_1(\omega)=\lim_{\epsilon\to 0^+}\frac{4\mu^2}{3\hbar\pi}i\int dk\,k^3\left[\frac{1}{\tilde{\omega}+k+i\epsilon}+\frac{1}{\tilde{\omega}-k+i\epsilon}\right]$$
$$\equiv\gamma_1(\omega)+i\Delta_1(\omega)\ , \tag{47}$$

with

$$\gamma_1(\omega)=\frac{4\mu^2}{3\hbar}|\tilde{\omega}|^3\ , \tag{48}$$

and

$$\Delta_1(\omega)=\frac{4\mu^2}{3\hbar\pi}\int dk\,k^3\left[\mathrm{P}\left[\frac{1}{\tilde{\omega}+k}\right]+\mathrm{P}\left[\frac{1}{\tilde{\omega}-k}\right]\right]\ . \tag{49}$$

P denotes the Cauchy principal value. $\gamma_1(\omega)$ is the frequency-dependent decay rate of $\langle\hat{\mathbf{V}}\rangle$, whereas $\Delta_1(\omega)$ is related to the Lamb shift. Clearly, the k integration has a *uv* divergence, which is usually taken care of by mass renormalization. The common result for the Lamb shift, obtained through the minimal-coupling Hamiltonian, diverges logarithmically in the upper boundary of the k integral. Our Δ_1, however, has a quadratic divergence. For the hydrogen atom, it has been shown[33] that the presence of an extra "self-energy" term in the multipolar Hamiltonian makes up for this difference. This extra term reads

$$2\pi\int d\mathbf{r}\sum_m|\hat{\mathbf{P}}_m^{\perp}(\mathbf{r})|^2\ ,$$

where $\hat{\mathbf{P}}_m^{\perp}(\mathbf{r})$ is the transverse polarization field due to molecule m only. For our model of two-level molecules,

$$\hat{\mathbf{P}}_m(\mathbf{r})=\boldsymbol{\mu}(\hat{B}_m+\hat{B}_m^{\dagger})\delta(\mathbf{r}-\mathbf{r}_m)\ ,$$

and it can be shown that the extra term in the Hamiltonian is an infinite constant, which thus cannot affect the dynamics. Obviously, the neglect of any detail about the charge distribution of the molecule by simply replacing it by a two-level system is a too severe simplification in order to deal with self-interactions in an exact way. We also note that Δ_1 does not appear as a real shift in the equations, since the equation for $\langle\hat{\mathbf{P}}\rangle$ does not contain a self-interaction term.

The kernels $K_2(\omega)$ and $K_3(\omega)$ are treated in the same way, and one finds

$$\gamma_2(\omega)=\frac{4\pi^2}{3\hbar}\begin{cases}(\tilde{\omega}+\tilde{\Omega})^3\quad(\omega>\Omega)\\(\tilde{\omega}+\tilde{\Omega})^3+(\tilde{\Omega}-\tilde{\omega})^3\quad(-\Omega<\omega<\Omega)\\(\tilde{\Omega}-\tilde{\omega})^3\quad(\omega<-\Omega)\ .\end{cases} \tag{50}$$

$\tilde{\Omega}=\Omega/c$, and $\Delta_2(\omega)$ is identical to $\Delta_1(\omega)$, except that k in the denominators of Eq. (49) is replaced by $k-\tilde{\Omega}$. Finally,

$$\gamma_3(\omega)=\frac{4\mu^2}{3\hbar}\begin{cases}(\tilde{\omega}-\tilde{\Omega})^3\quad(\omega>\Omega)\\0\quad(-\Omega<\omega<\Omega)\\-(\tilde{\omega}+\tilde{\Omega})^3\quad(\omega<-\Omega)\end{cases} \tag{51}$$

and $\Delta_3(\omega)$ is again given by Eq. (49), but now k is replaced by $k+\tilde{\Omega}$. Note that on the resonance frequency ($\tilde{\omega}=0$) of $\langle\hat{W}\rangle$, the decay rate of the upper molecular level is given by $\gamma_2(0)/2=4\mu^2\tilde{\Omega}^3/3\hbar$, which is the usual Markovian result,[50(a)] and the decay rate of the ground state is $\gamma_3(0)/2=0$, as one expects.

In concluding this section, we should note how Eqs. (39) may be used to derive expressions for molecular optical susceptibilities. To that end, we expand formally the molecular variables $\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle$, $\langle \hat{\mathbf{V}}(\mathbf{k},\omega)\rangle$, and $\langle \hat{W}(\mathbf{k},\omega)\rangle$ in a Taylor series in $\mathbf{E}_L(\mathbf{k},\omega)$. When these expansions are substituted in Eqs. (39), we can obtain the coefficients of expansion of the molecular variables order by order. The coefficients of expansion of $\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle$ constitute the molecular susceptibilities. Since Eqs. (39) are identical to the Bloch equations of a single molecule interacting with the field $\mathbf{E}_L$, these are actually the molecular polarizabilities. (This is no longer true once the kernel is evaluated to higher orders.) The macroscopic susceptibilities are defined in terms of the expansion of $\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle$ in a power series in the average Maxwell field $\mathbf{E}$, rather than the local field $\mathbf{E}_L$. Using the relation between $\mathbf{E}$ and $\mathbf{E}_L$ [Eq. (43)], we can expand $\mathbf{E}_L$ in powers of $\mathbf{E}$ and obtain the macroscopic susceptibilities.[2,20,22] The macroscopic susceptibility to order n is then given by sums of products of the molecular susceptibilities of order n and lower. It should further be noted that in this approximation we can express the susceptibilities in terms of correlation functions of the matter, as is common in linear- and nonlinear-response theory.[18,28,29] In Sec. VI we shall explicitly evaluate the linear susceptibility and the dielectric function for the present model.

VI. DIELECTRIC FUNCTION USING THE MULTIPOLAR HAMILTONIAN

The most straightforward application of the Bloch equations derived in Sec. V is the calculation of the linear susceptibility $\chi^{(1)}(\mathbf{k},\omega)$, which is defined by

$$\langle \hat{\mathbf{P}}^{(1)}(\mathbf{k},\omega)\rangle = \boldsymbol{\chi}^{(1)}(\mathbf{k},\omega)\cdot\langle \hat{\mathbf{E}}^{\perp}(\mathbf{k},\omega)\rangle \ , \tag{52a}$$

where $\langle \hat{\mathbf{P}}^{(1)}(\mathbf{k},\omega)\rangle$ stands for that part of the polarization that is linear in the electric field. $\boldsymbol{\chi}^{(1)}$ is a tensor, and, since we only consider transverse radiation fields, it should actually be referred to as the transverse susceptibility. Instead of $\boldsymbol{\chi}^{(1)}$ one often considers the dielectric function $\boldsymbol{\epsilon}(\mathbf{k},\omega)$, given by

$$\boldsymbol{\epsilon}(\mathbf{k},\omega) - \mathbf{1} = 4\pi\boldsymbol{\chi}^{(1)} \ . \tag{52b}$$

The linear susceptibility is easily obtained by linearizing the Bloch equations [Eqs. (39)], discarding all terms of second or higher order in the electric field. Since the molecules are nonpolar, $\langle \hat{\mathbf{P}}\rangle$ and $\langle \hat{\mathbf{V}}\rangle$ both vanish in the absence of electric fields, so that in lowest order they are linear in $\langle \hat{\mathbf{E}}^{\perp}\rangle$. The inversion $\langle \hat{W}_m\rangle$ for a given molecule is -1 in the absence of fields (molecule is in the ground state), and since it takes two interactions with the electromagnetic field to change the ground-state density operator $|0\rangle_{mm}\langle 0|$ into the excited state $|1\rangle_{mm}\langle 1|$, the next term in the expansion of $\langle \hat{W}_m\rangle$ in $\langle \mathbf{E}^{\perp}\rangle$ is quadratic. This is also clear from Eq. (39c): all terms to the right-hand side are at least quadratic in $\langle \hat{\mathbf{E}}^{\perp}\rangle$ (the spontaneous emission from the ground state given by the K_3 term can be neglected in practice, as mentioned above). Linearizing the Bloch equations is thus equivalent to invoking

$$\langle \hat{W}(\mathbf{k},\omega)\rangle = -2\pi\delta(\omega)N\sum_{\mathbf{G}}\delta_{\mathbf{k},2\pi\mathbf{G}} \ , \tag{53}$$

where $\mathbf{G}$ runs over the reciprocal lattice. Using the local-field expression, Eq. (43), one then obtains as linear equations

$$-i\omega\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle = -\Omega\langle \hat{\mathbf{V}}(\mathbf{k},\omega)\rangle - \Gamma\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle \ , \tag{54a}$$

$$\begin{aligned}-i\omega\langle \hat{\mathbf{V}}(\mathbf{k},\omega)\rangle = {} & \left[\Omega - \frac{8\pi}{3\hbar}\rho\mu^2\eta(\mathbf{k},\omega)\right]\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle \\ & -[\Gamma + K_1(\omega)]\langle \hat{\mathbf{V}}(\mathbf{k},\omega)\rangle \\ & -\frac{2}{\hbar}\rho\boldsymbol{\mu}\boldsymbol{\mu}\cdot\langle \hat{\mathbf{E}}^{\perp}(\mathbf{k},\omega)\rangle \ ,\end{aligned} \tag{54b}$$

where we omitted the superscripts 1 denoting the linear parts of $\mathbf{P}$ and $\mathbf{V}$ for brevity. Here

$$\eta(\mathbf{k},\omega) = [\boldsymbol{\mu}\cdot\boldsymbol{\eta}(\mathbf{k},\omega)\cdot\boldsymbol{\mu}]/\mu^2 \ , \tag{55}$$

and we used the fact that $\langle \hat{\mathbf{P}}\rangle \sim \boldsymbol{\mu}$ in identifying

$$\boldsymbol{\mu}\boldsymbol{\mu}\cdot\boldsymbol{\eta}\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle = \boldsymbol{\mu}\cdot\boldsymbol{\eta}\cdot\boldsymbol{\mu}\langle \hat{\mathbf{P}}(\mathbf{k},\omega)\rangle \ .$$

Eliminating $\langle \hat{\mathbf{V}}\rangle$ from Eqs. (54), and using Eq. (52b), we get

$$\frac{\boldsymbol{\epsilon}(\mathbf{k},\omega) - \mathbf{1}}{4\pi} = \frac{2\rho\Omega\boldsymbol{\mu}\boldsymbol{\mu}/\hbar}{-(\omega + i\Gamma)[\omega - \Delta_1(\omega) + i\Gamma + i\gamma_1(\omega)] + \Omega[\Omega - (8\pi/3\hbar)\rho\mu^2\eta(\mathbf{k},\omega)]} \ . \tag{56}$$

It appears that $\boldsymbol{\epsilon}(\mathbf{k},\omega)$ can be cast into a generalized Clausius-Mossotti relation

$$\frac{\boldsymbol{\mu}\cdot[\boldsymbol{\epsilon}(\mathbf{k},\omega) - \mathbf{1}]\cdot\boldsymbol{\mu}}{\boldsymbol{\mu}\cdot\{\mathbf{3} + \eta(\mathbf{k},\omega)[\boldsymbol{\epsilon}(\mathbf{k},\omega) - \mathbf{1}]\}\cdot\boldsymbol{\mu}} = \frac{4\pi}{3}\frac{\rho}{\mu^2}\boldsymbol{\mu}\cdot\boldsymbol{\alpha}(\omega)\cdot\boldsymbol{\mu} \ , \tag{57}$$

where $\boldsymbol{\alpha}(\omega)$ is the polarizability of a single molecule in a bath

$$\boldsymbol{\alpha}(\omega) = \frac{2\Omega\boldsymbol{\mu}\boldsymbol{\mu}/\hbar}{-(\omega + i\Gamma)[\omega - \Delta_1(\omega) + i\Gamma + i\gamma_1(\omega)] + \Omega^2} \ . \tag{58}$$

Equation (57) appears in a rather complicated form, because $\boldsymbol{\epsilon}(\mathbf{k},\omega)$ and $\boldsymbol{\alpha}(\omega)$ are tensors. This is a consequence of the fact that we describe an ordered system of molecules with only one nondegenerate accessible excited state, for which the polarization will always have a fixed direction, dictated by the orientation of the transition dipoles, and independent of the direction of the electric field. Only the magnitude of the polarization depends on the relative orientation of the dipoles and the electric field, which explains the dyadic $\boldsymbol{\mu}\boldsymbol{\mu}$ in Eqs. (56) and (58). One may also use our formalism, however, to describe the linear optics of a system with molecules (atoms) which have a spherically symmetric threefold degenerate excited state.[10] With only one macroscopic radiation field component $\mathbf{E}^{\perp}(\mathbf{k},\omega)$ present, only the excited state with its transition dipole parallel to this field is excited macroscopically, so that the dielectric function and the polarizability become scalars: $\boldsymbol{\epsilon}=\epsilon\mathbf{1}$, with $(\epsilon-1)/4\pi$ given by Eq. (56) with $\boldsymbol{\mu}\boldsymbol{\mu}$ replaced by μ^2, and analogous for $\boldsymbol{\alpha}$. One then also finds the Clausius-Mossotti relation in a scalar form,

$$(\epsilon-1)/[3+\eta(\epsilon-1)]=(4\pi/3)\rho\alpha\ ,$$

and for $k,\omega\rightarrow 0$, using Eqs. (46) and (55) with $\hat{\mathbf{k}}\cdot\boldsymbol{\mu}=0$, one has $\eta=1$, so that the usual expression is recovered.

Finally, we remark that, in view of the linearization, the results for $\epsilon(\mathbf{k},\omega)$ are not affected by the approximations made in the very beginning of Sec. V, leading to the local-field approximation [Eqs. (39)]. Direct linearization of Eqs. (31) will yield the same result for the dielectric function. Of course, this still does not mean that our result [Eq. (56)] is exact, because the kernel in Eqs. (31) was calculated to second order in the interaction only.

VII. REDUCED EQUATIONS OF MOTION AND THE DIELECTRIC FUNCTION USING THE MINIMAL-COUPLING HAMILTONIAN

The multipolar Hamiltonian used in this paper provides a convenient starting point for developing a theory for nonlinear-optical processes. An alternative Hamiltonian, frequently used in the literature, is the minimal-coupling Hamiltonian, where the interaction of matter with the radiation field is given by a $\mathbf{p}\cdot\mathbf{A}$ term. The two Hamiltonians are related by a canonical transformation.[32,33] In the minimal-coupling Hamiltonian, intermolecular Coulomb interactions are explicitly present, unlike the multipolar Hamiltonian, in which all interactions are mediated by the radiation field. It has been demonstrated that when the dipole approximation is made, both Hamiltonians may yield different predictions for optical line shapes.[31] A lively debate is going on regarding which form is to be preferred, following recent arguments made by Mandel.[38] Hopfield's celebrated calculations of the dielectric function in a crystal and the exciton-polariton model[10] were based on the minimal-coupling Hamiltonian. In order to shed some light on this issue, we derive in this section equations of motion and an expression for the dielectric function starting from the minimal-coupling Hamiltonian and compare them with the multipolar Hamiltonian. The minimal-coupling Hamiltonian is

$$\hat{H}_{\rm min}=\hat{H}_0+\hat{H}_1+\hat{V}_{\rm int}\ . \tag{59}$$

Here $\hat{H}_0$ is defined as in Eq. (2), $\hat{H}_1$ is the radiation-matter interaction

$$\hat{H}_1=-\frac{e}{Mc}\sum_m \hat{\mathbf{A}}(\mathbf{r}_m)\cdot\hat{\mathbf{p}}_m+\frac{e^2S}{2Mc^2}\sum_m \hat{\mathbf{A}}(\mathbf{r}_m)\cdot\hat{\mathbf{A}}(\mathbf{r}_m), \tag{60}$$

and

$$\hat{\mathbf{V}}_{\rm int}=\frac{\hbar}{2}\sum_{\substack{n,m\\ n\neq m}} J(\mathbf{r}_n-\mathbf{r}_m)(\hat{B}_n+\hat{B}_n^{\dagger})(\hat{B}_m+\hat{B}_m^{\dagger}) \tag{61}$$

is an instantaneous direct intermolecular interaction, with distance dependence $J(\mathbf{r})$. Note that in our case of nonpolar molecules the dipole-dipole interaction can be written in this form, with

$$\hbar J_{dd}(\mathbf{r})=\frac{\mu^2}{r^3}-3\frac{(\boldsymbol{\mu}\cdot\mathbf{r})^2}{r^5}\ . \tag{62}$$

In Eq. (60) the dipole approximation has been made by taking the value of the vector potential $\hat{\mathbf{A}}$ in the center $\mathbf{r}_m$ of every molecule. $\hat{\mathbf{p}}_m$ stands for the total canonical momentum of all S optically active electrons (mass M, charge e) of molecule m, and is written in second quantization as[11,50(a)]

$$\hat{\mathbf{p}}_m=\frac{-i\Omega M}{e}\boldsymbol{\mu}(\hat{B}_m-\hat{B}_m^{\dagger})\ . \tag{63}$$

The vector potential is again quantized as in Eq. (7a), and now its conjugate momentum is the transverse-electric field rather than the displacement.[33]

For the present Hamiltonian, we only give results by deriving the Heisenberg equations of motion for molecular and radiation operators and by factorizing all products when taking expectation values. We thus do not use a projection method, or alternatively, we only evaluate the mean-field term of the reduced equations of motion. Performing the second-order perturbation calculation for the minimal-coupling Hamiltonian would be a major task in view of the three interaction terms that are involved.

We obtain for the Heisenberg equations of motion for the electromagnetic fields

$$\frac{\partial}{\partial t}\hat{\mathbf{A}}^{\perp}(\mathbf{k},t)=-c\hat{\mathbf{E}}^{\perp}(\mathbf{k},t)\ , \tag{64a}$$

$$\begin{aligned}\frac{\partial}{\partial t}\hat{\mathbf{E}}^{\perp}(\mathbf{k},t)=&\ \frac{\omega_k^2}{c}\hat{\mathbf{A}}^{\perp}(\mathbf{k},t)\\ &+\frac{1}{c}\frac{4\pi e^2}{M}\rho S(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\sum_{\mathbf{G}}\hat{\mathbf{A}}^{\perp}(\mathbf{k}+2\pi\mathbf{G},t)\\ &+4\pi\Omega\hat{\mathbf{V}}^{\perp}(\mathbf{k},t)\ ,\end{aligned} \tag{64b}$$

and for the molecular operators

$$\begin{aligned}\frac{d}{dt}[\hat{B}_m(t)+\hat{B}_m^{\dagger}(t)]=&-\Omega i[\hat{B}_m(t)-\hat{B}_m^{\dagger}(t)]\\ &+\frac{2\Omega}{\hbar c}\boldsymbol{\mu}\cdot\hat{\mathbf{A}}^{\perp}(\mathbf{r}_m,t)\hat{W}_m(t)\ ,\end{aligned} \tag{65a}$$

$$\begin{aligned}\frac{d}{dt}i[\hat{B}_m(t)-\hat{B}_m^{\dagger}(t)]=&\ \Omega[\hat{B}_m(t)+\hat{B}_m^{\dagger}(t)]\\ &-2\sum_{n\neq m}J(\mathbf{r}_{nm})[\hat{B}_n(t)+\hat{B}_n^{\dagger}(t)]\\ &\times\hat{W}_m(t)\ ,\end{aligned} \tag{65b}$$

$$\begin{aligned}\frac{d}{dt}\hat{W}_m(t)=&-\frac{2\Omega}{\hbar c}\boldsymbol{\mu}\cdot\hat{\mathbf{A}}^{\perp}(\mathbf{r}_m,t)[\hat{B}_m(t)+\hat{B}_m^{\dagger}(t)]\\ &+2\sum_{n\neq m}J(\mathbf{r}_{nm})[\hat{B}_n(t)+\hat{B}_n^{\dagger}(t)]\\ &\times i[\hat{B}_m(t)-\hat{B}_m^{\dagger}(t)]\ .\end{aligned} \tag{65c}$$

The sum over $\mathbf{G}$ in Eq. (64b) extends over the reciprocal lattice, and the field $\hat{\mathbf{V}}^{\perp}(\mathbf{k},t)$ is defined analogous to Eq. (29). It is useful to give the material equations in $\mathbf{k}$ representation too:

$$\frac{\partial}{\partial t}\hat{\mathbf{P}}(\mathbf{k},t) = -\Omega\hat{\mathbf{V}}(\mathbf{k},t) + \frac{2\Omega}{\hbar c}\boldsymbol{\mu}\boldsymbol{\mu}\cdot\frac{1}{V}\sum_{k'}\hat{\mathbf{A}}^{\perp}(\mathbf{k}',t)\hat{W}(\mathbf{k}-\mathbf{k}',t) , \tag{66a}$$

$$\frac{\partial}{\partial t}\hat{\mathbf{V}}(\mathbf{k},t) = \Omega\hat{\mathbf{P}}(\mathbf{k},t) - \frac{2}{N}\sum_{\substack{\mathbf{k}'\\ 1\ \mathrm{BZ}}} J_0(\mathbf{k}')\hat{\mathbf{P}}(\mathbf{k}',t)\hat{W}(\mathbf{k}-\mathbf{k}',t) , \tag{66b}$$

$$\frac{\partial}{\partial t}\hat{W}(\mathbf{k},t) = -\frac{2\Omega}{\hbar c}\frac{1}{V}\sum_{\mathbf{k}'}\hat{\mathbf{A}}^{\perp}(\mathbf{k}',t)\cdot\hat{\mathbf{P}}(\mathbf{k}-\mathbf{k}',t) + \frac{2}{\mu^2 N}\sum_{\substack{\mathbf{k}'\\ 1\ \mathrm{BZ}}} J_0(\mathbf{k}')\hat{\mathbf{P}}(\mathbf{k}',t)\cdot\hat{\mathbf{V}}(\mathbf{k}-\mathbf{k}',t) , \tag{66c}$$

where $J_0(\mathbf{k}) = \sum_{m\neq 0} J(\mathbf{r}_m)\exp(-i\mathbf{k}\cdot\mathbf{r}_m)$.

Equations (64) are the radiation field equations in the crystal of point dipoles. They are linear in the operators, so that the expectation values of the electromagnetic fields obey the same equations. We show that these are consistent with Maxwell's equations. Obviously, after taking expectation values, Eq. (64a) is identical to Eq. (30a). The equivalence of Eqs. (64b) and (30b) is seen as follows. The current density may be written as

$$\hat{\mathbf{j}}(\mathbf{r},t) = \sum_m \left[\frac{e\hat{\mathbf{p}}_m(t)}{M} - \frac{Se^2}{Mc}\hat{\mathbf{A}}^{\perp}(\mathbf{r}_m,t)\right]\delta(\mathbf{r}-\mathbf{r}_m) . \tag{67}$$

Again using expression (63) for the momentum, performing a spatial Fourier transform and taking the transverse part, one finds

$$\frac{-4\pi}{c}\hat{\mathbf{j}}^{\perp}(\mathbf{k},t) = \frac{4\pi\Omega}{c}\hat{\mathbf{V}}^{\perp}(\mathbf{k},t) + \frac{4\pi e^2}{Mc^2}S\rho(1-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\sum_{\mathbf{G}}\hat{\mathbf{A}}(\mathbf{k}+2\pi\mathbf{G},t) . \tag{68}$$

One now readily recovers Eq. (30b) from Eq. (64b).

The material equations (65) in the absence of intermolecular interactions ($J=0$) are clearly different from the optical Bloch equations for isolated molecules [Eq. (34)]. Their physical content, however, is the same, since the $\boldsymbol{\mu}\cdot\mathbf{D}$ and the $\mathbf{p}\cdot\mathbf{A}$ Hamiltonians are related by a canonical transformation, even in the dipole approximation.[32,33] It is not obvious, however, how to define a local electric field from Eqs. (65).

Finally, we obtain the dielectric function by linearizing Eqs. (66a) and (66b), after taking expectation values and factorizing $\langle\hat{\mathbf{A}}\hat{W}\rangle$ and $\langle\hat{\mathbf{P}}\hat{W}\rangle$. Eliminating $\hat{\mathbf{V}}$ and using Eq. (64a), we find

$$\frac{\epsilon_{\min}(\mathbf{k},\omega)-1}{4\pi} = \frac{2\Omega\rho\boldsymbol{\mu}\boldsymbol{\mu}/\hbar}{-\omega^2+\Omega^2+2\Omega J_0(\mathbf{k})} , \tag{69}$$

which may be written as

$$\frac{\boldsymbol{\mu}\cdot[\epsilon_{\min}(\mathbf{k},\omega)-1]\cdot\boldsymbol{\mu}}{\boldsymbol{\mu}\cdot\{3+\eta_{\min}(\mathbf{k})[\epsilon_{\min}(\mathbf{k},\omega)-1]\}\cdot\boldsymbol{\mu}} = \frac{4\pi}{3}\frac{\rho}{\mu^2}\boldsymbol{\mu}\cdot\boldsymbol{\alpha}(\omega)\cdot\boldsymbol{\mu} , \tag{70}$$

with

$$\eta_{\min}(\mathbf{k}) = -\frac{3}{4\pi}\frac{\hbar J_0(\mathbf{k})}{\rho\mu^2} \tag{71a}$$

and $\boldsymbol{\alpha}(\omega)$ again the molecular polarizability [cf. Eq. (58)], without the dephasing and self-interaction parameters:

$$\boldsymbol{\alpha}(\omega) = \frac{2\Omega\boldsymbol{\mu}\boldsymbol{\mu}/\hbar}{-\omega^2+\Omega^2} . \tag{71b}$$

Clearly, the present result for $\epsilon(\mathbf{k},\omega)$ differs from the one obtained in Sec. VI, even if we neglect dephasing and self-interactions in the latter: $\eta_{\min}$ does not contain any signature of retarded interactions, in contrast to η, obtained from Eqs. (44) and (55). This is reflected in the fact that η depends on $\mathbf{k}$ and ω, whereas $\eta_{\min}$ depends only on $\mathbf{k}$. Furthermore, $\boldsymbol{\alpha}(\omega)$ [Eq. (71b)] does not include self-interactions (spontaneous emission and Lamb shift). Hopfield concluded that spontaneous emission is suppressed in a crystal and that the electromagnetic field, coupled with the polarization wave (polariton), propagates freely. In contrast, our result using the $\boldsymbol{\mu}\cdot\mathbf{D}$ Hamiltonian [Eq. (58)] contains the spontaneous emission. A discussion of spontaneous emission in large aggregates was given recently.[53] If $J(\mathbf{r})$ is the dipole-dipole interaction [Eq. (62)], then one finds in the limit $k\rightarrow 0$ (Ref. 54)

$$\hbar J_0(k\rightarrow 0) = \frac{4\pi}{3}\rho\boldsymbol{\mu}\cdot(3\hat{\mathbf{k}}\hat{\mathbf{k}}-1)\cdot\boldsymbol{\mu} . \tag{72}$$

Thus, in this limit, the minimal-coupling result agrees with the $\mathbf{k},\omega\rightarrow 0$ result from the multipolar Hamiltonian [cf. Eq. (46)]. Of course, in this limit retardation effects are not important. The dielectric function Eq. (69), restricted to spherical atoms, exactly matches the result that Hopfield obtained in his treatment of the exciton polariton,[10] which is not surprising, since his model system and Hamiltonian are the same as ours. The only difference between Hopfield's approach and ours is that he linearizes the equations of motion on the level of the operators, i.e., he assumes that excitons in $\mathbf{k}$ space behave like bosons. One then obtains a set of four equations [Eqs. (64), (65a), and (65b)—the last two in linearized form) from which one derives the elementary excitations as mixed eigenmodes of molecular and radiation operators. The dispersion relation of these modes gives $\epsilon(\mathbf{k},\omega)$ as in Eq. (69). It should be noted, however, that, although a rationale is given in Ref. 10 for the approximate behavior of excitons as bosons, there is no systematic expansion that justifies the linearization on the operator level. This can only be given for expectation values ($\langle\hat{W}\rangle$ can be expanded in $\langle\hat{\mathbf{E}}\rangle$); the step from operators to expectation values necessarily involves a factorization approximation.

VIII. CONCLUDING REMARKS

The Bloch-Maxwell equations are usually derived for an *isolated* molecule (a two-level system) interacting with an *external* electromagnetic field. In the limit of low molecular density, where intermolecular forces may be neglected, we, indeed, recover the Bloch-Maxwell equations [Eqs. (34)]. In this case, the polarization density $\langle \mathbf{P} \rangle$ is very small, and all the fields $\langle \hat{\mathbf{E}} \rangle$, $\mathbf{E}_L$, $\langle \hat{\mathbf{D}} \rangle$ are equal to the external field $\mathbf{E}_{\text{ex}}$. The main problem which we addressed in this paper is how to extend these equations in a systematic way to incorporate properly intermolecular forces.

The local-field approximation is a mean-field procedure which is widely used in the calculation of molecular susceptibilities at finite densities, when intermolecular forces are important. The Bloch-Maxwell equations in the local-field approximation [Eqs. (39) and (43)] may alternatively be derived in the following phenomenological way. Suppose we apply an external field $\mathbf{E}_{\text{ex}}$ on our optical medium. The Maxwell equations may be formally solved, resulting in (see Appendix B)

$$\mathbf{E}(\mathbf{k},\omega)=\mathbf{E}_{\text{ex}}(\mathbf{k},\omega)+[\mathbf{F}_c(\mathbf{k},\omega)-\tfrac{4}{3}\pi\mathbf{1}]\cdot\mathbf{P}(\mathbf{k},\omega) \;. \tag{73}$$

We now make the following argument: the local field that a given molecule feels is the external field plus the field originating from all other molecules. We thus define

$$\mathbf{E}_L(\mathbf{k},\omega)=\mathbf{E}_{\text{ex}}(\mathbf{k},\omega)+\mathbf{F}_l(\mathbf{k},\omega)\cdot\mathbf{P}(\mathbf{k},\omega) \;, \tag{74}$$

where, in r representation, $\mathbf{E}_{\text{ex}}$ is defined throughout space, but the second term is defined on lattice sites only. Combining Eqs. (73) and (74), we get

$$\mathbf{E}_L(\mathbf{k},\omega)=\mathbf{E}(\mathbf{k},\omega)+[\tfrac{4}{3}\pi\mathbf{1}+\mathbf{F}_l(\mathbf{k},\omega)-\mathbf{F}_c(\mathbf{k},\omega)]\cdot\mathbf{P}(\mathbf{k},\omega) \;. \tag{75}$$

Alternatively, we may express $\mathbf{E}_L$ in $\mathbf{E}^{\perp}$ by combining the transverse part of Eq. (73) with Eq. (74), and using the fact that $\mathbf{E}_{\text{ex}}$ is a transverse field. Then we obtain

$$\mathbf{E}_L(\mathbf{k},\omega)=\mathbf{E}^{\perp}(\mathbf{k},\omega)+[\tfrac{4}{3}\pi\mathbf{1}-4\pi\hat{\mathbf{k}}\hat{\mathbf{k}}+\mathbf{F}_l(\mathbf{k},\omega)-\mathbf{F}_c(\mathbf{k},\omega)]\cdot\mathbf{P}(\mathbf{k},\omega) \;, \tag{76}$$

which exactly agrees with Eq. (43). We thus model the nonlinear response of an interacting system by that of a single molecule interacting with the local field $\mathbf{E}_L$ rather than $\mathbf{E}_{\text{ex}}$, resulting in Eqs. (39), without the self-interaction terms. It should be noted that Eq. (73) is purely macroscopic and is obtained from the Maxwell equations without any reference to a specific microscopic model. Equation (74), on the other hand, assumes that the medium consists of point dipoles.

The local-field model provides a simple way to relate the polarizabilities of isolated molecules to the macroscopic susceptibilities. In fact, the susceptibility at some order is given in terms of sums of products of molecular polarizabilities of that order and lower orders.[2,20–22] This provides a simple, back of the envelope, calculation of macroscopic susceptibilities. It is clear, however, that this procedure is not rigorous. It fails to take properly into account the correlated dynamics of the interacting many-body system, i.e., correlations among the molecules, as well as correlations between the molecules and the radiation field. Short-range forces (e.g., exchange) are totally neglected in this procedure. Moreover, even the dipole-dipole forces are not fully taken into account. The resulting susceptibilities do not depend at all on the wave vectors, apart from the local-field contribution through $\eta(\mathbf{k},\omega)$, but just on the frequencies. This indicates that processes such as exciton migration and energy transfer and transport (e.g., the Förster transfer[55]) are neglected in this procedure. Such processes are often added phenomenologically in order to interpret transient grating spectroscopy, which is a four-wave-mixing technique that measures transport processes by following the wave-vector dependence of the susceptibilities. The derivation given by Eqs. (73)–(76) cannot be extended to include these processes, since it is intrinsically a mean-field single-molecule theory.

The theory developed in this paper provides for the first time a microscopic derivation which allows for a systematic incorporation of intermolecular forces in nonlinear optics and avoids overcounting or undercounting of interactions. We clearly show what approximations need to be made in order to recover the local-field approximation [Eqs. (39) and (43)]. The most significant contribution of this paper is the development of a rigorous way to improve upon these approximations. In general, the response functions and susceptibilities should be calculated using our more general reduced equations of motion [Eqs. (31)]. One then solves self-consistently for the field and the material variables as was done by Hopfield for linear optics. The susceptibilities cannot, therefore, be written in terms of correlation functions of the field-free system. In addition, in contrast to the local-field approximation, the macroscopic susceptibilities cannot be expressed as simple functionals of the single-molecule polarizabilities. The role of intermolecular forces and the relation between single-molecule polarizabilities and macroscopic susceptibilities is rigorously established.

Since in the present approach we work with the fields $\mathbf{D}$, $\mathbf{E}$, and $\mathbf{E}_L$ directly, we do not need to introduce an external field $\mathbf{E}_{\text{ex}}$ at all. This way, we can focus on an infinite medium and obtain susceptibilities which do not depend on geometry or shape. The shape may enter, when the Bloch-Maxwell equations are solved, but we need not address it in defining the susceptibilities.

Another point that should be stressed is that the molecular susceptibilities do depend on the retarded interactions through the kernel $(\mathbf{M})$. Knowledge of the eigenstates of the molecular Hamiltonian with instantaneous Coulomb interactions is not sufficient to get the susceptibilities. In contrast, in the local-field model, the susceptibilities do not depend on retarded interactions. The latter are only included in the local field. Strong evidence for the necessity of incorporating retarded interactions in susceptibilities is provided by some recent nonlinear-optical measurements involving exciton polaritons.[56–58] The analysis of Small and Agranovich strongly suggests that polariton effects should be included in the susceptibilities. This is impossible using the conventional local-field approximation, but such effects are naturally included in the present formalism. In the present paper we evaluated the kernel to second order in the dipole μ. We thus did not recover transport. Förster transfer will enter, when the kernel is evaluated to fourth order in the dipole.

Finally, our formulation can be generalized without major difficulty to treat the optical properties of disordered media (doped crystals, solutions, glasses). In that case, the projection operator should be extended to include an ensemble average over the disordered systems.[22,59–63]

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APPENDIX A

In this appendix we derive Eq. (20) of the main text. Let

$$\hat\sigma(t)=P(t)\hat\rho(t)\ ,$$

and

$$\hat\tau(t)=Q(t)\hat\rho(t)=\hat\rho(t)-\hat\sigma(t)\ ,$$

with $Q(t)\equiv 1-P(t)$ the complementary projection. First act on the Liouville equation (19) with $P(t)$, and use Eq. (17) to find

$$\frac{d}{dt}\hat\sigma(t)=-iP(t)L\hat\rho(t) =-iP(t)L\hat\sigma(t)-iP(t)L\hat\tau(t)\ . \tag{A1}$$

Analogously, by acting with $Q(t)$:

$$\frac{d}{dt}\hat\tau(t)=-iQ(t)L\hat\rho(t) =-iQ(t)L\hat\sigma(t)-iQ(t)L\hat\tau(t)\ . \tag{A2}$$

Solving $\hat\tau(t)$ formally from Eq. (A2), and substituting the result into Eq. (A1), gives

$$\frac{d}{dt}\hat\sigma(t)= -iP(t)L\hat\sigma(t) -\int_{t_0}^{t}dt'P(t)L\tilde G(t,t')Q(t')L\hat\sigma(t')\ , \tag{A3}$$

where

$$\tilde G(t,t')=\exp_+\left[-i\int_{t'}^{t}ds\, Q(s)L\right]\ ,$$

with $\exp_+$ the exponential with positive time ordering.[48] As usual, it is assumed in the derivation of Eq. (A3) that $\hat\sigma(t_0)=\hat\rho(t_0)$, i.e., $\hat\tau(t_0)=0$, which is reasonable if fields are turned on adiabatically at t_0, and blackbody radiation may be neglected (absence of continuum).

The Liouville operator may be split into $L=L_0+L_{\rm int}$, with $\hbar L_0\hat C=[\hat H_0,\hat C]$ and $\hbar L_{\rm int}\hat C=[\hat H_{\rm int},\hat C]$, $\hat C$ being an arbitrary operator. Furthermore, we pose here, again without derivation, two other properties of the projection, namely,

$$P(t)L_0\hat\rho(t)=L_0P(t)\hat\rho(t) \tag{A4}$$

and

$$Q(t)L_0Q(t')=L_0Q(t') \tag{A5}$$

for arbitrary t and t'. Using the first identity, it is obvious that the second L in the integrand of Eq. (A3) may be replaced by $L_{\rm int}$ [since $Q(t)P(t)=0$]. Moreover, using Eq. (A5), in combination with the form of $\tilde G(t,t')$, the expansion of which yields terms of the form $Q(\bar t)L\cdots$ for certain $\bar t$, it is easily shown that also the first L in this integrand can be replaced by $L_{\rm int}$. Finally, one may again use Eq. (A5) and the expansion of $\tilde G(t,t')$ to show that this operator in Eq. (A3) may be replaced by

$$G(t,t')=\exp_+\left[-i\int_{t'}^{t}ds[L_0+Q(s)L_{\rm int}]\right]\ . \tag{A6}$$

This proves Eq. (20).

APPENDIX B

In this appendix we derive more explicit expressions for the tensor **M**, as defined in Eq. (32), in **r** as well as in **k** representation. After performing a temporal Fourier transform, we obtain

$$\mathbf{M}(\mathbf{r},\omega)=\lim_{\epsilon\to 0^+}\frac{4\pi}{V}\sum_{\mathbf{k}}{}^{*}\frac{k^2\mathbf{1}-\mathbf{k}\mathbf{k}}{k^2-(\tilde\omega+i\epsilon)^2}e^{i\mathbf{k}\cdot\mathbf{r}}\ , \tag{B1}$$

where $\tilde\omega\equiv\omega/c$, and we used the fact that if **k** is special, also $-\mathbf{k}$ is taken in the special set. We write $\mathbf{M}=\mathbf{F}-\mathbf{H}$, where **F** is defined as **M**, except that the sum extends over all modes, and **H** is the sum over the special modes only. Converting the summation in **F** to an integration ($V\to\infty$), one finds

$$\mathbf{F}(\mathbf{r},\omega)=\lim_{\epsilon\to 0}\frac{2}{\pi}\int_0^\infty dk\frac{k^4}{k^2-(\tilde\omega+i\epsilon)^2}\boldsymbol{\tau}(kr)\ , \tag{B2}$$

with

$$\boldsymbol{\tau}(kr)\equiv\frac{1}{4\pi}\int d\Omega_{\mathbf{k}}(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})e^{i\mathbf{k}\cdot\mathbf{r}} =\boldsymbol{\alpha}\frac{\sin(kr)}{kr}+\boldsymbol{\beta}\left[\frac{\cos(kr)}{k^2r^2}-\frac{\sin(kr)}{k^3r^3}\right]\ . \tag{B3}$$

Here

$$\boldsymbol{\alpha}=\mathbf{1}-\hat{\mathbf{r}}\hat{\mathbf{r}} \tag{B4}$$

and

$$\boldsymbol{\beta}=\mathbf{1}-3\hat{\mathbf{r}}\hat{\mathbf{r}}\ , \tag{B5}$$

with $\hat{\mathbf{r}}$ denoting the unit vector in the **r** direction.[32(b)] The integral in Eq. (B2) is easily extended to run from $-\infty$ to $+\infty$ and is then evaluated in the complex plane.

One obtains, for $\epsilon \to 0^+$,

$$\mathbf{F}(\mathbf{r},\omega) = [-\boldsymbol{\beta} + i(\tilde{\omega} r)\boldsymbol{\beta} + (\tilde{\omega} r)^2 \boldsymbol{\alpha}] \frac{e^{i\tilde{\omega} r}}{r^3} ,$$

$$= (\nabla\nabla + \tilde{\omega}^2 \mathbf{1}) \frac{e^{i\tilde{\omega} r}}{r} + \frac{4\pi}{3}\delta(\mathbf{r})\mathbf{1} . \qquad \text{(B6)}$$

The last identity is valid throughout space and is easily checked by explicit differentiation. The Dirac δ function is added to cancel against the one that arises from $\nabla\nabla(r^{-1})$. This proves Eq. (37) in the main text.

For purpose of reference, it is useful to evaluate the continuous space Fourier transform of $\mathbf{F}(\mathbf{r},\omega)$. From Eq. (B6) it readily follows that

$$\mathbf{F}_c(\mathbf{k},\omega) = (-\mathbf{k}\mathbf{k} + \tilde{\omega}^2 \mathbf{1}) \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{e^{i\tilde{\omega} r}}{r} + \frac{4\pi}{3}\mathbf{1} . \qquad \text{(B7)}$$

The angular integrations are easily performed, and the remaining r integration is straightforward after adding a convergence factor $e^{-\epsilon r}$ $(\epsilon \to 0^+)$. One finds

$$\mathbf{F}_c(\mathbf{k},\omega) = -4\pi \lim_{\epsilon \to 0^+} \frac{\mathbf{k}\mathbf{k} - \tilde{\omega}^2 \mathbf{1}}{k^2 - (\tilde{\omega} + i\epsilon)^2} + \frac{4\pi}{3}\mathbf{1} . \qquad \text{(B8)}$$

The first term on the right-hand side is recognized as the Green function of the Maxwell equation.[7(b),9,18,20] It is not surprising that this enters here, because, as is well known, the source of the Maxwell equation (the polarization) behaves as a dipole.[6] The extra term $(4\pi/3)\mathbf{1}$ corrects for the fact that $\mathbf{F}(\mathbf{r},\omega)$ does not contain a δ function in the origin. In fact, the Fourier transform leading to Eq. (B8) would have given the same result if an arbitrarily small sphere surrounding $\mathbf{r}=0$ had been excluded from the Fourier integral. The contribution of this sphere vanishes, as is easily shown from the first form of Eq. (B6) by performing the angular integration first. This is equivalent to the well-known fact that an arbitrarily small sphere for the Green function of the Maxwell equation has a contribution $-(4\pi/3)\mathbf{1}$ in $\mathbf{k}$ space.

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[51] A more careful treatment of the continuum **k** limit is possible if one considers small wave packets of special modes, so that the summation in **H** is converted to an integration over small regions in **k** space. This method is more cumbersome, however, and its final results would not differ from those of our approach.

[52] We use a lattice Fourier transform of **M** because the second part of Eq. (35) is only defined on the lattice ($\mathbf{r}_m$). One *could* extend the definition to an arbitrary point **r**, changing the sum $\sum_{n \neq m}$ to an integral, excluding a sphere with radius $\delta \rightarrow 0$ around **r**. The sums over k' in Eqs. (39) would then run over all Brillouin zones. This approach would formally lead to the same results but proves to be impractical, e.g., in the linearization of the Bloch equations [Eq. (53)].

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