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Microscopic theory of quantization of radiation in molecular dielectrics: Normal-mode representation of operators for local and averaged (macroscopic) fields

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Quantization of radiation has been performed from first principles in a realistic molecular medium, represented by an arbitrary number of energy levels (electronic, vibrational, rotational, etc.) for each constituent molecule. Adopting a polariton model, the field operators have been expanded in terms of normal Bose operators for polariton creation and annihilation. The expansion coefficients have been derived explicitly for the normal modes characterized by wavelengths exceeding considerably the characteristic distance of separation between the molecules. Accordingly, the formalism applies to the long-wavelength region of the spectrum for which description in terms of the macroscopic refractive index is relevant; furthermore, consideration is restricted to the nonabsorbing areas of the spectrum. The theory has been formulated in a manner that made possible a parallel and comparative consideration of operators for both the averaged (macroscopic) and local fields. Consequently, the mode expansions derived cover both the local displacement-field operator and also the averaged (macroscopic) operators for the electric, displacement, magnetic, and polarization fields, and the vectorial potential. The expansions, involving summation over an arbitrary number of branches of polariton dispersion, manifestly embody the refractive influences as well. To this end, the local-field effects intrinsically emerge within the present formalism that treats systematically the photon umklapp processes. Relations have been established between the expansion components of the local and averaged field operators. The relationships support some previous attempts to link the amplitudes of local and macroscopic field operators phenomenologically, and are also consistent with the familiar results of classical electrodynamics. Equal-time commutation relations have been demonstrated to be preserved, expressing the operators for the averaged fields in terms of the normal Bose operators. On the other hand, the commutation relations between the macroscopic fields are of the same form as those for their microscopic counterparts, subject to the coarse-graining procedure. Finally, the present study dealing with the macroscopic and local operators provides a tool for combined investigation of both propagation of the quantized fields in molecular dielectrics and also interaction of the fields with the embedded molecules or atoms.

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I. INTRODUCTION

The presence of a polarizable medium alters the quantum fluctuations of the radiation field. Hence, the proper understanding of a quantized electromagnetic field in the medium is important in quantum optics. The usual method to quantize the radiation introduces the matter phenomenologically through the linear [1–5] or nonlinear [6–8] susceptibilities. The approach, initially suggested by Ginzburg [9] and by Jauch and Watson [10], relies on the phenomenological quantization of the macroscopic electromagnetic field. An alternative procedure, originating from the classical works by Fano [11], Hopfield [12], and Agranovich [13], introduces the matter explicitly. Here the quantized radiation field is considered to be in mutual interaction with the atomic (or molecular) medium, both constituting a single dynamical system. The dressed normal modes of such a combined system are known as polaritons.

Polaritons are a familiar subject in solid-state physics [12–18]. In recent years the polariton concept has been applied to the problems of quantization of radiation in linear dielectrics [19–23]. Here an important aspect is how to represent the field operators in terms of normal polariton modes. Huttner and co-workers [20–22] considered the canonical quantization of the radiation field in a uniform dielectric medium, modeled by a harmonic oscillator field. As a result, the normal-mode expansions have been obtained for the macroscopic field operators in such a dielectric. It is to be pointed out that the formalism did not reflect effects due to discreteness of the atomic or molecular medium, including the local-field effects. The related study by Ho and Kumar [23] extended the analysis to the case of a nonuniform medium consisting of discrete quantum oscillators (atoms or molecules) with one resonance frequency. Another development by Knoester and Mukamel [19], also based on the two-level (one resonance frequency) representation of each atom or molecule of the medium, involved a consideration of operators for the microscopic displacement field calculated at the lattice sites, i.e., the local-field operators. This facilitated the subsequent analysis of polariton-mediated intermolecular processes.

The present paper deals with the normal-mode representation of electromagnetic and polarization fields in a discrete molecular medium. The study extends in a number of ways the existent theories [19–23] on the microscopic quantization of radiation in dielectrics. Unlike the previous works [19–23], the theory is formulated in a manner that allows a parallel and comparative analysis of normal-mode expansions of operators for both the averaged (macroscopic) fields and also

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the local displacement field. Consequently, relations are established between the mode components of operators for macroscopic and local fields. Refractive contributions, including the local-field factors, emerge intrinsically in the relationships. At the same time, the relations are consistent with the familiar results of classic electrodynamics. Next, the paper considers a discrete molecular medium without any restriction to a number of excitation frequencies (electronic, vibrational, rotational, etc.) for each individual molecule. The arising mathematical difficulties are dealt with through the application of a matrix formulation [17,24] of the polariton problem and subsequent Green's function development. (The Green's-function technique is related to some extent with that suggested recently by Juzeliūnas and Andrews [24] in the quantum-electrodynamics study of intermolecular energy transfer in the condensed phases.) As a result, an arbitrary number of polariton branches may be accommodated within the present approach, in contrast to two dispersion branches that feature in the theories by Knoester and Mukamel [19] and Ho and Kumar [23].

Finally, the present study is based on the multipolar formulation of quantum electrodynamics (QED), unlike some of the previous theories employing the minimum coupling QED [21–23]. This facilitates representation of the operator for the local displacement field in a form explicitly accommodating the local-field factors and other refractive contributions: It is the local displacement operator that describes the coupling of individual molecules with the radiation field in the multipolar QED. Hence, the subsequent applications of the theory to various molecule-radiation processes in the media, such as spontaneous emission or linear absorption, are then straightforward [25]. That contrasts with lengthy and complicated analysis of the spontaneous emission within the minimal coupling formulation of the QED [23], in which the instantaneous Coulomb interaction is to be considered between the molecules. In this way, our formalism giving the normal-mode representations of operators for both the macroscopic (averaged) and local fields provides a tool for combined consideration of the problems involving both the propagation of the quantized fields in molecular dielectrics and also the interaction of the fields with the embedded molecules or atoms.

The paper is organized as follows. Section II A introduces the operators for the electric, electric displacement, and polarization fields. In Sec. II B the second-quantized (polariton) Hamiltonian is defined for a system comprising a quantized electromagnetic field coupled to a discrete molecular (atomic) medium. In Secs. III A and III B the matrix formulation of the polariton problem is outlined, followed by the formal derivation in Sec. III C of the normal-mode expansion of the field operators in terms of the appropriate Green's functions. The expansion coefficients are then determined in Secs. IV A and IV B; the results for the electric, displacement, and polarization fields are summarized in Sec. IV C. In Sec. IV D the operators for the electric and displacement fields are transformed from the original Schrödinger to the Heisenberg representation. The normal-mode representations of the magnetic-field operators are then determined using the Maxwell equations relating the field operators in the Heisenberg representation. Section IV E considers the commutation relations between the field operators: The original commutation relations are demonstrated to be preserved expressing the field operators in terms of normal operators for polariton creation and annihilation. The concluding remarks are placed in Sec. V. Appendixes A and B contain details of the derivation of the mode representation of macroscopic operators for the displacement and polarization fields.

II. FORMULATION

A. Operators for the electric displacement and polarization fields

In the minimal coupling formulation of the nonrelativistic QED, the momentum density canonical to the transverse vectorial potential $\mathbf{a}^{\perp}(\mathbf{r})$ is $-\varepsilon_0$ times the electric field $\mathbf{e}^{\perp}(\mathbf{r})$ [26–28]. In this QED formulation, the radiation-matter coupling is represented by the familiar $\mathbf{p}\cdot\mathbf{a}^{\perp}$ and also $\mathbf{a}^{\perp 2}$ terms. In addition, an instantaneous Coulombic interaction couples the electric charges of the system. Another QED representation, related to the minimal coupling QED by a canonical transformation [28,29], entails the full multipolar expansion of electric, magnetic, and diamagnetic densities of molecules interacting with the quantized radiation field. In such a multipolar QED formulation, an instantaneous electrostatic interaction is cancelled between the molecules, the intermolecular coupling being exclusively due to the exchange of transverse photons. The present study makes use of the electric-dipole approximation of the multipolar QED. This is normally sufficient for the situations where the radiation wavelength is long compared to the dimensions of molecules (or their chromophoric groups), so that the variation of the vectorial potential over a molecule may be neglected. The momentum conjugated to $\mathbf{a}^{\perp}(\mathbf{r})$ is now given by $-\mathbf{d}^{\perp}(\mathbf{r})$, where $\mathbf{d}^{\perp}(\mathbf{r})$ is the operator for the transverse microscopic displacement field [28];

$$\mathbf{d}^{\perp}(\mathbf{r})=\varepsilon_0\mathbf{e}^{\perp}(\mathbf{r})+\mathbf{p}^{\perp}(\mathbf{r}), \tag{2.1}$$

and $\mathbf{e}^{\perp}(\mathbf{r})$ is the operator for the transverse electric field. For the time being, we shall consider the full polarization field,

$$\mathbf{p}(\mathbf{r})=\sum_{\zeta}\boldsymbol{\mu}(\zeta)\,\delta(\mathbf{r}-\mathbf{r}_{\zeta}), \tag{2.2}$$

rather than its solenoidal (divergence-free) component $\mathbf{p}^{\perp}(\mathbf{r})$ featured in Eq. (2.1). The above $\boldsymbol{\mu}(\zeta)$ is the operator for the electric dipole moment of molecule ζ positioned at $\mathbf{r}_{\zeta}$, and the summation over ζ extends to all the molecules of the system, the term ''molecule'' being used generically to also encompass other quantum species such as atoms or chromophoric groups.

The operators $\mathbf{d}^{\perp}(\mathbf{r})$ and $\mathbf{p}(\mathbf{r})$ may be represented as a Fourier series in $\mathbf{k}+\mathbf{G}$ modes, allowed by the periodic boundary conditions (chosen to be the same both for the radiation field and the matter),

$$\mathbf{d}^{\perp}(\mathbf{r})=i\sum_{\mathbf{k},\mathbf{G}}\sum_{\lambda=1}^{2}\left(\frac{\hbar c|\mathbf{k}+\mathbf{G}|\varepsilon_0}{2V_0}\right)^{1/2}\mathbf{e}^{(\lambda)}(\mathbf{k}+\mathbf{G})\times[a^{(\lambda)}(\mathbf{k}+\mathbf{G})-a^{\dagger(\lambda)}(-\mathbf{k}-\mathbf{G})]e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \tag{2.3}$$

and

$$\mathbf{p}(\mathbf{r})=\rho N^{-1/2}\sum_{\mathbf{k},\mathbf{G}} \boldsymbol{\mu}_{\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \tag{2.4}$$

with

$$\boldsymbol{\mu}_{\mathbf{k}}\equiv\boldsymbol{\mu}_{\mathbf{k}+\mathbf{G}}=N^{-1/2}\sum_{\zeta} \boldsymbol{\mu}(\zeta)e^{-\mathbf{ik}\cdot\mathbf{r}_{\zeta}}, \tag{2.5}$$

where

$$\rho=N/V_0 \tag{2.6}$$

is the mean number density, N being the number of molecules per quantization volume V_0. For convenience, the above wave vector $\mathbf{k}+\mathbf{G}$ has been partitioned into the first Brillouin-zone vector $\mathbf{k}$ and the inverse lattice vector $\mathbf{G}$ $[\exp(i\mathbf{G}\cdot\mathbf{r}_{\zeta})=1]$, reflecting the lattice symmetry imposed at this stage on the molecular system: Nevertheless, the results based on such a model can describe adequately the quantized fields in a variety of less regular media, as will be discussed later in this section.

The expansion (2.3) casts the operator for the displacement field $\mathbf{d}^{\perp}(\mathbf{r})$ in a usual way [28] in terms of Bose operators $a^{\dagger(\lambda)}(\mathbf{k}+\mathbf{G})$ and $a^{(\lambda)}(\mathbf{k}+\mathbf{G})$ for creation and annihilation of a photon with wave vector $\mathbf{k}+\mathbf{G}$ and polarization $\mathbf{e}^{(\lambda)}(\mathbf{k}+\mathbf{G})$ ($\lambda=1,2$); the latter is chosen to be real and such that $\mathbf{e}^{(\lambda)}(-\mathbf{k}-\mathbf{G})=\mathbf{e}^{(\lambda)}(\mathbf{k}+\mathbf{G})$. As regards the polarization field of the medium, $\mathbf{p}(\mathbf{r})$, it will be presented explicitly in terms of the molecular creation and annihilation operators in the equation (2.16). Ultimately, both the displacement and polarization fields will be expressed in terms of the normal Bose operators for polariton creation and annihilation. The mode expansion of the electric-field operator $\mathbf{e}^{\perp}(\mathbf{r})$ will then be obtained straightforwardly exploiting the general relationship (2.1).

B. Hamiltonian

The full Hamiltonian of the system comprises the radiation (H_{rad}) and molecular (H_{mol}) Hamiltonians, and the coupling operator H_{coup},

$$H=H_{\text{rad}}+H_{\text{mol}}+H_{\text{coup}}. \tag{2.7}$$

Here, according to the electric-dipole approximation [17,28,29], the Hamiltonian H_{coup} for the radiation-matter coupling originates from the contributions by the individual molecules, as

$$H_{\text{coup}}=-\varepsilon_0^{-1}\sum_{\zeta} \boldsymbol{\mu}(\zeta)\cdot\mathbf{d}^{\perp}(\mathbf{r}_{\zeta}). \tag{2.8}$$

In second quantization, the radiation and molecular Hamiltonians, as well as the molecular operator for the dipole moment $\boldsymbol{\mu}(\zeta)$ may be expressed as

$$H_{\text{rad}}=\sum_{\mathbf{k},\mathbf{G}}\sum_{\lambda=1}^{2} \hbar c|\mathbf{k}+\mathbf{G}|[a^{\dagger(\lambda)}(\mathbf{k}+\mathbf{G})a^{(\lambda)}(\mathbf{k}+\mathbf{G})+a^{(\lambda)}(\mathbf{k}+\mathbf{G})a^{\dagger(\lambda)}(\mathbf{k}+\mathbf{G})] \tag{2.9}$$

$$H_{\text{mol}}=E_g+\sum_{\zeta,\gamma}\sum_{j=1}^{3} \hbar\Omega_{\gamma}B^{\dagger}_{\zeta,\gamma,j}B_{\zeta,\gamma,j}, \tag{2.10}$$

$$\boldsymbol{\mu}(\zeta)=\sum_{\gamma}\sum_{j=1}^{3} (B^{\dagger}_{\zeta,\gamma,j}+B_{\zeta,\gamma,j})\mu_{\gamma}\mathbf{e}_j, \tag{2.11}$$

where E_g denotes the ground-state energy of the molecular subsystem, $\mathbf{e}_j$ is the unit vector along a Cartesian axis j, and $B^{\dagger}_{\zeta,\gamma,j}$ ($B_{\zeta,\gamma,j}$) is the Bose operator for creation (annihilation) of an excitation at the molecule ζ [30]. When acting on a ground molecular state, the creation operator $B^{\dagger}_{\zeta,\gamma,j}$ promotes the molecule ζ to an excited electronic state, characterized by indexes γ and j. It is to be emphasized that an arbitrary number of excitation frequencies Ω_{γ} has been included for each individual molecule. An additional index $j=1,2,3$ explicitly refers to the triple degeneracy of the excited molecular states, the associated transition dipole moments $\mu_{\gamma}\mathbf{e}_j$ being mutually perpendicular: For convenience, the transition dipoles μ_{γ} have been chosen to be real.

In this way, the molecules have been assumed to be characterized by isotropic polarizabilities. Such a model may also represent a common situation where the nonisotropic species are randomly oriented in their sites. As regards the spatial arrangement, the molecules are supposed to constitute a simple cubic lattice. Nevertheless, the main results to come seem to be insensitive to the possible lack of such a translational symmetry in a number of important situations. The potential applications of the theory to spontaneous emission and other molecule-radiation processes will involve the photonic areas of polariton dispersion, away from any exciton resonances. Accordingly, the effects of exciton coherence (i.e., delocalization of the excited molecular states due to the lattice symmetry) then do not play a significant role. The effects of coherence are of minimum importance for exciton regions of dispersion as well, provided the molecular linewidths exceed the characteristic value of the resonance coupling between the molecules. It is therefore expected that the present analysis of the quantized radiation field in an isotropic medium with cubic symmetry may also represent adequately the radiation modes in a variety of amorphous media constituted of randomly situated and oriented molecules.

Transforming the molecular Bose operators to the momentum space,

$$B_{\mathbf{k},\gamma,j}=N^{-1/2}\sum_{\zeta} B_{\zeta,\gamma,j}e^{-i\mathbf{k}\cdot\mathbf{r}_{\zeta}}, \tag{2.12}$$

$$B_{\mathbf{k},\gamma,\lambda'}=\sum_{j=1}^{3} [\mathbf{e}^{(\lambda')}(k)\cdot\mathbf{e}_j]B_{\mathbf{k},\gamma,j} \tag{2.13}$$

[with $\mathbf{e}^{(\lambda')}(\mathbf{k})=\hat{\mathbf{k}}\equiv\mathbf{k}/k$, for $\lambda'=3$], the molecular Hamiltonian (2.10), the coupling operator (2.8), and the polarization field (2.4) acquire a form, through Eqs. (2.3), (2.5), and (2.11),

$$H_{\mathrm{mol}}=\sum_{\mathbf{k},\gamma}\sum_{\lambda'=1}^{3}\hbar\Omega_{\gamma}(B^{\dagger}_{\mathbf{k},\gamma,\lambda'}B_{\mathbf{k},\gamma,\lambda'}+B_{\mathbf{k},\gamma,\lambda'}B^{\dagger}_{\mathbf{k},\gamma,\lambda'}), \tag{2.14}$$

$$H_{\mathrm{coup}}=\sum_{\mathbf{k},\mathbf{G},\gamma}\sum_{\lambda'=1}^{3}\sum_{\lambda=1}^{2}\hbar[C_{(\mathbf{k},\gamma,\lambda')(\mathbf{k},\mathbf{G},\lambda)}(B^{\dagger}_{\mathbf{k},\gamma,\lambda'}+B_{-\mathbf{k},\gamma,\lambda'})a^{(\lambda)}(\mathbf{k}+\mathbf{G})+C^{*}_{(\mathbf{k},\gamma,\lambda')(\mathbf{k},\mathbf{G},\lambda)}a^{\dagger(\lambda)}(\mathbf{k}+\mathbf{G})(B_{\mathbf{k},\gamma,\lambda'}+B^{\dagger}_{-\mathbf{k},\gamma,\lambda'})], \tag{2.15}$$

$$\mathbf{p}(\mathbf{r})=\rho N^{-1/2}\sum_{\mathbf{k},\mathbf{G}}\sum_{\gamma}\sum_{\lambda'=1}^{3}\mu_{\gamma}\mathbf{e}^{(\lambda')}(\mathbf{k})(B_{\mathbf{k},\gamma,\lambda'}+B^{\dagger}_{-\mathbf{k},\gamma,\lambda'})e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \tag{2.16}$$

where

$$C_{(\mathbf{k},\gamma,\lambda')(\mathbf{k},\mathbf{G},\lambda)}=-i\left(\frac{c|\mathbf{k}+\mathbf{G}|}{2\varepsilon_0\hbar}\rho\right)^{1/2}\mu_{\gamma}[\mathbf{e}^{(\lambda')}(\mathbf{k})\cdot\mathbf{e}^{(\lambda)}(\mathbf{k}+\mathbf{G})] \tag{2.17}$$

is the radiation-matter coupling matrix. Accordingly, the coupling Hamiltonian (2.15) manifestly accommodates photon umklapp processes ($\mathbf{k}\rightarrow\mathbf{k}+\mathbf{G}$). Here also a specific zero-point energy E_g has been chosen in the molecular Hamiltonian (2.14) to make it symmetric with respect to the molecular creation and annihilation operators. It is to be noted that the full Hamiltonian H should also contain a field-independent contribution, represented by the last term of Eq. (3.6.31) of Ref. [28]. Yet, such a contribution, essential for the calculations of the radiative Lamb shift, is not important for the present purposes.

Equations (2.14) and (2.15), together with (2.9) and (2.7), define the full second-quantized Hamiltonian of the system. The matrix formulation of the problem will be outlined next.

III. MATRIX REPRESENTATION

A. Matrix Hamiltonian

Let us now introduce a uniform notation for the Bose molecular and radiative operators:

$$A_{\alpha}=\begin{cases} a^{(\lambda)}(\mathbf{k}+\mathbf{G}) & \text{for } \alpha=(\mathbf{k},\mathbf{G},\lambda) \\ B_{\mathbf{k},\gamma,\lambda'} & \text{for } \alpha=(\mathbf{k},\gamma,\lambda'). \end{cases} \tag{3.1}$$

Adopting also the tilde convention to indicate momentum reversal,

$$\widetilde{(\mathbf{k},\gamma,\lambda')}=(-\mathbf{k},\gamma,\lambda'),\quad \widetilde{(\mathbf{k},\mathbf{G},\lambda)}=(-\mathbf{k},-\mathbf{G},\lambda) \tag{3.2}$$

the second-quantized Hamiltonian may be expressed in a compact manner through the matrix product [24],

$$H=\frac{\hbar}{2}(A^{\dagger},\widetilde{A}|h|A,\widetilde{A}^{\dagger}), \tag{3.3}$$

where $|A,\widetilde{A}^{\dagger})$ is the row matrix of the creation and annihilation operators,

$$|A,\widetilde{A}^{\dagger})=(A_{\alpha_1},A_{\alpha_2},\ldots;A^{\dagger}_{\widetilde{\alpha}_1},A^{\dagger}_{\widetilde{\alpha}_2},\ldots), \tag{3.4}$$

$(A^{\dagger},\widetilde{A}|$ is its column counterpart, and h is the matrix Hamiltonian to be defined later; for more details see also Ref. [24].

It is convenient to make use of the following expansion of the matrix vectors:

$$|A,\widetilde{A}^{\dagger})=\sum_{\alpha}[|\alpha,1)A_{\alpha}+|\alpha,2)A^{\dagger}_{\widetilde{\alpha}}], \tag{3.5}$$

$$(A^{\dagger},\widetilde{A}|=\sum_{\alpha}[A^{\dagger}_{\alpha}(\alpha,1|+A_{\widetilde{\alpha}}(\alpha,2|], \tag{3.6}$$

where the summation over α extends to all α_t ($t=1,2,3,\ldots$): An additional index $i=1,2$ is due to the involvement of the double-basis set of the original (molecular and radiation) modes α in the matrix formulation of the problem. Here $|\alpha,i)$ [$(\alpha,i|$] is the orthogonal set of unit row (column) vectors. (These are not to be confused with the quantum-mechanical bra and ket state vectors, such as those featured in Ref. [25].) For instance,

$$|\alpha_4,2)=(0,0,\ldots;0,0,0,1,0,..). \tag{3.7}$$

The expanded matrix Hamiltonian is given by [24]

$$h=h_r+h_m+h_{m-r}+h_{r-m}, \tag{3.8}$$

with

$$h_r=\sum_{\mathbf{k},\mathbf{G}}\sum_{\lambda=1}^{2}\sum_{i=1}^{2}|\mathbf{k},\mathbf{G},\lambda,i)c|\mathbf{k}+\mathbf{G}|(\mathbf{k},\mathbf{G},\lambda,i|, \tag{3.9}$$

$$h_m=\sum_{\mathbf{k},\gamma}\sum_{\lambda'=1}^{3}\sum_{i=1}^{2}|\mathbf{k},\gamma,\lambda',i)\Omega_\gamma(\mathbf{k},\gamma,\lambda',i|, \tag{3.10}$$

$$h_{m-r}=-i\sum_{\mathbf{k}}\sum_{j=1}^{3}|\mathbf{k},\mathrm{matt})_{jj}(\mathbf{k},\mathrm{rad}|, \tag{3.11}$$

and

$$h_{r-m}=i\sum_{\mathbf{k}}\sum_{j=1}^{3}|\mathbf{k},\mathrm{rad})_{jj}(\mathbf{k},\mathrm{matt}|. \tag{3.12}$$

Here h_r and h_m are the diagonal matrices of radiative and molecular frequencies; h_{r-m} and h_{m-r} are the off-diagonal matrices that describe the radiation-matter coupling, with

$$|\mathbf{k},\mathrm{matt})_j=\sum_{\gamma}\sum_{\lambda'=1}^{3}[|\mathbf{k},\gamma,\lambda',1)+|\mathbf{k},\gamma,\lambda',2)]\times e_j^{(\lambda')}(\mathbf{k})\mu_\gamma, \tag{3.13}$$

$$|\mathbf{k},\mathrm{rad})_j=\sum_{\mathbf{G}}\sum_{\lambda=1}^{2}[|\mathbf{k},\mathbf{G},\lambda,1)-|\mathbf{k},\mathbf{G},\lambda,2)]e_j^{(\lambda)}(\mathbf{k}+\mathbf{G})\times\left(\frac{c|\mathbf{k}+\mathbf{G}|}{2\varepsilon_0\hbar}\rho\right)^{1/2}, \tag{3.14}$$

the radiative and molecular raw matrices, ${}_j(\mathbf{k},\mathrm{rad}|$ and ${}_j(\mathbf{k},\mathrm{matt}|$ being their column counterparts. Note that the summation over the inverse lattice vector $\mathbf{G}$, featured in the radiative matrix vectors $|\mathbf{k},\mathrm{rad})_j$ and ${}_j(\mathbf{k},\mathrm{rad}|$, represents the photon umklapp processes in the interaction terms (3.11) and (3.12) of the matrix Hamiltonian.

B. Formal diagonalization

We shall search for a new set of Bose creation and annihilation operators diagonalizing the Hamiltonian. The following transformation of the Bogliubov-Tyablikov type relates the old and new sets of operators:

$$P_\sigma=\sum_{\alpha}[(\sigma,1|S|\alpha,1)A_\alpha+(\sigma,1|S|\alpha,2)A^\dagger_{\tilde\alpha}], \tag{3.15}$$

$$P^\dagger_{\tilde\sigma}=\sum_{\alpha}[(\sigma,2|S|\alpha,1)A_\alpha+(\sigma,2|S|\alpha,2)A^\dagger_{\tilde\alpha}], \tag{3.16}$$

where $(\sigma,i|S|\alpha,i')$ are the transformation coefficients (i, $i'=1,2$) and the index σ labels the normal polariton modes σ_t ($t=1,2,3,\ldots$): At this stage, the quasimomentum $\mathbf{k}$ of the polariton is implicitly incorporated into the mode index σ. The linear relation (3.15) and (3.16) may be compactly expressed as

$$|P,\tilde P^\dagger)=S|A,\tilde A^\dagger), \tag{3.17}$$

or

$$(P^\dagger,\tilde P|=(A^\dagger,\tilde A|{}^tS^*, \tag{3.18}$$

with

$$|P,\tilde P^\dagger)=\sum_{\sigma}[|\sigma,1)P_\sigma+|\sigma,2)P^\dagger_{\tilde\sigma}], \tag{3.19}$$

$$(P^\dagger,\tilde P|=\sum_{\sigma}[P^\dagger_\sigma(\sigma,1|+P_{\tilde\sigma}(\sigma,2|], \tag{3.20}$$

where S is a transformation matrix, and $|\sigma,i)$ $[(\sigma,i|]$ is an orthogonal set of unit row (column) vectors, $i=1,2$.

The transformed second-quantized Hamiltonian is required to take a diagonal form,

$$H=(P^\dagger,\tilde P|\Lambda|P,\tilde P^\dagger), \tag{3.21}$$

where

$$\Lambda=\sum_{\sigma}\sum_{i=1}^{2}|\sigma,i)\Pi_\sigma(\sigma,i| \tag{3.22}$$

is a diagonal matrix Hamiltonian and Π_σ is a polariton frequency. Accordingly, the original matrix Hamiltonian h is related to its diagonal counterpart Λ, as

$$h={}^tS^*\Lambda S. \tag{3.23}$$

The Bose commutation relations are to be obeyed by both the original and transformed sets of operators, A_α, $A^\dagger_\sigma$ and P_σ, $P^\dagger_\sigma$. This leads to a condition on S,

$$Q=SQ{}^tS^* \quad \text{or} \quad S^{-1}=Q({}^tS^*)Q, \tag{3.24}$$

with

$$Q=\sum_{i=1}^{2}\sum_{\sigma}|\sigma,i)(-1)^{i+1}(\sigma,i|\equiv\begin{pmatrix}\mathbf{1}&0\\0&-\mathbf{1}\end{pmatrix} \tag{3.25}$$

a diagonal matrix. Other conditions imposed on the transformation matrix S are [24]

$$(\sigma,1|S^*|\alpha,1)=(\sigma,2|S|\alpha,2), \tag{3.26}$$

$$(\sigma,1|S^*|\alpha,2)=(\sigma,2|S|\alpha,1), \tag{3.27}$$

and

$$(\tilde\sigma,i|S|\tilde\alpha,j)=(\sigma,i|S|\alpha,j) \quad (i,j=1,2). \tag{3.28}$$

Finally, performing the inverse transformation, one obtains the following for the combinations of molecular and radiative operators that feature in the mode expansions (2.3) and (2.16) of $\mathbf{d}^\perp(\mathbf{r})$ and $\mathbf{p}(\mathbf{r})$,

$$a^{(\lambda)}(\mathbf{k}+\mathbf{G})-a^{\dagger(\lambda)}(-\mathbf{k}-\mathbf{G})=\sum_{\sigma}\{[(\mathbf{k},\mathbf{G},\lambda,1|-(\mathbf{k},\mathbf{G},\lambda,2|]S^{-1}|\sigma,1)P_{\sigma}$$
$$-(\sigma,1|QSQ[|-\mathbf{k},-\mathbf{G},\lambda,1)-|-\mathbf{k},-\mathbf{G},\lambda,2)]P_{\sigma}^{\dagger}\}, \tag{3.29}$$

and

$$B_{\mathbf{k},\gamma,\lambda'}+B^{\dagger}_{-\mathbf{k},\gamma,\lambda'}=\sum_{\sigma}\{[(\mathbf{k},\gamma,\lambda',1|+(\mathbf{k},\gamma,\lambda',2|]S^{-1}|\sigma,1)P_{\sigma}+(\sigma,1|QSQ[|-\mathbf{k},\gamma,\lambda',1)+|-\mathbf{k},\gamma,\lambda',2)]P_{\sigma}^{\dagger}\}, \tag{3.30}$$

where the use has also been made of the above equations (3.24) and (3.26)–(3.28) for S.

C. Field operators

The operators for the electric displacement and polarization fields may now be formally represented through the polariton Bose operators $P_{\mathbf{k},m,\lambda}$ and $P^{\dagger}_{\mathbf{k},m,\lambda}$. [From now on, the $\mathbf{k}$ dependence will be displayed explicitly in the mode index $\sigma\equiv(\mathbf{k},m,\lambda)$: here the subindex m will refer to branches of polariton dispersion ($m=1,2,3,...$), the third subindex λ being reserved to label the degenerate sublevels within the branches]. Consider the operators for the mean (i.e., macroscopic) displacement and polarization fields, $\overline{\mathbf{d}^{\perp}}(\mathbf{r})$ and $\overline{\mathbf{p}}(\mathbf{r})$, as well as the operator $\mathbf{d}^{\perp}(\mathbf{r}_{\zeta})$ for the local displacement field: The latter, representing the displacement field at the molecular sites ζ, describes coupling of the radiation field with the individual molecules. Calling on Eqs. (2.3), (2.16), (3.29), and (3.30), one finds for the Cartesian components of the field operators,

$$d_j^{\perp}(\mathbf{r}_{\zeta})=i\hbar\varepsilon_0 N^{-1/2}\sum_{\mathbf{k},m,\lambda}[_j(\mathbf{k},\mathrm{rad}|S^{-1}|\mathbf{k},m,\lambda,1)P_{\mathbf{k},m,\lambda}e^{i\mathbf{k}\cdot\mathbf{r}_{\zeta}}-(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\mathrm{rad})_j P^{\dagger}_{\mathbf{k},m,\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}_{\zeta}}], \tag{3.31}$$

$$\overline{d_j^{\perp}}(\mathbf{r})=i\hbar\varepsilon_0 N^{-1/2}\sum_{\mathbf{k},m,\lambda}[_j(\mathbf{k},\mathrm{rad}_0|S^{-1}|\mathbf{k},m,\lambda,1)P_{\mathbf{k},m,\lambda}e^{i\mathbf{k}\cdot r}-(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\mathrm{rad}_0)_j P^{\dagger}_{\mathbf{k},m,\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}}], \tag{3.32}$$

and

$$\overline{p_j}(\mathbf{r})=\rho N^{-1/2}\sum_{\mathbf{k},m,\lambda}[_j(\mathbf{k},\mathrm{matt}|S^{-1}|\mathbf{k},m,\lambda,1)P_{\mathbf{k},m,\lambda}e^{i\mathbf{k}\cdot\mathbf{r}}+(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\mathrm{matt})_j P^{\dagger}_{\mathbf{k},m,\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}}], \tag{3.33}$$

where

$$|\mathbf{k},\mathrm{rad}_0)_j\equiv I_{r_0}|\mathbf{k},\mathrm{rad})_j=\sum_{\lambda=1}^{2}[|\mathbf{k},\mathbf{0},\lambda,1)-|\mathbf{k},\mathbf{0},\lambda,2)]e_j^{(\lambda)}(\mathbf{k})$$
$$\times\left(\frac{ck}{2\varepsilon_0\hbar}\rho\right)^{1/2}, \tag{3.34}$$

and $|\mathbf{k},\mathrm{matt})_j$ is as in Eq. (3.13), the matrix I_{r_0} being defined by Eq. (A6) in Appendix A. The latter I_{r_0} projects the full radiative matrix vector $|\mathbf{k},\mathrm{rad})_j$ [given by Eq. (3.14)] onto the subspace of the first-Brillouin-zone photons, producing $|\mathbf{k},\mathrm{rad}_0)_j$. Consequently, the expansion of the new radiative matrix vector $|\mathbf{k},\mathrm{rad}_0)_j$ involves only the $\mathbf{G}=\mathbf{0}$ term.

In this way, the macroscopic fields $\overline{\mathbf{d}^{\perp}}(\mathbf{r})$ and $\overline{\mathbf{p}}(\mathbf{r})$ no longer contain summations over the inverse lattice vector $\mathbf{G}$, since all the contributions from the terms with $\mathbf{G}\neq\mathbf{0}$ vanish during the averaging over the elementary cell [$\overline{\exp(i\mathbf{G}\cdot\mathbf{r})}=\delta_{\mathbf{G},\mathbf{0}}$]. Furthermore, it is implied that the first-Brillouin-zone vector $\mathbf{k}$ covers the region where

$$k\ll 2\pi(N/V)^{1/3}\equiv 2\pi/a \quad (N/V\equiv\rho=a^{-3}), \tag{3.35}$$

in the mode expansions (3.32) and (3.33) of the averaged fields, so that $\overline{\exp(i\mathbf{k}\cdot\mathbf{r})}\approx\exp(i\mathbf{k}\cdot\mathbf{r})$. The condition (3.35), which will be extended subsequently to the local-field expansion (3.31) as well, is fully appropriate for the consideration of the infrared, optical, or ultraviolet modes of light in the condensed media: In these regions of the spectrum, the radiation wavelength $\lambda=2\pi/k$ exceeds greatly the characteristic distance a of intermolecular separation in the condensed molecular system.

To deal with the matrix elements of S entering the above mode expansions, let us consider the following Green function:

$$\ddot{G}^{\varphi}_{lj}(\mathbf{k},\omega)=\sum_{m,\lambda}\left[\frac{{}_l(\mathbf{k},\varphi|S^{-1}|\mathbf{k},m,\lambda,1)(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\varphi)_j}{\omega-\omega_k^{(m)}}+\frac{{}_l(\mathbf{k},\varphi|S^{-1}|\mathbf{k},m,\lambda,2)(\mathbf{k},m,\lambda,2|QSQ|\mathbf{k},\varphi)_j}{-\omega-\omega_k^{(m)}}\right]$$

$$\equiv{}_l(\mathbf{k},\varphi|\ddot{G}(\omega)|\mathbf{k},\varphi)_j, \tag{3.36}$$

where

$$\omega_k^{(m)}\equiv\Pi_{\mathbf{k},m,\lambda}, \quad m=1,2,3,\ldots \tag{3.37}$$

will denote the eigenfrequency of the $(\mathbf{k},m,\lambda)\equiv\sigma$ mode: $\omega_k^{(m)}$ depends on $k\equiv|\mathbf{k}|$, since the system in question is isotropic. Here also $|\mathbf{k},\varphi)_j$ is the following abbreviation for the radiative matrix vectors:

$$|\mathbf{k},\varphi)_j=\begin{cases}|\mathbf{k},\mathrm{rad})_j & \text{for} \quad \varphi=\mathrm{rad}\\ |\mathbf{k},\mathrm{rad}_0)_j & \text{for} \quad \varphi=\mathrm{rad}_0,\end{cases} \tag{3.38}$$

and

$$\ddot{G}(\omega)=[\omega Q-h]^{-1} \tag{3.39}$$

is the Green's matrix corresponding to the matrix Hamiltonian h, with Q as in Eq. (3.25). Note that the umlaut has been placed over the Green's matrix $\ddot{G}(\omega)$ to differentiate it from the inverse lattice vector $\mathbf{G}$.

For each eigenfrequency $\omega_k^{(m)}$ in the dispersion branch m, one has

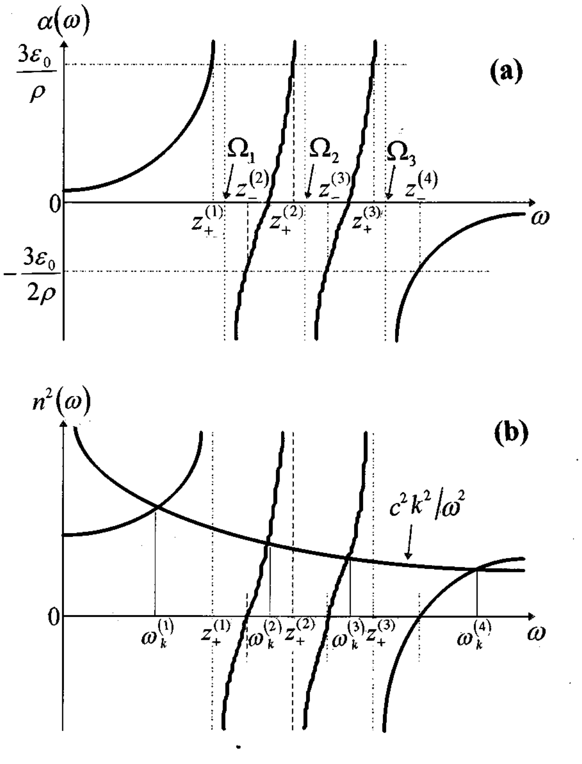

FIG. 1. Graphical solution of Eq. (4.4) for $M_{\mathrm{mol}}=3$. (a) Molecular polarizability $\alpha(\omega)$, Eq. (4.3), plotted schematically as a function of frequency ω. Vertical dashed lines at molecular frequencies Ω_1, Ω_2, and Ω_3 correspond to the infinities of $\alpha(\omega)$. The polarizability curves cross the horizontal dashed lines at the points $\omega=z_+^{(j)}$ and $\omega=z_-^{(j+1)}$ $(j=1,2,3)$, representing, respectively, infinities and zeros of the relative dielectric permittivity $\varepsilon_r\equiv n^2=(1+2\alpha\rho/3\varepsilon_0)/(1-\alpha\rho/3\varepsilon_0)$. (b) Subsequent plot of $n^2(\omega)$ as a function of ω. The eigenfrequencies $\omega_k^{(m)}$ $(m=1,2,3,4)$ are then determined by the intersection points with the curve c^2k^2/ω^2.

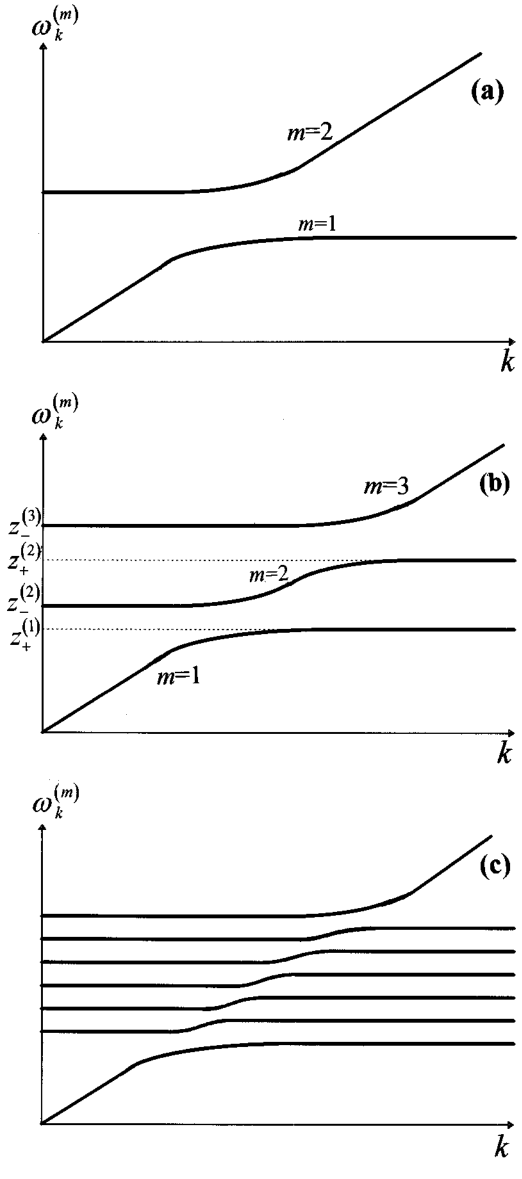

FIG. 2. Schematic plot of the dispersion curves $\omega_k^{(m)}$ $(m=1,\ldots,M_{\mathrm{mol}}+1)$ for (a) $M_{\mathrm{mol}}=1$ (Hopfield model) and (b) $M_{\mathrm{mol}}=2$. The third diagram (c) illustrates a situation in which a dense set of dispersion curves is featured. Note that all the diagrams represent the long-wavelength region of the spectrum $(k\ll 2\pi/a)$ under consideration. For greater values of k, the effects of spatial dispersion are to be considered.

$$\sum_{\lambda} {}_l(\mathbf{k},\varphi|S^{-1}|\mathbf{k},m,\lambda,1)(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\varphi)_j = \lim_{\omega\to\omega_k^{(m)}} (\omega-\omega_k^{(m)})\ddot{G}^{\varphi}_{lj}(\mathbf{k},\omega), \tag{3.40}$$

where the summation on the left-hand side extends to the degenerate sublevels of the branch, characterized by different polarization indexes λ. The above equation relates the matrix elements entering the expansions (3.31) and (3.32) to the Green's function $\ddot{G}^{\varphi}_{lj}(\mathbf{k},\omega)$. The relationship (3.40) will be exploited in the following derivations of the mode expansions.

IV. NORMAL-MODE REPRESENTATION OF THE FIELD OPERATORS

A. Local displacement field

We shall first search for the normal-mode expansion of the operator $\mathbf{d}^{\perp}(\mathbf{r}_{\zeta})$ for the local displacement field. For $k \ll 2\pi/a$, the corresponding Green's function $\ddot{G}^{\varphi}_{lj}(\mathbf{k},\omega)$ (with φ=rad) has been obtained previously [24] giving [31]

$$\ddot{G}^{\mathrm{rad}}_{lj}(\mathbf{k},\omega) = \frac{\rho}{3\hbar\varepsilon_0}\frac{1}{n^2}\left(\frac{n^2+2}{3}\right)^2 \frac{[2(n\omega/c)^2+k^2]\delta_{lj}-3k_lk_j}{(n\omega/c)^2-k^2}, \tag{4.1}$$

where $n \equiv n(\omega)$ is the refractive index,

$$n^2=\varepsilon_r=1+\frac{\alpha\rho/\varepsilon_0}{1-\alpha\rho/3\varepsilon_0}, \tag{4.2}$$

with

$$\alpha\equiv\alpha(\omega)=\alpha(-\omega)=\frac{1}{\hbar}\sum_{\gamma}\left(\frac{\mu_\gamma^2}{\Omega_\gamma-\omega}+\frac{\mu_\gamma^2}{\Omega_\gamma+\omega}\right) \tag{4.3}$$

being the molecular polarizability. The above $\varepsilon_r=\varepsilon/\varepsilon_0$ is the relative dielectric permittivity that apparently satisfies the Clausius-Mossotti relation: This is due to the systematic incorporation of photon umklapp processes into the theory. Note that the effects of the spatial dispersion (dependence of ε_r on k) are beyond the scope of the present study.

Our analysis will concentrate on the transverse normal modes of the system: Only these modes contribute to the operators for the transverse quantized fields under consideration. The corresponding eigenfrequencies are the poles of the Green's function (4.1) at

$$\omega_k^{(m)}=ck/n(\omega_k^{(m)}). \tag{4.4}$$

The graphical solution of Eq. (4.4) is depicted in Fig. 1. It is obvious that more than one normal frequency $\omega_k^{(m)}$ $(m=1,2,\ldots,M_{\mathrm{mol}}+1)$ corresponds to each value of k, M_{mol} being a number of molecular frequencies Ω_γ involved [32]. For instance, the single-frequency (Hopfield) model employed by Knoester and Mukamel [19] and also Ho and Kumar [23], provides two polariton branches. Examples of dispersion curves with various values of M_{mol} are presented in Fig. 2. As the number of molecular frequencies increases, the dispersion branches may start to form dense sets of dispersion curves, as illustrated in Fig. 2(c). Hence, the present theory may accommodate adequately the contributions due to densely spaced molecular sublevels of vibrational, rotational, and other origins.

Substituting Eqs. (4.1) and (4.4) into Eq. (3.40), one finds

$$\sum_{\lambda} {}_l(\mathbf{k},\mathrm{rad}|S^{-1}|\mathbf{k},m,\lambda,1)(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\mathrm{rad})_j=\frac{\rho\omega_k^{(m)}v_g^{(m)}}{2c\varepsilon_0\hbar n(\omega_k^{(m)})}\left[\frac{[n(\omega_k^{(m)})]^2+2}{3}\right]^2(\delta_{lj}-\hat{k}_l\hat{k}_j) \tag{4.5}$$

with $\hat{k}_l=k_l/k$, where

$$v_g^{(m)}=c\left\{\frac{d[\omega n(\omega)]}{d\omega}\right\}^{-1}\Bigg|_{\omega=\omega_k^{(m)}}=\frac{d\omega_k^{(m)}}{dk} \tag{4.6}$$

is the group velocity of polariton in the mth branch of dispersion. Solutions of Eq. (4.5) are characterized by two independent polarization components (λ=1,2) for each eigenfrequency $\omega_k^{(m)}$,

$${}_j(\mathbf{k},\mathrm{rad}|S^{-1}|\mathbf{k},m,\lambda,1)=[(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\mathrm{rad})_j]^*=\left(\frac{\rho\omega_k^{(m)}v_g^{(m)}}{2c\varepsilon_0\hbar n(\omega_k^{(m)})}\right)^{1/2}\left[\frac{[n(\omega_k^{(m)})]^2+2}{3}\right]e_j^{(\lambda)}(\mathbf{k}). \tag{4.7}$$

Here use has been made of the following:

$$\sum_{\lambda=1}^{2} e_l^{(\lambda)}(\mathbf{k})\cdot e_j^{(\lambda)}(\mathbf{k})=(\delta_{lj}-\hat{k}_l\hat{k}_j), \tag{4.8}$$

where the transverse polarization vectors, $\mathbf{e}^{(\lambda)}(\mathbf{k})\perp\mathbf{k}$ (with λ=1,2), have already featured in Eq. (2.3). The explicit mode representation of the local operator $\mathbf{d}^{\perp}(\mathbf{r}_{\zeta})$ is now straightforward. This will be carried out in the summarizing Sec. IV C.

B. Mean displacement and polarization fields

Consider next the mode expansion of the operator $\overline{\mathbf{d}^{\perp}}(\mathbf{r})$ for the averaged (macroscopic) displacement field. The corresponding Green's function $\ddot{G}^{\varphi}_{lj}(\mathbf{k},\omega)$ (with $\varphi=\mathrm{rad}_0$) has been derived in Appendix A, giving

$$\ddot{G}^{\mathrm{rad}_0}_{lj}(\mathbf{k},\omega)=\frac{\rho n^2}{\hbar\varepsilon_0}\frac{k^2\delta_{lj}-k_lk_j}{(n\omega/c)^2-k^2} \tag{4.9}$$

for $k\ll 2\pi/a$. Repeating the procedure outlined above, one finds

$${}_j(\mathbf{k},\mathrm{rad}_0|S^{-1}|\mathbf{k},m,\lambda,1)=[(\mathbf{k},m,\lambda,1|QSQ|\mathbf{k},\mathrm{rad}_0)_j]^*=\left(\frac{\rho\omega_k^{(m)}\nu_g^{(m)}}{2c\varepsilon_0\hbar n(\omega_k^{(m)})}\right)^{1/2}[n(\omega_k^{(m)}]^2e_j^{(\lambda)}(k) \tag{4.10}$$

($\lambda=1,2$), where the phase of the above matrix element has been chosen demanding that the mode expansions for the local and averaged displacement fields [determined by Eqs. (4.10) and (4.7), respectively] should coincide in the limit of an infinitely dilute medium ($n\rightarrow 1$). Finally, to determine the polarization field $\overline{\mathbf{p}^{\perp}}(\mathbf{r})$, Eq. (3.33), we shall make use of the following (see Appendix B):

$${}_j(\mathbf{k},\mathrm{matt}|S^{-1}|\mathbf{k},m,\lambda,1)={}_j(\mathbf{k},\mathrm{rad}|S^{-1}|\mathbf{k},m,\lambda,1)i\hbar\alpha(\omega_k^{(m)}), \tag{4.11}$$

$\alpha(\omega_k^{(m)})$ being the molecular polarizability at $\omega=\omega_k^{(m)}$. The above relates the material matrix element of interest to its radiative counterpart ${}_j(\mathbf{k},\mathrm{rad}|S^{-1}|\mathbf{k},m,\lambda,1)$: The latter has been already obtained in Eq. (4.7).

C. Summary of results on electric, displacement, and polarization fields

Substituting Eqs. (4.7), (4.10), and (4.11) into (3.31)–(3.33), the operators for the displacement and polarization fields take the form

$$\mathbf{d}^{\perp}(\mathbf{r}_\zeta)=i\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\varepsilon_0\hbar\omega_k^{(m)}\nu_g^{(m)}}{2cV_0n(\omega_k^{(m)})}\right)^{1/2}\left[\frac{[n(\omega_k^{(m)})]^2+2}{3}\right]\mathbf{e}^{(\lambda)}(\mathbf{k})(e^{i\mathbf{k}\cdot\mathbf{r}_\zeta}P_{\mathbf{k},m,\lambda}-e^{-i\mathbf{k}\cdot\mathbf{r}_\zeta}P^{\dagger}_{\mathbf{k},m,\lambda}), \tag{4.12}$$

$$\overline{\mathbf{d}^{\perp}}(\mathbf{r})=i\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\varepsilon_0\hbar\omega_k^{(m)}\nu_g^{(m)}}{2cV_0n(\omega_k^{(m)})}\right)^{1/2}[n(\omega_k^{(m)})]^2\mathbf{e}^{(\lambda)}(\mathbf{k})(e^{i\mathbf{k}\cdot\mathbf{r}}P_{\mathbf{k},m,\lambda}-e^{-i\mathbf{k}\cdot\mathbf{r}}P^{\dagger}_{\mathbf{k},m,\lambda}), \tag{4.13}$$

and

$$\overline{\mathbf{p}^{\perp}}(\mathbf{r})=i\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\varepsilon_0\hbar\omega_k^{(m)}\nu_g^{(m)}}{2cV_0n(\omega_k^{(m)})}\right)^{1/2}\{[n(\omega_k^{(m)})]^2-1\}\mathbf{e}^{(\lambda)}(\mathbf{k})(e^{i\mathbf{k}\cdot\mathbf{r}}P_{\mathbf{k},m,\lambda}-e^{-i\mathbf{k}\cdot\mathbf{r}}P^{\dagger}_{\mathbf{k},m,\lambda}), \tag{4.14}$$

where, in the last equation, we have exploited the following relation:

$$\frac{\alpha\rho}{\varepsilon_0}\left(\frac{n^2+2}{3}\right)=n^2-1. \tag{4.15}$$

The above summations over $\mathbf{k}$ extend to $k\ll 2\pi/a$: As discussed earlier, this restriction is fully appropriate for consideration of infrared, optical, and ultraviolet modes of radiation in the condensed molecular systems. The mode expansions manifestly accommodate summations over the branch index m, the emerging refractive index $n(\omega_k^{(m)})$, and group velocity $\nu_g^{(m)}\equiv\nu_g(\omega_k^{(m)})$ being the branch-dependent quantities.

The electric-field operator may now be determined using the general relationship (2.1) between the electric, displacement, and polarization fields, to yield

$$\overline{\mathbf{e}^{\perp}}(\mathbf{r})=i\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\hbar\omega_k^{(m)}\nu_g^{(m)}}{2\varepsilon_0cV_0n(\omega_k^{(m)})}\right)^{1/2}\mathbf{e}^{(\lambda)}(\mathbf{k})(e^{i\mathbf{k}\cdot\mathbf{r}}P_{\mathbf{k},m,\lambda}-e^{-i\mathbf{k}\cdot\mathbf{r}}P^{\dagger}_{\mathbf{k},m,\lambda}), \tag{4.16}$$

which is consistent with the previous result by Ho and Kumar [23] based on the model restricted to two branches ($m=1,2$) of polariton dispersion. Recasting the field operators in terms of ($\mathbf{k}$,m) mode components,

$$\mathbf{d}^{\perp}(\mathbf{r}_\zeta)=\sum_{\mathbf{k},m}\mathbf{d}^{\perp}_{\mathbf{k},m}(\mathbf{r}_\zeta),\quad \overline{\mathbf{d}^{\perp}}(\mathbf{r})=\sum_{\mathbf{k},m}\overline{\mathbf{d}^{\perp}_{\mathbf{k},m}}(\mathbf{r}), \tag{4.17}$$

etc., it is straightforward to find the following relationships between the mode components of various field operators:

$$\mathbf{d}^{\perp}_{\mathbf{k},m}(\mathbf{r}_{\zeta})=\frac{1}{\varepsilon_r^{(m)}}\left(\frac{\varepsilon_r^{(m)}+2}{3}\right)\overline{\mathbf{d}}^{\perp}_{\mathbf{k},m}(\mathbf{r}_{\zeta}), \tag{4.18}$$

$$\overline{\mathbf{d}}^{\perp}_{\mathbf{k},m}(\mathbf{r})=\varepsilon_0\varepsilon_r^{(m)}\overline{\mathbf{e}}^{\perp}_{\mathbf{k},m}(\mathbf{r}), \tag{4.19}$$

$$\overline{\mathbf{p}}^{\perp}_{\mathbf{k},m}(\mathbf{r})=\varepsilon_0(\varepsilon_r^{(m)}-1)\overline{\mathbf{e}}^{\perp}_{\mathbf{k},m}(\mathbf{r}), \tag{4.20}$$

where

$$\varepsilon_r^{(m)}\equiv\varepsilon_r(\omega_k^{(m)})=[n(\omega_k^{(m)})]^2 \tag{4.21}$$

is an abbreviation for the relative dielectric permittivity in the dispersion branch m. Equations (4.18)–(4.20) are apparently the quantum version of the familiar formulas of the classical electrodynamics relating electric, displacement, and polarization fields. It is instructive to note that the branch index m explicitly features in these expressions.

D. Heisenberg representation and magnetic operators

Performing a transformation from the original Schrödinger representation to the Heisenberg representation, the time variable emerges in the field operators. The operators for the electric and displacement fields become then

$$\overline{\mathbf{e}}^{\perp}(\mathbf{r},t)=i\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\hbar\omega_k^{(m)}\nu_g^{(m)}}{2\varepsilon_0 cV_0 n(\omega_k^{(m)})}\right)^{1/2}\mathbf{e}^{(\lambda)}(\mathbf{k})\left(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P_{\mathbf{k},m,\lambda}-e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P^{\dagger}_{\mathbf{k},m,\lambda}\right), \tag{4.22}$$

and

$$\overline{\mathbf{d}}^{\perp}(\mathbf{r},t)=i\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\varepsilon_0\hbar\omega_k^{(m)}\nu_g^{(m)}}{2cV_0 n(\omega_k^{(m)})}\right)^{1/2}[n(\omega_k^{(m)})]^2\mathbf{e}^{(\lambda)}(\mathbf{k})\left(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P_{\mathbf{k},m,\lambda}-e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P^{\dagger}_{\mathbf{k},m,\lambda}\right). \tag{4.23}$$

The mode expansion of the magnetic operators $\overline{\mathbf{h}}^{\perp}(\mathbf{r},t)$ and $\overline{\mathbf{b}}^{\perp}(\mathbf{r},t)$ may now be obtained using the Maxwell equations for the field operators in the Heisenberg representation,

$$\boldsymbol{\nabla}\times\overline{\mathbf{h}}^{\perp}(\mathbf{r},t)=\frac{\partial\overline{\mathbf{d}}^{\perp}(\mathbf{r},t)}{\partial t}, \tag{4.24}$$

$$\boldsymbol{\nabla}\times\overline{\mathbf{e}}^{\perp}(\mathbf{r},t)=-\frac{\partial\overline{\mathbf{b}}^{\perp}(\mathbf{r},t)}{\partial t}. \tag{4.25}$$

The first equation determines the magnetic-field operator as

$$\overline{\mathbf{h}}^{\perp}(\mathbf{r},t)=i\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\hbar\omega_k^{(m)}\nu_g^{(m)}n(\omega_k^{(m)})}{2\mu_0 cV_0}\right)^{1/2}\hat{\mathbf{k}}\times\mathbf{e}^{(\lambda)}(\mathbf{k})\left(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P_{\mathbf{k},m,\lambda}-e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P^{\dagger}_{\mathbf{k},m,\lambda}\right), \tag{4.26}$$

with $\mu_0=1/\varepsilon_0c^2$ being the magnetic permeability of vacuum. The second Maxwell equation defines the magnetic induction vector $\overline{\mathbf{b}}^{\perp}(\mathbf{r},t)$: For the nonmagnetic medium under consideration, we have $\overline{\mathbf{b}}^{\perp}(\mathbf{r},t)=\mu_0\overline{\mathbf{h}}^{\perp}(\mathbf{r},t)$. Finally, the familiar expressions relate the operators for the magnetic induction and electric fields to the vectorial potential, as

$$\overline{\mathbf{b}}^{\perp}=\nabla\times\overline{\mathbf{a}}^{\perp}, \tag{4.27}$$

$$\overline{\mathbf{e}}^{\perp}=-\frac{\partial\overline{\mathbf{a}}^{\perp}}{\partial t}, \tag{4.28}$$

giving the following normal-mode representation for the latter:

$$\overline{\mathbf{a}}^{\perp}(\mathbf{r},t)=\sum_{\mathbf{k}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\hbar\nu_g^{(m)}}{2\varepsilon_0 cV_0\omega_k^{(m)}n(\omega_k^{(m)})}\right)^{1/2}\mathbf{e}^{(\lambda)}(\mathbf{k})\left(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P_{\mathbf{k},m,\lambda}+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k^{(m)}t)}P^{\dagger}_{\mathbf{k},m,\lambda}\right). \tag{4.29}$$

Note, that at $t=0$ the Heisenberg operators reduce to those of the original Schrödinger representation, so that $\overline{\mathbf{h}}^{\perp}(\mathbf{r})=\overline{\mathbf{h}}^{\perp}(\mathbf{r},0)$, $\overline{\mathbf{b}}^{\perp}(\mathbf{r})=\overline{\mathbf{b}}^{\perp}(\mathbf{r},0)$, and $\overline{a}^{\perp}(\mathbf{r})=\overline{a}^{\perp}(\mathbf{r},0)$.

E. Commutation relations between the field operators

The commutation relations between various field operators should be retained recasting the field operators in terms of normal operators for polariton creation and annihilation. To demonstrate this, consider the commutation relation between the averaged operators for the vectorial potential and displacement fields: These two quantities constitute a pair of canonical variables in the multipolar formulation of QED under consideration [28]. The averaged field operators read, in terms of the original Bose operators for photon creation and annihilation,

$$\overline{\mathbf{d}}^{\perp}(\mathbf{r})=i\sum_{\mathbf{k}}\sum_{\lambda=1}^{2}\left(\frac{\hbar ck\varepsilon_0}{2V_0}\right)^{1/2}\mathbf{e}^{(\lambda)}(\mathbf{k})[a^{(\lambda)}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}-a^{\dagger(\lambda)}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}}], \tag{4.30}$$

$$\overline{\mathbf{a}}^{\perp}(\mathbf{r})=\sum_{\mathbf{k}}\sum_{\lambda=1}^{2}\left(\frac{\hbar}{2\varepsilon_0 ckV_0}\right)^{1/2}\mathbf{e}^{(\lambda)}(\mathbf{k})[a^{(\lambda)}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}+a^{\dagger(\lambda)}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}}], \tag{4.31}$$

where the summation over the wave vector is restricted to the first-Brillouin-zone vector $\mathbf{k}$ (with $k\ll 2\pi/a$), as the terms with $\mathbf{G}\neq\mathbf{0}$ disappear during the procedure of averaging over the elementary cell. The following commutation relation is held between the Cartesian components of the averaged operators:

$$[\overline{a_l^{\perp}}(\mathbf{r}),\overline{d_j^{\perp}}(\mathbf{r}')]=-i\hbar\frac{1}{V_0}\sum_{\mathbf{k}}(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \tag{4.32}$$

$$=-i\hbar\,\overline{\delta_{lj}^{\perp}}(\mathbf{r}-\mathbf{r}'). \tag{4.33}$$

Here $\overline{\delta_{lj}^{\perp}}(\mathbf{r}-\mathbf{r}')$ is the smoothened (coarse-grained) transverse δ function that replaces the ordinary transverse δ function,

$$\delta_{lj}^{\perp}(\mathbf{r})=\frac{1}{V_0}\sum_{\mathbf{k},\mathbf{G}}(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{4.34}$$

featuring in the commutation relation [28] between the microscopic (nonaveraged) field operators $a_l^{\perp}(\mathbf{r})$ and $d_j^{\perp}(\mathbf{r}')$.

Next we shall exploit the normal-mode expansions (4.23) and (4.29) for the averaged operators. The equal-time commutation relation then takes the form

$$[\overline{a_l^{\perp}}(\mathbf{r}),\overline{d_j^{\perp}}(\mathbf{r}')]=-i\hbar\frac{1}{cV_0}\sum_{\mathbf{k}}(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\sum_m \nu_g^{(m)}n(\omega_k^{(m)}). \tag{4.35}$$

Employing the equality [22]

$$\sum_m \nu_g^{(m)}n(\omega_k^{(m)})=c, \tag{4.36}$$

the commutation relations (4.32) and (4.35) prove to be identical. This is a consequence of the canonical nature of the transformation from the original set of molecular and radiative Bose operators to the set of normal Bose operators for polaritons.

On a similar basis, one can check other commutation relations. Since [22]

$$\sum_m \nu_g^{(m)}\Big/n(\omega_k^{(m)})=c, \tag{4.37}$$

the equal-time commutator between the averaged fields (4.22) and (4.29) is

$$[\overline{a_l^{\perp}}(\mathbf{r}),\overline{e_j^{\perp}}(\mathbf{r}')]=-i\hbar\frac{1}{\varepsilon_0 cV_0}\sum_{\mathbf{k}}(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\sum_m \nu_g^{(m)}\Big/n(\omega_k^{(m)}) \tag{4.38}$$

$$=-\frac{i\hbar}{\varepsilon_0}\overline{\delta_{lj}^{\perp}}(\mathbf{r}-\mathbf{r}'), \tag{4.39}$$

so that the operators for the vectorial potential and the material polarization field commute, as required

$$[\overline{a_l^{\perp}}(\mathbf{r}),\overline{p_j^{\perp}}(\mathbf{r}')]\equiv[\overline{a_l^{\perp}}(\mathbf{r}),\overline{d_j^{\perp}}(\mathbf{r}')]-[\overline{a_l^{\perp}}(\mathbf{r}),\varepsilon_0\overline{e_j^{\perp}}(\mathbf{r}')]=0. \tag{4.40}$$

It is noteworthy that Eqs. (4.36) and (4.37) represent general relationships, established by Huttner and Barnett [22] utilizing the analytical properties of $\varepsilon_r(\omega) \equiv n^2(\omega)$. On the other hand, demanding now that the commutation relations are to be preserved, one arrives then to the same relationships (4.36) and (4.37), confirming their validity.

V. CONCLUDING REMARKS

Microscopic quantization of radiation has been carried out in a realistic molecular medium, represented by an arbitrary number of energy levels (electronic, vibrational, rotational, etc.) for each molecule of the system. Adopting a polariton model, the field operators have been expanded in terms of normal Bose operators for polariton creation and annihilation. The expansion coefficients have been explicitly derived for the normal modes that are characterized by wavelengths exceeding considerably the characteristic distance a of separation between the molecules constituting the dielectric medium. Accordingly, the formalism applies to the long-wavelength region of the spectrum for which description in terms of the macroscopic refractive index is relevant. The theory has been formulated in a manner that made possible a parallel comparative consideration of operators for both the averaged (macroscopic) fields and also the local displacement field. Consequently, the relationships [given by Eqs. (4.18)–(4.20)] have been established between the mode components of macroscopic and local-field operators: Refractive contributions, including the local-field factors, explicitly feature in these relations. The relationships support some previous attempts to link the amplitudes of local and macroscopic field operators phenomenologically (see, for instance, Refs. [33, 34]) and are consistent with the familiar results of the classical electrodynamics as well.

Equal-time commutation relations have been demonstrated to be preserved, expressing the operators for the averaged fields in terms of the normal Bose operators for polariton creation and annihilation. This is due to the fact that more than one normal frequency $\omega_k^{(m)}$ $(m=1,2,\dots,M_{\mathrm{mol}}+1)$ corresponds to each wave vector k in our field expansions, M_{mol} being the number of molecular frequencies involved. Ignoring any of the $M_{\mathrm{mol}}+1$ dispersion branches would alter the commutation relations leading to violation of microcausality: As discussed earlier [22,23], this happens in the quantization schemes with one-to-one correspondence between the wave vector and the frequency. On the other hand, the commutation relations between the macroscopic fields are of the same form as those for their microscopic counterparts, subject to the coarse-graining procedure. For example, the transverse δ function, featuring in the canonical commutation relation between the microscopic operators for the vectorial potential and the displacement field, is now to be replaced by the course-grained transverse δ function (4.33).

The mode-expansion expansion (4.12) of $\mathbf{d}^{\perp}(\mathbf{r}_\zeta)$ may be applied analyzing various molecule-radiation processes and also field-assisted molecule-molecule process. [It is the operator for the local displacement field $\mathbf{d}^{\perp}(\mathbf{r}_\zeta)$ that describes the coupling of the electromagnetic field with individual molecules ζ.] One may thus arrive quite straightforwardly [25] to the $n[(n^2+2))/3]^2$ refractive modification of the rate of spontaneous emission by a guest molecule embedded in a host molecular dielectric. The result is consistent with the conclusions by previous microscopic QED considerations of spontaneous emission in the condensed phases [19,23], based on one-frequency (two-level) representations for each molecule constituting the dielectric medium. Note that our formalism provides more realistic representation of the host medium, as now an arbitrary number of molecular levels contributes to the refractive index n. Next, addressing the mode expansion (4.12) to the linear absorption, the molecular absorption cross section can be shown [25] to experience the $n^{-1}[(n^2+2)/3]^2$ modification in a dielectric medium. It is to be emphasized that the present theory (like the previous ones [19–23]) deals with the normal modes for which $ka \ll \pi$. Hence, the above consideration of the spontaneous emission (as well as the linear absorption) does not apply to the absorbing areas of the spectrum in which the excitonlike modes with $k \cong \pi/a$ play an important role. Indeed, as demonstrated in Fig. 2(c), absorbing regions of the spectrum are characterized by dense sets of flat excitonlike dispersion curves with vanishing group velocities. Hence, for spontaneous emission within such an absorption region, the polariton modes with large values of k $(k \cong \pi/a)$ may play an important role, as they might be in resonance with the emission frequency. However, these modes have not been accommodated in the present theory concentrating on the modes with $k \ll \pi/a$ for which description in terms of the refractive index n is relevant.

Finally, the time and space evolution of macroscopic field operators can be analyzed utilizing the appropriate normal-mode expansions for the averaged fields. In this way, the present study, giving the normal-mode representations of operators for both the macroscopic (averaged) and local fields, provides a tool for a combined investigation of both propagation of the quantized fields in molecular dielectrics and also the interaction of the fields with the embedded molecules or atoms.

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APPENDIX A: DERIVATION OF THE GREEN'S FUNCTION $\ddot{G}_{lj}^{\mathrm{rad}_0}$

1. Alternative partitioning of the system

The representation (3.8) of the matrix Hamiltonian is based on partitioning of the full system into the material and radiative subsystems. In this Appendix, the full system will be divided in an alternative way into another two subsystems: The first one, denoted by s, will now comprise a material part m coupled to the subspace r_0 of the first-Brillouin-zone photons, the second subsystem r_x consisting of other photons that do not belong to the first Brillouin zone. The full matrix Hamiltonian may be cast then in terms of its components, as

$$h = h_{r_x} + h_s + h_{m-r_x} + h_{r_x-m}, \tag{A1}$$

where h_s is the matrix Hamiltonian for the subsystem s,

$$h_s=h_m+h_{r_0}+h_{m-r_0}+h_{r_0-m}. \qquad \text{(A2)}$$

The remaining new components can also be expressed through the old ones, featured in the original representation (3.8) of the matrix Hamiltonian, as

$$h_{r_0}=I_{r_0}h_rI_{r_0}, \quad h_{r_x}=I_{r_x}h_rI_{r_x}, \qquad \text{(A3)}$$

$$h_{m-r_0}=h_{m-r}I_{r_0}, \quad h_{r_0-m}=I_{r_0}h_{r-m}, \qquad \text{(A4)}$$

$$h_{m-r_x}=h_{m-r}I_{r_x}, \quad h_{r_x-m}=I_{r_x}h_{r-m}, \qquad \text{(A5)}$$

where I_{r_0}, I_{r_x}, and I_m are the following matrices for projection onto the subsystems r_0, r_x, and m, respectively:

$$I_{r_0}=\sum_{\mathbf{k}}\sum_{\lambda=1}^{2}\sum_{i=1}^{2}|\mathbf{k},\mathbf{0},\lambda,i)(\mathbf{k},\mathbf{0},\lambda,i|, \qquad \text{(A6)}$$

$$I_{r_x}=I_r-I_{r_0}=\sum_{\mathbf{k}}\sum_{\mathbf{G}\neq 0}\sum_{\lambda=1}^{2}\sum_{i=1}^{2}|\mathbf{k},\mathbf{G},\lambda,i)(\mathbf{k},\mathbf{G},\lambda,i|, \qquad \text{(A7)}$$

and

$$I_m=\sum_{\mathbf{k},\gamma}\sum_{\lambda'=1}^{3}\sum_{i=1}^{2}|\mathbf{k},\gamma,\lambda',i)(\mathbf{k},\gamma,\lambda',i|. \qquad \text{(A8)}$$

The matrix for projection onto the subsystem s is then

$$I_s=I_{r_0}+I_m. \qquad \text{(A9)}$$

In this way, the terms h_{m-r_x} and h_{r_x-m} for the interaction between the two subsystems, s and r_x, have been defined by Eqs. (A.5) excluding the contributions by the non-first-Brillouin-zone photons from the original interaction matrices h_{m-r} and h_{r-m}. The excluded terms h_{m-r_0} and h_{r_0-m} have been incorporated into the Hamiltonian h_s. Accordingly, the matrix Hamiltonian splits naturally into the zero-order Hamiltonian $h^{0\prime}$ and the interaction matrix ν', as

$$h=h^{0\prime}+\nu', \qquad \text{(A10)}$$

with

$$h^{0\prime}=h_s+h_{r_x}, \qquad \text{(A11)}$$

and

$$\nu'=h_{r_x-m}+h_{m-r_x}, \qquad \text{(A12)}$$

where the primes refer to the alternative partitioning of the full system.

2. Effective Dyson equation for the subsystem *s* and its formal solution

The Dyson equation may now be written for the Green's matrix (3.39) of the partitioned matrix Hamiltonian (A10),

$$\ddot{G}=\ddot{G}^{0\prime}+\ddot{G}^{0\prime}\nu'\ddot{G}, \qquad \text{(A13)}$$

with

$$\ddot{G}^{0\prime}\equiv\ddot{G}^{0\prime}(\omega)=[\omega Q-h^{0\prime}]^{-1} \qquad \text{(A14)}$$

being the zero-order Green's matrix: The prime over $\ddot{G}^{0\prime}$ will help to differentiate it from the ordinary zero-order Green's matrix,

$$\begin{aligned}\ddot{G}^{0}\equiv\ddot{G}^{0}(\omega)&=[\omega Q-(h_m+h_r)]^{-1}\\&=[\omega Q-(h_m+h_{r_0}+h_{r_x})]^{-1},\end{aligned} \qquad \text{(A15)}$$

that will feature later in Eq. (A30). Note that unlike $\ddot{G}^{0}$, the primed Green's matrix $\ddot{G}^{0\prime}$ accommodates the coupling terms h_{m-r_0} and h_{r_0-m}, featured in Eq. (A2).

Recursive substitution of the left-hand side of the Dyson equation (A.13) into its right-hand side with subsequent projection onto the subsystem s, produces a Dyson-type equation for the projected Green's function $\ddot{G}_s\equiv I_s\ddot{G}I_s$,

$$\ddot{G}_s=\ddot{G}_s^{0\prime}+\ddot{G}_s^{0\prime}\nu_m^{\mathrm{eff}}\ddot{G}_s, \qquad \text{(A16)}$$

where

$$\nu_m^{\mathrm{eff}}=h_{m-r_x}\ddot{G}^{0\prime}h_{r_x-m} \qquad \text{(A17)}$$

$$=\sum_{\mathbf{k}}\sum_{l=1}^{3}\sum_{j=1}^{3}|\mathbf{k},\mathrm{matt})_{ll}(\mathbf{k},\mathrm{rad}|I_{r_x}\ddot{G}^{0\prime}I_{r_x}|\mathbf{k},\mathrm{rad})_{jj}(\mathbf{k},\mathrm{matt}| \qquad \text{(A18)}$$

is the operator for the effective interaction within the subsystem s due to the influences of the subsystem x. In Eq. (A18), use has been made of Eqs. (A5), (3.11), and (3.12) to explicitly represent the coupling matrices h_{m-r_x}, and h_{r_x-m}. Since

$$I_{r_x}\ddot{G}^{0\prime}I_{r_x}=I_{r_x}\ddot{G}^{0}I_{r_x}, \qquad \text{(A19)}$$

the radiative Green's function entering Eq. (A18) is

$${}_l(\mathbf{k},\mathrm{rad}|I_{r_x}\ddot{G}^{0\prime}I_{r_x}|\mathbf{k},\mathrm{rad})_j=\frac{\rho}{\varepsilon_0\hbar}\sum_{\mathbf{G}\neq 0}\frac{|\mathbf{k}+\mathbf{G}|^2\delta_{lj}-(\mathbf{k}+\mathbf{G})_l(\mathbf{k}+\mathbf{G})_j}{(\omega/c)^2-|\mathbf{k}+\mathbf{G}|^2}, \qquad \text{(A20)}$$

where the contribution by the $\mathbf{G}=\mathbf{0}$ term has been excluded due to the matrix I_{r_x} projecting the radiative matrix vector $|\mathbf{k},\mathrm{rad})_j$ [given by Eq. (3.14)] onto the subspace r_x. Performing summation over the inverse lattice vector $\mathbf{G}$ [19,24], Eq. (A20) takes the form for $k \ll G$,

$$ {}_l(\mathbf{k},\mathrm{rad}\,|I_{r_x}\ddot{G}^{0\prime}I_{r_x}|\mathbf{k},\mathrm{rad})_j=\frac{\rho}{3\varepsilon_0\hbar}\,\frac{[2(\omega/c)^2+k^2]\delta_{lj}-3k_lk_j}{(\omega/c)^2-k^2}-\frac{\rho}{\varepsilon_0\hbar}\,\frac{k^2\delta_{lj}-k_lk_j}{(\omega/c)^2-k^2}=\frac{2}{3}\,\frac{\rho}{\varepsilon_0\hbar}\,\delta_{lj}. \tag{A21}$$

Substituting Eq. (A21) into (A18), one finds a final expression for the matrix ν_m^{eff},

$$\nu_m^{\mathrm{eff}}=\frac{2}{3}\,\frac{\rho}{\varepsilon_0\hbar}\sum_{\mathbf{k}}\sum_{j=1}^{3}|\mathbf{k},\mathrm{matt})_{jj}(\mathbf{k},\mathrm{matt}|, \tag{A22}$$

so that the effective Dyson equation (A16) for the subsystem s has now been fully determined. Its formal solution reads

$$\ddot{G}_s\equiv\ddot{G}_s(\omega)=[\omega QI_s-h_s^{\mathrm{eff}}]^{-1}, \tag{A23}$$

where h_s^{eff} is the effective Hamiltonian for the subsystem s,

$$h_s^{\mathrm{eff}}=h_s^{\mathrm{eff}^0}+(h_{m-r_0}+h_{r_0-m}) \tag{A24}$$

and

$$h_s^{\mathrm{eff}^0}=(h_m+\nu_m^{\mathrm{eff}})+h_{r_0}. \tag{A25}$$

In this way, the coupling of the subsystem s with the high-frequency (non-first-Brillouin zone) photons has been described in an effective manner through the operator ν_m^{eff}. Retention of this operator is essential for a proper description of the local-field effects.

3. Green's matrix for the radiative subspace r_0

The effective Hamiltonian h_s^{eff} of the system s has been partitioned by Eq. (A24) into the zero-order effective Hamiltonian $h_s^{\mathrm{eff}^0}$ and the interaction term $(h_{m-r_0}+h_{r_0-m})$: The latter term represents coupling of the material part of the subsystem s to the subspace r_0 of the first-Brillouin-zone photons. The material subsystem may now be excluded applying a procedure analogous to that outlined in the previous subsection eliminating the subspace r_x. As a result, the following effective Dyson equation is obtained for the projected Green's matrix $\ddot{G}_{r_0}$,

$$\ddot{G}_{r_0}=\ddot{G}_{r_0}^{0}+\ddot{G}_{r_0}^{0}(h_{r_0-m}\ddot{G}_m^{\mathrm{eff}^0}h_{m-r_0})\ddot{G}_{r_0}, \tag{A26}$$

where

$$\ddot{G}_{r_0}^{0}=[\omega QI_{r_0}-h_{r_0}]^{-1} \tag{A27}$$

is the zero-order Green's matrix for the radiative subsystem, and

$$\ddot{G}_m^{\mathrm{eff}^0}=[\omega QI_m-h_m-\nu_m^{\mathrm{eff}}]^{-1} \tag{A28}$$

is the zero-order effective Green's matrix for the material subsystem. Substituting Eqs. (A4), (A6), (3.11)–(3.14) and (3.34) into Eq. (A26), one finds a closed equation for the radiative Green's function $\ddot{G}_{lj}^{\mathrm{rad}_0}(\mathbf{k},\omega)\equiv{}_l(\mathbf{k},\mathrm{rad}_0|\ddot{G}_{r_0}|\mathbf{k},\mathrm{rad}_0)_j$,

$$\ddot{G}_{lj}^{\mathrm{rad}_0}(\mathbf{k},\omega)=\ddot{G}_{lj}^{0}(\mathbf{k},\omega)+\sum_{p=1}^{3}\sum_{q=1}^{3}\ddot{G}_{lp}^{0}(\mathbf{k},\omega)\,{}_p(\mathbf{k},\mathrm{matt}|\ddot{G}_m^{\mathrm{eff}^0}|\mathbf{k},\mathrm{matt})_q\,\ddot{G}_{qj}^{\mathrm{rad}_0}(\mathbf{k},\omega). \tag{A29}$$

$\ddot{G}_{lj}^{0}(\mathbf{k},\omega)$ being the zero-order Green's function for the subsystem r_0,

$$\ddot{G}_{lj}^{0}(\mathbf{k},\omega)\equiv{}_l(\mathbf{k},\mathrm{rad}_0|\ddot{G}_{r_0}^{0}|\mathbf{k},\mathrm{rad}_0)_j=\frac{\rho}{\varepsilon_0\hbar}\,\frac{k^2\delta_{lj}-k_lk_j}{(\omega/c)^2-k^2}. \tag{A30}$$

To make further progress, the material Green's function ${}_p(\mathbf{k},\mathrm{matt}|\ddot{G}_m^{\mathrm{eff}^0}|\mathbf{k},\mathrm{matt})_q$ is to be determined. The following effective Dyson equation holds for the Green's matrix (A28):

$$\ddot{G}_m^{\mathrm{eff}^0}=\ddot{G}_m^{0}+\ddot{G}_m^{0}\nu_m^{\mathrm{eff}}\ddot{G}_m^{\mathrm{eff}^0}, \tag{A31}$$

with

$$\ddot{G}_m^{0}=[\omega QI_m-h_m]^{-1}. \tag{A32}$$

Substituting Eq. (A22) for ν_m^{eff} into Eq. (A31), one obtains

$$ {}_l(\mathbf{k},\mathrm{matt}|\ddot{G}_m^{\mathrm{eff}^0}|\mathbf{k},\mathrm{matt})_j=-\hbar\alpha\delta_{lj}-\frac{2}{3}\,\frac{\alpha\rho}{\varepsilon_0}\,{}_l(\mathbf{k},\mathrm{matt}|\ddot{G}_m^{\mathrm{eff}^0}|\mathbf{k},\mathrm{matt})_j, \tag{A33}$$

where use has been made of the following:

$$ {}_l(\mathbf{k},\mathrm{matt}|\ddot{G}_m^{0}|\mathbf{k},\mathrm{matt})_j=-\hbar\alpha(\omega)\delta_{lj}, \tag{A34}$$

with $\alpha(\omega)\equiv\alpha$ being the molecular polarizability given by Eq. (4.3). Hence,

$$ {}_l(\mathbf{k},\text{matt}|\ddot{G}_m^{\text{eff}^0}|\mathbf{k},\text{matt})_j = -\hbar\alpha'\delta_{lj}, \tag{A35}$$

with

$$\alpha' = \alpha\left(1+\frac{2}{3}\frac{\alpha\rho}{\varepsilon_0}\right)^{-1}. \tag{A36}$$

Substituting Eq. (A35) into Eq. (A29), the formal solution of the resulting equation reads

$$\ddot{G}_{lj}^{\text{rad}_0}(\mathbf{k},\omega) = (\hbar\alpha')^{-1}\{\delta_{lj} - [\mathbf{1}+\hbar\alpha'\ddot{G}^0(\mathbf{k},\omega)]_{lj}^{-1}\}, \tag{A37}$$

where $\ddot{G}^0(\mathbf{k},\omega)$ is the abbreviation for the 3×3 matrix given by Eq. (A30). Inverting the matrix in the square brackets yields

$$[\mathbf{1}+\hbar\alpha'\ddot{G}^0(\mathbf{k})]_{lj}^{-1} = \frac{[(\omega/c)^2-k^2]\delta_{lj}-k_lk_j\alpha'\rho/\varepsilon_0}{(\omega/c)^2-k^2(1-\alpha'\rho/\varepsilon_0)}. \tag{A38}$$

Finally, substituting the last result into Eq. (A37) and using the identity for the refractive index (4.2),

$$n^{-2}=1-\alpha'\rho/\varepsilon_0, \tag{A39}$$

one arrives to the required result (4.9) for the Green's function $\ddot{G}_{lj}^{\text{rad}_0}$.

APPENDIX B: RELATIONSHIP BETWEEN THE MATERIAL AND RADIATIVE MATRIX ELEMENTS

Combining the basic equations for diagonalization (3.23) and (3.24), it follows that

$$hS^{-1}=QS^{-1}Q\Lambda. \tag{B1}$$

Multiplying Eq. (B1) on the right by $|\sigma',1\rangle$ and making use of Eqs. (3.22) and (3.25), one has

$$(Q\Pi_\sigma-h)S^{-1}|\sigma,1)=0. \tag{B2}$$

Employing the partitioning (3.8) for the matrix Hamiltonian h, Eq. (B2) may be rewritten as

$$S^{-1}|\sigma,1)=\ddot{G}^0(\Pi_\sigma)(h_{m-r}+h_{r-m})S^{-1}|\sigma,1), \tag{B3}$$

where $\ddot{G}^0(\Pi_\sigma)$ is the zero-order Green's matrix given by Eq. (A15). Accordingly,

$$\begin{aligned}&{}_j(\mathbf{k},\text{matt}|S^{-1}|\sigma,1)\\&\quad=-i\sum_{l=1}^{3}{}_j(\mathbf{k},\text{matt}|\ddot{G}_m^0(\Pi_\sigma)|\mathbf{k},\text{matt})_l\,{}_l(\mathbf{k},\text{rad}|S^{-1}|\sigma,1),\end{aligned} \tag{B4}$$

where use has been made of Eq. (3.11) for h_{m-r}. Using Eq. (A34), one finds

$${}_j(\mathbf{k},\text{matt}|S^{-1}|\sigma,1)=i\hbar\alpha(\Pi_\sigma)\,{}_j(\mathbf{k},\text{rad}|S^{-1}|\sigma,1). \tag{B5}$$

Finally, since $\sigma\equiv(\mathbf{k},m,\lambda)$ and $\Pi_\sigma\equiv\omega_k^{(m)}$, the above is equivalent to Eq. (4.11) of the main text.

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[30] At this stage, the Bose approximation has been adopted for the molecular creation and annihilation operators, replacing the exact Pauli commutation rules by those of the Bose type. This is a common approach (see, e.g., Refs. [19, 24]), producing a good model representation for three-dimensional molecular systems at relatively low occupation numbers of molecular modes. Accordingly, the medium is considered to be linear. Such a linear approximation has been also utilized in the previous theories [19–23] on the microscopic quantization of radiation in dielectrics.

[31] In Eq. (4.1) we disregard the constant (**k**-independent) term featured in Eq. (B8) of Ref. [24]. This term, associated with energy shift, is not important for the present purposes.

[32] The dispersion relation (4.4) does not cover the polariton branches with extremely high frequencies. These branches, ranging in the areas of photon umklapp frequencies cG (with $G \neq 0$), are well above the frequencies of infrared, optical, or ultraviolet modes of interest and hence are beyond the scope of the present study.

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