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Excitation Spectrum of Interacting Polaritons in Dielectric Crystals*

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The excitation spectrum of interacting polariton waves in the infrared region of frequencies of dielectric crystals has been studied using the double-time Green's-function method. The Dyson equation describing the spectrum of interacting polariton fields is derived in a general form, and then the polarization operator and the polariton Green's function are evaluated in two successive approximations. Use has been made of two "equivalent" renormalized Hamiltonian representations, which are correct in the lowest and first approximations, respectively. The polariton Green's function is expressed, in the second approximation, in terms of the renormalized polariton frequencies, where the frequency of each polariton mode contains anharmonic corrections to all orders. Expressions are developed for the frequency shift and spectral width of the fundamental absorption bands. It is shown that the renormalization of the polariton frequencies directly affects the temperature dependence of the frequency shift and width of the infrared absorption bands. The retardation effects reduce the magnitudes of the anharmonic coupling functions. In the region of wave vectors where retardation may be neglected, the phonon excitation spectrum has been considered and compared with the results derived from previous studies.

I. INTRODUCTION

In the infrared range of frequencies of dielectric crystals, polaritons are defined as quasiparticles which consist of long wavelength transverse photons dressed by the harmonic field of optical phonons, and they propagate in the medium with energies and wave vectors that satisfy the linear Maxwell equations.[1] Mathematically, polaritons are elementary excitations which satisfy dispersion relations derived from the exact diagonalization of the Hamiltonian that consists of the harmonic Hamiltonians corresponding to the optical phonon and transverse electromagnetic field, respectively, plus the interaction between them in the zero approximation, i.e., when scattering processes[2] due to phonon-photon interactions are neglected. The diagonalization can be done by means of either a canonical transformation[3] or the Green's function method.[4] Since the total Hamiltonian consists of the lattice Hamiltonian plus the phonon-photon interaction Hamiltonian, the theory of polaritons is equivalent to considering retardation effects in lattice dynamics.[4–6] We refer to the review article by Kwok[4] for the discussion on retardation effects in the harmonic approximation. The existence of polaritons has been demonstrated by Henry and Hopfield[7] through Raman scattering experiments on GaP.

The propagation of polariton modes in the medium is damped. In pure crystals and at finite temperatures, the damping is mainly due to the polariton-polariton interactions. Burstein *et al.*[8] have recently presented a theory of Raman scattering by polaritons. They introduced a phenomenological dispersion relation for the polariton spectrum and pointed out that the damping constant is the inverse of the lifetime of the transverse optical phonons. This hypothesis is not justifiable, because in the range of wave vectors were retardation effects are important only polariton modes exist and not optical phonons; therefore, the lifetime of polaritons may differ considerably from that of optical phonons.

In the present study, an attempt is made to develop a general microscopic theory regarding the excitation spectrum of interacting polaritons in dielectric crystals. The expression for the total polariton Hamiltonian is developed in Sec. II consisting of the harmonic and anharmonic parts with respect to the polariton operators which describe the polariton-polariton interactions. Using the polariton Hamiltonian, the Dyson equation for the polariton spectrum is derived in Sec. III by considering the equations of motion for the polariton Green's function with respect to both time arguments. The expression for the polarization operator is found to have two kinds of terms: The first group consists of the sum of terms linear with respect to the anharmonic coupling functions multiplied by the average values of commutators involving polariton operators with equal-time arguments. The second group is composed of a series of terms which are quadratic with respect to the anharmonic coupling functions and they are proportional to two-, three-, and many-polariton Green's functions.

The polarization operator and, hence, the polariton Green's function are evaluated in two successive approximations by means of constructed equivalent renormalized Hamiltonians which are correct in the lowest

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and first approximation, respectively. In the first approximation the polariton Green's function is expressed in terms of the frequencies for the polariton modes which are only partly renormalized, while in the second approximation, the frequencies for the polariton modes are correct to the second order. In this case, the frequency of each polariton mode in the new representation includes anharmonic corrections to all orders and the resulting elementary excitation may be called the "dressed" or the "physical polariton." In the limiting case where retardation effects may be neglected, the expression for the polarization operator is reduced to that for the bare phonon spectrum and is compared with those derived by Wehner[9] and Kowk.[4]

The polariton excitation spectrum is discussed in Sec. IV by considering the expression for the spectral representation. In the transparent range of frequencies for the crystal expressions for the scattering amplitudes are derived which describe all the possible polariton-polariton scattering processes. Formulas are developed for the frequency shift and spectral width of the fundamental absorption bands. It is found that one of the effects arising from the renormalization of the frequency modes is to change the temperature dependence for the polariton and, consequently, the phonon excitation spectrum. Comparison has been made with those results derived for the phonon spectrum by means of diagram techniques.[10] In general, retardation effects are found to reduce the magnitudes of the anharmonic coupling functions; rough estimates indicate that, for example, the square of the cubic and quartic anharmonic functions, $|V_3|^2$ and $|V_4|^2$, can be reduced by as much as 12 and 6%, respectively, owing to retardation. The actual effects on the excitation spectrum arising from the renormalization of the frequency modes as well as the effects due to retardation can be established only by direct computation of the quantities in question; this will be the subject of a later publication.

II. POLARITON HAMILTONIAN

The Hamiltonian of the coupled system, crystal plus radiation, can be written in the form

$$\mathcal{H}=\mathcal{H}_l+\mathcal{H}_\gamma+\mathcal{H}_{l\gamma}, \tag{1}$$

where the lattice Hamiltonian, in terms of phonon annihilation and creation operators, is known to be[10]

$$\begin{aligned}\mathcal{H}_l=&\sum_{\mathbf{k}j}\omega_{\mathbf{k}j}{}^0(a_{\mathbf{k}j}{}^\dagger a_{\mathbf{k}j}+\tfrac{1}{2})\\&+\sum_{n=3}^{\infty}\sum_{\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_nj_n}V_n(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_nj_n)\\&\times(a_{\mathbf{k}_1j_1}+a_{-\mathbf{k}_1j_1}{}^\dagger)\cdots(a_{\mathbf{k}_nj_n}+a_{-\mathbf{k}_nj_n}{}^\dagger).\end{aligned} \tag{2}$$

In (2), the first term describes the Hamiltonian of the free phonon assembly, and the remaining terms describe the interactions between them. $\omega_k{}^0$ is the energy of the bare phonon of wave vector $\mathbf{k}$ and polarization j. We use $\hbar=1$ throughout. The Hamiltonian for the radiation field is[3]

$$\mathcal{H}_\gamma=\sum_{\mathbf{k}\lambda}ckb_{\mathbf{k}\lambda}{}^\dagger b_{\mathbf{k}\lambda}, \tag{3}$$

where $b_{\mathbf{k}\lambda}$ and $b_{\mathbf{k}\lambda}{}^\dagger$ are the annihilation and creation operators for the bare photon of momentum $\mathbf{k}$ and transverse polarization λ $(=1, 2)$; c denotes velocity of light in vacuum. The interaction Hamiltonian due to the electromagnetic field can be represented as[2]

$$\mathcal{H}_{l\gamma}=\sum_{l\kappa}\frac{Z_\kappa}{M_\kappa c}\mathbf{A}(\mathbf{R}(l,\kappa))\cdot\mathbf{p}(l,\kappa)+\sum_{l\kappa}\frac{Z_\kappa{}^2}{2M_\kappa c^2}A^2(\mathbf{R}(l,\kappa)), \tag{4}$$

where $\mathbf{A}(\mathbf{R}(l,\kappa))$ is the vector potential of the electromagnetic field evaluated at the instantaneous position

$$\mathbf{R}(l,\kappa)=\mathbf{X}(l,\kappa)+\mathbf{U}(l,\kappa)=\mathbf{X}(\kappa)+\mathbf{X}(l)+\mathbf{U}(l,\kappa). \tag{5}$$

Here, $\mathbf{X}(l,\kappa)$ is the equilibrium position of the κth ion in the lth unit cell, $\mathbf{U}(l,\kappa)$ is the displacement from the equilibrium position, and Z_κ is the effective charge of the κth ion. We consider N unit cells in volume V, and there are r atoms per unit cell. The displacement, momentum amplitude, and vector potential can be expressed in the second-quantized representation, respectively, as[10,3]

$$\mathbf{U}(l,\kappa)=\left(\frac{1}{2M_\kappa N}\right)^{1/2}\sum_{\mathbf{k}j}\frac{\mathbf{e}(\kappa|\mathbf{k}j)}{(\omega_{\mathbf{k}j}{}^0)^{1/2}}(a_{\mathbf{k}j}+a_{-\mathbf{k}j}{}^\dagger)e^{i\mathbf{k}\cdot\mathbf{X}(l)}, \tag{6a}$$

$$\begin{aligned}\mathbf{p}(l,\kappa)=\frac{1}{i}\left(\frac{M_\kappa}{2N}\right)^{1/2}&\sum_{\mathbf{k}j}\mathbf{e}(\kappa|\mathbf{k}j)(\omega_{\mathbf{k}j}{}^0)^{1/2}\\&\times(a_{\mathbf{k}j}-a_{-\mathbf{k}j}{}^\dagger)e^{i\mathbf{k}\cdot\mathbf{X}(l)},\end{aligned} \tag{6b}$$

and

$$\mathbf{A}(\mathbf{R}(l,\kappa))=\sum_{\mathbf{k}\lambda}\left(\frac{2\pi c^2}{Vck}\right)^{1/2}\boldsymbol{\xi}(\mathbf{k}\lambda)(b_{\mathbf{k}\lambda}+b_{-\mathbf{k}\lambda}{}^\dagger)e^{i\mathbf{k}\cdot\mathbf{R}(l,\kappa)}. \tag{6c}$$

In Eq. (6), $\mathbf{e}(\kappa|\mathbf{k}j)$ is the polarization vector for the phonons and satisfies the usual orthonormality and closure relations; $\boldsymbol{\xi}(\mathbf{k}\lambda)$ denotes the unit photon polarization vector. We substitute the expression for $\mathbf{R}(l,\kappa)$ from Eq. (5) into (6c) and expand the exponential in powers of the displacement amplitude $\mathbf{U}(l,\kappa)$ from the equilibrium position $\mathbf{X}(l,\kappa)$. The first term in this expansion corresponds to the usual long wavelength approximation, i.e., the vector potential is evaluated at the equilibrium position. In this approximation, the interaction Hamiltonian (4) can be easily expressed in the form

$$\begin{aligned}\mathcal{H}_{l\gamma}{}^0=&\frac{\omega_p{}^2}{4}\sum_{\mathbf{k}\lambda}\frac{1}{ck}(b_{\mathbf{k}\lambda}+b_{-\mathbf{k}\lambda}{}^\dagger)(b_{\mathbf{k}\lambda}{}^\dagger+b_{-\mathbf{k}\lambda})\\&-\frac{i}{2}\sum_{\mathbf{k},j,\lambda}\left(\frac{\omega_{\mathbf{k}j}{}^0}{kc}\right)^{1/2}x_j(\mathbf{k}\lambda)(b_{\mathbf{k}\lambda}{}^\dagger+b_{-\mathbf{k}\lambda})(a_{\mathbf{k}j}-a_{-\mathbf{k}j}{}^\dagger),\end{aligned} \tag{7}$$

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where the coupling constant $x_j(\mathbf{k}\lambda)$ is expressed as

$$x_j(\mathbf{k}\lambda)=\left(\frac{4\pi N}{V}\right)^{1/2}\sum_{\kappa=1}^{r}\frac{Z_\kappa}{\sqrt{M_\kappa}}\times e^{-i\mathbf{k}\cdot\mathbf{X}(\kappa)}[\mathbf{e}(\kappa|\mathbf{k}j)\cdot\boldsymbol{\xi}(\mathbf{k}\lambda)], \quad (8)$$

from which it follows that photons interact only with the transverse optical phonons. It is easy to see that the plasma frequency of the ions satisfies the relation

$$\omega_p^2=\frac{4\pi N}{V}\sum_\kappa\frac{Z_\kappa^2}{M_\kappa}=\sum_j|x_j(\mathbf{k}\lambda)|^2. \quad (9)$$

The higher-order terms arising from the interaction Hamiltonian (4) can be written in the general form

$$\mathcal{H}_{l\gamma}'=-\sum_{n=3}^{\infty}\sum_{\mathbf{q}\lambda,\mathbf{k}_1j_1,\cdots,\mathbf{k}_{n-1}j_{n-1}}\phi_n(\mathbf{q}\lambda,\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_{n-1}j_{n-1})(b_{\mathbf{q}\lambda}+b_{-\mathbf{q}\lambda}^\dagger)(a_{\mathbf{k}_1j_1}-a_{-\mathbf{k}_1j_1}^\dagger)(a_{\mathbf{k}_2j_2}+a_{-\mathbf{k}_2j_2}^\dagger)\cdots$$
$$\times(a_{\mathbf{k}_{n-1}j_{n-1}}+\mathbf{a}^\dagger_{\mathbf{k}_{n-1}j_{n-1}})+\sum_{n=3}^{\infty}\sum_{\substack{\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2\\ \mathbf{k}_3j_3,\cdots,\mathbf{k}_{n4_2}j_{n4_2}}}g_n(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,\mathbf{k}_3j_3,\cdots,\mathbf{k}_{n-2}j_{n-2})$$
$$\times(b_{\mathbf{q}_1\lambda_1}+b_{-\mathbf{q}_1\lambda_1}^\dagger)(b_{\mathbf{q}_2\lambda_2}+b_{-\mathbf{q}_2\lambda_2}^\dagger)(a_{\mathbf{k}_3j_3}+a_{-\mathbf{k}_3j_3}^\dagger)(\cdots a_{\mathbf{k}_{n-2}j_{n-2}}+a_{-\mathbf{k}_{n-2}j_{n-2}}^\dagger), \quad (10a)$$

where the coupling functions $\phi_n(\mathbf{q}\lambda,\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_{n-1}j_{n-1})$ and $g_n(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,\mathbf{k}_3j_3,\cdots,\mathbf{k}_{n-2}j_{n-2})$ result from terms in the expression (4) which are linear and quadratic with respect to the vector potential, respectively, and are equal to

$$\phi_n(\mathbf{q}\lambda,\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_{n-1}j_{n-1})=i\sum_\kappa\left(\frac{\pi Z_\kappa^2N}{M_\kappa V}\right)^{1/2}e^{i\mathbf{q}\cdot\mathbf{X}(\kappa)}[\boldsymbol{\xi}(\mathbf{q}\lambda)\cdot\mathbf{e}(\kappa|\mathbf{k}_1j_1)][\mathbf{q}\cdot\mathbf{e}(\kappa|\mathbf{k}_1j_1)]\cdots[\mathbf{q}\cdot\mathbf{e}(\kappa|\mathbf{k}_{n-1}j_{n-1})]$$
$$\times\frac{(i)^{n-2}}{(n-2)!}(2M_\kappa N)^{-(n-2)/2}(\omega_{\mathbf{k}_1j_1}{}^0)^{1/2}(cq\omega_{\mathbf{k}_2j_2}{}^0\omega_{\mathbf{k}_3j_3}{}^0\cdots\omega_{\mathbf{k}_{n-1}j_{n-1}}{}^0)^{-1/2}\boldsymbol{\Delta}(\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2+\cdots+\mathbf{k}_{n-1}), \quad (10b)$$

$$g_n(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,\mathbf{k}_3j_3,\cdots,\mathbf{k}_{n-2}j_{n-2})=\sum_\kappa\left(\frac{Z_\kappa^2N}{2M_\kappa c}\right)e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{X}(\kappa)}[\boldsymbol{\xi}(\mathbf{q}_1\lambda_1)\cdot\boldsymbol{\xi}(\mathbf{q}_2\lambda_2)]$$
$$\times\left(\frac{4\pi^2Z_\kappa^2}{V^2\mathbf{q}_1\mathbf{q}_2}\right)^{1/2}\frac{(i)^{n-2}}{(n-2)!}(2M_\kappa N)^{-(n-2)/2}(\omega_{\mathbf{k}_3j_3}{}^0\omega_{\mathbf{k}_4j_4}{}^0\cdots\omega^0{}_{\mathbf{k}_{n-2}j_{n-2}})^{-1/2}[(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{e}(\kappa|k_3j_3)]\cdots$$
$$\times[(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{e}(\kappa|\mathbf{k}_{n-2}j_{n-2})]\boldsymbol{\Delta}(\mathbf{q}_1+\mathbf{q}_2+\mathbf{k}_3+\mathbf{k}_4+\cdots+\mathbf{k}_{n-2}). \quad (10c)$$

The interaction Hamiltonian (10a) describes all the possible photon-phonon scattering processes. The function $\boldsymbol{\Delta}(\mathbf{k})$ appearing in (10) is equal to unity when $\mathbf{k}$ is equal to a reciprocal-lattice vector, and vanishes otherwise.

It is now well known that the quadratic parts of the Hamiltonian can be diagonalized with a canonical transformation to exhibit the independent polariton modes. Hence we diagonalize the Hamiltonian consisting of the harmonic parts of (2) and (3) for the lattice and the radiation field, respectively, plus the interaction between them, (7), by using the canonical transformation[3]

$$a_{\mathbf{k}j}=\sum_\rho[u_j(\mathbf{k}\rho)\alpha_{\mathbf{k}\rho}+v_j^*(-\mathbf{k}\rho)\alpha_{-\mathbf{k}\rho}{}^\dagger] \quad (11a)$$

and

$$b_{\mathbf{k}\lambda}=\sum_\rho[u_\lambda(\mathbf{k}\rho)\alpha_{\mathbf{k}\rho}+v_\lambda^*(-\mathbf{k}\rho)\alpha_{-\mathbf{k}\rho}{}^\dagger], \quad (11b)$$

where u_j, v_j, and u_λ, v_λ are the transformation amplitudes for phonons and photons, respectively, and are determined by solving a set of four simultaneous equations; ρ designates the polariton bands. In the long-wavelength approximation the Hamiltonian is now expressed in the polariton representation as

$$\mathcal{H}_0=\text{const}+\sum_{\mathbf{k}\rho}\omega_{\mathbf{k}\rho}\alpha_{\mathbf{k}\rho}{}^\dagger\alpha_{\mathbf{k}\rho}, \quad (12)$$

where $\omega_{\mathbf{k}\rho}$ are the energies of excitation derived from the solutions of Maxwell's equations

$$c^2k^2=\omega_{\mathbf{k}\rho}{}^2\tilde{\epsilon}(\mathbf{k},\omega_{\mathbf{k}\rho}), \quad (13a)$$

$$\tilde{\epsilon}(\mathbf{k},\omega_{\mathbf{k}\rho})=1+\sum_j\frac{|x_j(\mathbf{k})|^2}{(\omega_{\mathbf{k}j}{}^0)^2-\omega_{\mathbf{k}\rho}{}^2}. \quad (13b)$$

The polariton operators $\alpha_{\mathbf{k}\rho}{}^\dagger$ and $\alpha_{\mathbf{k}\rho}$ satisfy Bose commutation relations, while the summation in (13b) is over those phonon branches which interact with the photons of the electromagnetic field. Because of the presence of anharmonicity both in the expression for the lattice Hamiltonian as well as in that for the coupled photon-phonon field, polaritons are no longer independent but interact with each other. To derive the expression for the polariton interaction Hamiltonian, we express both the anharmonic lattice Hamiltonian and the photon-phonon interaction Hamiltonian in the polariton representation with the result

$$\mathcal{H}_{\text{int}}=\sum_{n=3}^{\infty}\sum_{k_1,k_2,\cdots,k_n}\{\tilde{V}_n(k_1,k_2,\cdots,k_n)A_{k_1}A_{k_2}\cdots A_{k_n}$$
$$-\tilde{\phi}_n(k_1,k_2,\cdots,k_n)B_{k_1}A_{k_2}A_{k_3}\cdots A_{k_n}\}\,,\quad(14)$$

where the following notation has been introduced:

$$\tilde{V}_n(k_1,k_2,\cdots,k_n)=\bar{V}_n(k_1,k_2,\cdots,k_n)$$
$$+\bar{g}_n(k_1,k_2,\cdots,k_n)\,,\quad(15\text{a})$$

$$\bar{V}_n(k_1,k_2,\cdots,k_n)=\sum_{j_1,j_2,\cdots,j_n}U_{j_1}(k_1)U_{j_2}(k_2)\cdots$$
$$\times U_{j_n}(k_n)V_n(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_nj_n)\,,\quad(15\text{b})$$

$$\bar{g}_n(k_1,k_2,\cdots,k_n)=\sum_{\lambda_1,\lambda_2,j_3,\cdots,j_{n-2}}U_{\lambda_1}(k_1)U_{\lambda_2}(k_2)U_{j_3}(k_3)\cdots$$
$$\times U_{j_{n-2}}(k_n)g_n(\mathbf{k}_1\lambda_1,\mathbf{k}_2\lambda_2,\mathbf{k}_3j_3,\cdots,\mathbf{k}_nj_{n-2})\,,\quad(15\text{c})$$

$$\tilde{\phi}_n(k_1,k_2,\cdots,k_n)=\sum_{\lambda_2,j_1,j_2,\cdots,j_{n-1}}\bar{U}_{j_1}(k_1)U_{\lambda_2}(k_2)U_{j_3}(k_3)\cdots$$
$$\times U_{j_{n-1}}(k_n)\phi_n(\mathbf{k}_1j_1,\mathbf{k}_2\lambda_2,\mathbf{k}_3j_3,\cdots,\mathbf{k}_nj_{n-1})\,,\quad(15\text{d})$$

$$U_j(k)=u_j(k)+v_j(-k)$$
$$=i\frac{[(\omega_{\mathbf{k}j}{}^0)^2\omega_k]^{1/2}x_j(\mathbf{k}\lambda)}{(\omega_{\mathbf{k}j}{}^0)^2-\omega_k{}^2}\left(\frac{d\omega^2\tilde{\epsilon}(\mathbf{k},\omega)}{d\omega^2}\right)_{\omega=\omega_k}^{-1/2},\quad(15\text{e})$$

$$\bar{U}_j(k)=u_j(k)-v_j(-k)$$
$$=i\left(\frac{\omega_{\mathbf{k}j}{}^0}{\omega_k}\right)\frac{(\omega_{\mathbf{k}j}{}^0\omega_k)^{1/2}x_j(\mathbf{k}\lambda)}{\omega_k{}^2-(\omega_{\mathbf{k}j}{}^0)^2}\left(\frac{d\omega^2\tilde{\epsilon}(\mathbf{k},\omega)}{d\omega^2}\right)_{\omega=\omega_k}^{-1/2},\quad(15\text{f})$$

$$U_\lambda(k)=u_\lambda(k)+v_\lambda(-k)=\left(\frac{ck}{\omega_k}\right)^{1/2}\left(\frac{d\omega^2\tilde{\epsilon}(\mathbf{k},\omega)}{d\omega^2}\right)_{\omega=\omega_k}^{-1/2},\quad(15\text{g})$$

$$A_k\equiv\alpha_k+\alpha_{-\mathbf{k}}{}^\dagger,\quad B_k\equiv\alpha_k-\alpha_{-\mathbf{k}}{}^\dagger,\quad k\equiv(\mathbf{k},\rho)\,.$$

In (15a)–(15d), $V_n(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_nj_n)$ is the anharmonic potential for the phonon field,[10] while the coupling functions $\phi_n(\mathbf{k}_1j_1,\mathbf{k}_2\lambda_2,\mathbf{k}_3j_3,\cdots,\mathbf{k}_nj_{n-1})$ and $g_n(\mathbf{k}_1\lambda_1,\mathbf{k}_2\lambda_2,\mathbf{k}_3j_3,\cdots,\mathbf{k}_nj_{n-2})$ are given by (10b) and (10c), respectively. The quantities $\bar{V}_n(k_1,k_2,\cdots,k_n)$, $\tilde{\phi}_n(k_1,k_2,\cdots,k_n)$, and $\bar{g}_n(k_1,k_2,\cdots,k_n)$ are the anharmonic coupling functions corresponding to the polariton field; their explicit expressions can be easily derived from (15b)–(15d), respectively, by making use of (15e)–(15g). For example, the expression for $\bar{V}_n(k_1,k_2,\cdots k_n)$ becomes

$$\bar{V}_n(k_1,k_2,\cdots,k_n)$$
$$=(i)^n\frac{(\omega_{\mathbf{k}_1j_1}{}^0\omega_{\mathbf{k}_2j_2}{}^0\cdots\omega_{\mathbf{k}_nj_n}{}^0\omega_{k_1}\omega_{k_2}\cdots\omega_{k_n})^{1/2}}{[(\omega_{\mathbf{k}_1j_1}{}^0)^2-\omega_{k_1}{}^2][(\omega_{\mathbf{k}_2j_2}{}^0)^2-\omega_{k_2}{}^2]\cdots[(\omega_{\mathbf{k}_nj_n}{}^0)^2-\omega_{k_n}{}^2]}$$
$$\times x_{j_1}(k_1)x_{j_2}(k_2)\cdots x_{j_n}(\mathbf{k}_n)\left(\frac{d\omega^2\tilde{\epsilon}(\mathbf{k}_1,\omega)}{d\omega^2}\right)_{\omega=\omega_{k_1}}^{-1/2}\cdots$$
$$\times\left(\frac{d\omega^2\tilde{\epsilon}(\mathbf{k}_n,\omega)}{d\omega^2}\right)_{\omega=\omega_{k_n}}^{-1/2}V_n(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_nj_n)\,.\quad(16)$$

In the range of wave vectors where retardation effects can be neglected, i.e., in the limit when $\omega_k\to\omega_{\mathbf{k}j}{}^0$ and $\tilde{\epsilon}(\mathbf{k},\omega_k)\to 1$, then

$$\tilde{\phi}_n(k_1,k_2,\cdots,k_n)\to 0,\quad\bar{g}_n(k_1,k_2,\cdots,k_n)\to 0\,,$$
$$\tilde{V}_n(k_1,k_2,\cdots,k_n)\to V_n(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\cdots,\mathbf{k}_nj_n)$$

and the interaction Hamiltonian (14) describes the anharmonic phonon field.

III. DYSON'S EQUATION

In this section we derive the Dyson equation and, consequently, the polarization operator describing the polariton spectrum. The retarded polariton Green's function is defined as[11]

$$G(k,\,t-t')\equiv\langle\langle A_k;\,A_{k'}{}^\dagger\rangle\rangle$$
$$=-i\theta(t-t')\langle[A_k(t),A_{k'}{}^\dagger(t')]_-\rangle\,,\quad(17\text{a})$$

where the angular brackets denote the average over the canonical ensemble appropriate to the total Hamiltonian $\mathcal{H}$; the factor $\theta(t)$ is the usual step function, and the operators A_k and $A_{k'}{}^\dagger$ are in the Heisenberg representation. In (17a) and in what follows, the time arguments of the operators have been suppressed for convenience. The Fourier transform of the polariton Green's function with respect to the argument t satisfies the equation of motion

$$\omega G(k,\omega)=(1/2\pi)\langle[A_k,A_{k'}{}^\dagger]_-\rangle_{t=t'}$$
$$+\langle\langle[A_k,\mathcal{H}]_-;\,A_{k'}{}^\dagger\rangle\rangle\,.\quad(17\text{b})$$

Using (12), (14), and (17b), the equation of motion for the polariton Green's function is found to be

$$G_{00}{}^{-1}(k,\omega)G(k,\omega)=1+\langle\langle F(k);\,A_{k'}{}^\dagger\rangle\rangle\,,\quad(18)$$

where

$$G_{00}(k,\omega)=\frac{\omega_k}{\pi}(\omega^2-\omega_k{}^2)^{-1}\delta_{kk'}\quad(19)$$

is the unperturbed polariton Green's function and

$$F(k)=2\pi\sum_{n=3}^{\infty}\sum_{k_1,k_2,\cdots,k_{n-1}}[Q_n(k_1,\,k_2,\,\cdots,\,k_{n-1},\,-k;\,\omega)$$
$$\times A_{k_1}A_{k_2}\cdots A_{k_{n-1}}-(n-1)\tilde{\phi}_n(k_1,\,k_2,\,\cdots,\,k_{n-2},\,-k)$$
$$\times B_{k_1}A_{k_2}\cdots A_{k_{n-2}}]\,,\quad(20\text{a})$$

$$Q_n(k_1,\,k_2,\,\cdots,\,k_{n-1},\,-k;\,\omega)\equiv n\tilde{V}_n(k_1,\,k_2,\,\cdots,\,k_{n-1},\,-k)$$
$$+(\omega/\omega_k)\tilde{\phi}_n(k_1,\,k_2,\,\cdots,\,k_{n-1},\,-k)\,,\quad(20\text{b})$$

$$n\bar{g}_n(k_1,\,k_2,\,\cdots,\,k_{n-1},\,-k)$$
$$\equiv 2\sum_{\lambda_1,\lambda_2,j_3,\cdots,j_{n-2}}U_{\lambda_1}(-k)U_{\lambda_2}(k_1)U_{j_3}(k_2)\cdots$$
$$\times U_{j_{n-2}}(k_{n-1})g(-k_{\lambda_1},\mathbf{k}_2\lambda_2,\mathbf{k}_2j_3,\cdots,\mathbf{k}_{n-1}j_{n-2})$$
$$+(n-2)\sum_{\lambda_1,\lambda_2,j_3,\cdots,j_{n-2}}U_{\lambda_1}(k_1)U_{\lambda_2}(k_2)U_{j_3}(-k)\cdots$$
$$\times U_{j_{n-2}}(k_{n-1})g(\mathbf{k}_1\lambda_1,\,\mathbf{k}_2\lambda_2,\,-\mathbf{k}j_3,\,\cdots,\,\mathbf{k}_{n-1}j_{n-2})\,.\quad(20\text{c})$$

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[11] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Uspekhi **3**, 320 (1960)].

Considering the equation of motion for the Green's function that appears on the right-hand side of (18) with respect to the argument t' and substituting the resulting expression into (18), we derive Dyson's equation

$$\begin{aligned} G(k,\omega) &= G_{00}(k,\omega)+G_{00}(k,\omega)\tilde{P}(k,\omega)G_{00}(k,\omega) \\ &= G_{00}(k,\omega)+G_{00}(k,\omega)\Pi(k,\omega)G(k,\omega)\,, \end{aligned} \tag{21}$$

where the polarization operator $\Pi(k,\omega)$ is equal to

$$\Pi(k,\omega)=\tilde{P}(k,\omega)[1+G_{00}(k,\omega)\tilde{P}(k,\omega)]^{-1}, \tag{22}$$

and

$$\begin{aligned} \tilde{P}(k,\omega)=\tfrac{1}{2}[\langle[F(k),B_k{}^\dagger]_-\rangle+(\omega/\omega_k)\langle[F(k),A_k{}^\dagger]_-\rangle]_{t=t'} \\ +\langle\langle F(k);\, F^\dagger(k)\rangle\rangle. \end{aligned} \tag{23}$$

In the range of frequencies ω far from the zeros of the denominator appearing in the expression for the polarization operator (22), we may expand the denominator of (22) in a power series of $\tilde{P}(k,\omega)$ as

$$\Pi(k,\omega)\approx\tilde{P}(k,\omega)[1-G_{00}(k,\omega)\tilde{P}(k,\omega)+\cdots]. \tag{24}$$

In what follows, we shall retain only the first term in the expression (24). Then Dyson's equation (21) may be written as

$$G(k,\omega)=(\omega_k/\pi)\delta_{kk'}[\omega^2-\tilde{\omega}_k{}^2-2\omega_k P(k,\omega)]^{-1}, \tag{25}$$

where the energies $\tilde{\omega}_k$ are determined from the solutions of the equation

$$\begin{aligned} \tilde{\omega}_k{}^2=\omega_k{}^2+(\omega_k/2\pi)[\langle[F(k),B_k{}^\dagger]_-\rangle^{(0)} \\ +(\omega/\omega_k)\langle[F(k),A_k{}^\dagger]_-\rangle^{(0)}]_{\omega=\tilde{\omega}_k,\,t=t'}\,, \end{aligned} \tag{26}$$

and $P(k,\omega)$ is given by

$$P(k,\omega)=(1/2\pi)\langle\langle F(k);\, F^\dagger(k)\rangle\rangle. \tag{27}$$

The solutions of the Eq. (26) determine the frequencies $\tilde{\omega}_k$ for the renormalized mode k in the lowest approximation of perturbation theory, and the renormalization is caused by the terms arising from the evaluation of the commutators.[12] The polarization operator $P(k,\omega)$ will be calculated in successive approximations, i.e., it may be written as

$$P(k,\omega)\approx P^{(0)}(k,\omega)+P^{(1)}(k,\omega)+\cdots, \tag{28}$$

where the superscripts (0) and (1) indicate that the various Green's functions that appear in (27) must be evaluated in the lowest and first approximation, respectively, in the manner which shall be described below.

A. Lowest Approximation for $P(k,\omega)$

In the first approximation the Green's function (25) may be written as

$$G^{(1)}(k,\omega)=(\omega_k/\pi)\delta_{kk'}[\omega^2-\tilde{\omega}_k{}^2-2\omega_k P^{(0)}(k,\omega)]^{-1}. \tag{29}$$

From Eq. (29) we observe that when $P^{(0)}(k,\omega)$ is taken equal to zero, then the zeroth-order renormalized polariton Green's function is given by

$$G^{(0)}(k,\omega)=(\omega_k/\pi)\delta_{kk'}[\omega^2-\tilde{\omega}_k{}^2]^{-1}. \tag{30}$$

The excitation spectrum described by (30) results from an equivalent zeroth-order renormalized Hamiltonian which has the form

$$\mathcal{H}_{\mathrm{ren}}{}^{(0)}=\mathrm{const}+\tfrac{1}{4}\sum_k\left[\left(\frac{\tilde{\omega}_k{}^2}{\omega_k}\right)1_k{}^\dagger A_k+\omega_k B_k{}^\dagger B_k\right]. \tag{31}$$

Therefore, the Hamiltonian (31) must be used for the evaluation of $P^{(0)}(k,\omega)$. Because of the form of the Hamiltonian (31), only the Green's functions appearing in (27) with $n=n'$ give contributions while terms with $n\neq n'$ disappear. In the Appendix, an example is carried out where the various two- and three-polariton Green's functions are evaluated via the Hamiltonian (31). Substituting (A5) and (A9) into (27) we obtain

$$\begin{aligned} P^{(0)}(k,\omega)=2\sum_{k_1,k_2}\{&[\tilde{Q}_3{}^{(+)}(k_1,\,k_2,\,-k;\,\omega)(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})-2\omega\hat{Q}_3{}^{(+)}(k_1,\,k_2,\,-k;\,\omega)](\tilde{\eta}_{k_1}+\tilde{\eta}_{k_2})[\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2]^{-1} \\ &+[\tilde{Q}_3{}^{(-)}(k_1,\,k_2,\,-k;\,\omega)(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})-2\omega\hat{Q}_3{}^{(-)}(k_1,\,k_2,\,-k;\,\omega)](\tilde{\eta}_{k_2}-\tilde{\eta}_{k_1})[\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2]^{-1}\} \\ &+2\sum_{k_1,k_2,k_3}\{[\tilde{Q}_4{}^{(+)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})-2\omega\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)](1+\tilde{\eta}_{k_1}\tilde{\eta}_{k_2}+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}+\tilde{\eta}_{k_1}\tilde{\eta}_{k_3}) \\ &\times[\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2]^{-1}+[\tilde{Q}_4{}^{(-)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})-2\omega\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)] \\ &\times(1+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_3}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_2})[\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})^2]^{-1}+(\tilde{\omega}_{k_2}\leftrightarrow-\tilde{\omega}_{k_2})+(\tilde{\omega}_{k_3}\leftrightarrow-\tilde{\omega}_{k_3})\} \\ &+(\text{terms with } n>4)\,. \end{aligned} \tag{32}$$

The coupling functions

$$\tilde{Q}_3{}^{(\pm)}(k_1,\,k_2,\,-k;\,\omega),\quad \hat{Q}_3{}^{(\pm)}(k_1,\,k_2,\,-k;\,\omega)\,,$$
$$\tilde{Q}_4{}^{(\pm)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)\,,$$

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[12] In (26), $\omega=\varpi_k$ and the superscript (0) indicate that the polariton occupation numbers, $N_q=\langle A_q{}^\dagger A_q\rangle$, resulting from the calculation of the commutators have to be evaluated by means of the zeroth-order Green's function (30) or the renormalized Hamiltonian (31); for example, $N_q{}^{(0)}=(\omega_q/\varpi_q)\coth\tfrac{1}{2}\beta\varpi_q$. In this approximation the correlation functions with $n>4$ have to be decoupled in the usual way into products of polariton occupation numbers, $N_q{}^{(0)}$, and hence, only correlation functions with even number of operators give nonzero contributions. In this manner, the second term on the right-hand side of (26) can be easily expressed as a function of the polariton occupation numbers and ϖ_k, including terms up to any desired value of n, then the final solution for the frequencies ϖ_k has to be derived from Eq. (26) by computation.

and $\hat{Q}_4(k_1, k_2, k_3, -k\colon \omega)$ are given by the expressions (A10a)–(A10d) in the Appendix, respectively. In Eq. (32), $(\tilde{\omega}_{k_2} \leftrightarrow -\tilde{\omega}_{k_2})$ and $(\tilde{\omega}_{k_3} \leftrightarrow -\tilde{\omega}_{k_3})$ for the quartic anharmonic terms indicate that there are two further terms obtained by changing the signs of $\tilde{\omega}_{k_2}$ and $\tilde{\omega}_{k_3}$ in the first terms, respectively. Hence, the excitation spectrum in the first approximation is described by the expression (29) with $P^{(0)}(k,\omega)$ given by (32) and is a function of the frequency modes, the $\tilde{\omega}_k$'s, which are renormalized in the lowest order of perturbation theory. In this approximation (29) may be written as

$$G^{(1)}(k,\omega) = (\omega_k/\pi)\delta_{kk'}[\omega^2 - \tilde{\omega}_k^2 - 2\omega_k \operatorname{Re}P^{(0)}(k,\omega) \\ -2\omega_k \operatorname{Im}P^{(0)}(k,\omega)]^{-1}, \quad \text{(32a)}$$

where $\operatorname{Re}P^{(0)}(k,\omega)$ and $\operatorname{Im}P^{(0)}(k,\omega)$ indicate the real and imaginary parts of (32), respectively. If $\operatorname{Im}P^{(0)}(k,\omega)$ is small but finite, $\operatorname{Im}P^{(0)}(k,\omega) \ll \omega_k$ and varies slowly with ω in the vicinity of frequencies $\omega \sim \tilde{\omega}_k$, then the energy spectrum described by (32a) is a Lorentzian line peaked at $\omega \sim \tilde{\omega}_k$ with a width of the order of $\operatorname{Im}P^{(0)}(k,\tilde{\omega}_k)$ in energy units.

An alternative approach to calculating the Green's function

$$G(k,\omega) = (\omega_k/\pi)\delta_{kk'}[\omega^2 - \omega_k^2 - (\omega_k/\pi)\tilde{P}(k,\omega)]^{-1} \quad \text{(32b)}$$

is the following: If the frequency $\tilde{\omega}_k$ is replaced by Ω_k in the expression for the Hamiltonian (31), where Ω_k is the polariton energy of excitation which has yet to be determined self-consistently, then using this Hamiltonian to evaluate (32b) we find

$$G(k,\omega) = (\omega_k/\pi)\delta_{kk'}[\omega^2 - \Omega_k^2 - 2\omega_k \operatorname{Im}P(k,\omega)]^{-1}, \quad \text{(32c)}$$

where Ω_k is determined by the solutions of the equation

$$\Omega_k^2 - \omega_k^2 - P_1(k, N_q;\ \omega = \Omega_k) \\ -2\omega_k \operatorname{Re}P(k,\ \omega = \Omega_k) = 0. \quad \text{(32d)}$$

The function $P_1(k,\ N_q;\ \omega = \Omega_k)$ results from the evaluation of the last term on the right-hand side of (26) in the manner described in Ref. 12 and is a function of the polariton occupation numbers, $N_q = (\omega_q/\Omega_q) \coth\frac{1}{2}\beta\Omega_q$, and the frequency Ω_k. The function $P(k,\ \omega = \Omega_k)$ is given by the expression (32) if all the frequencies $\tilde{\omega}_{k_1}$, $\tilde{\omega}_{k_2}$, and $\tilde{\omega}_{k_3}$ are replaced everywhere by Ω_{k_1}, Ω_{k_2}, and Ω_{k_3}, respectively. It is easily seen that when $\operatorname{Im}P(k,\omega)$ is small but finite then the excitation spectrum described by (32c) is reduced to that of (32a). In the limiting case when $\operatorname{Im}P(k,\omega)$ tends to zero for any value of $\omega = \Omega_k$, then the energies of excitation Ω_k, corresponding to a quasiparticle with infinite lifetime, are determined by the solutions of the equation

$$\Omega_k^2 - \omega_k^2 - P_1(k,\ N_q;\ \omega = \Omega_k) - 2\omega_k P(k,\ \omega = \Omega_k) = 0. \quad \text{(32e)}$$

In principle, Eq. (32e) can be solved self-consistently by means of computing methods to obtain numerical results. In practice, not only the frequency Ω_k but also all the frequencies Ω_{k_1}, Ω_{k_2}, $\cdots$, $\Omega_{k_{n-1}}$ have to be determined self-consistently, therefore, for the general solution of (32e) one has to deal with an infinite number of variables (frequencies). Hence, approximate methods have to be developed for the calculation of (32c).

B. First Approximation for $P(k,\omega)$

In the case when the imaginary part of $P^{(0)}(k,\omega)$ tends to zero for some frequency, say ϵ_k $(\neq \tilde{\omega}_k)$, then the expression (29) takes the form

$$G^{(1)}(k,\omega) = (\omega_k/\pi)\delta_{kk'}[\omega^2 - \epsilon_k^2]^{-1}, \quad \text{(33)}$$

where the energies of excitation ϵ_k are determined by the roots of the equation

$$\epsilon_k^2 - \tilde{\omega}_k^2 - 2\omega_k P^{(0)}(k,\epsilon_k) = 0. \quad \text{(34a)}$$

Considering that when the system resonates in the neighborhood of frequencies $\omega \sim \tilde{\omega}_k$ the expressions (32a) and (32c) coincide, then far from resonance the inclusion in (34a) of the term $2\omega_k P^{(0)}(k,\epsilon_k)$, in which all the frequencies $\Omega_{k'}$ have been replaced by their corresponding values at resonance $\tilde{\omega}_{k'}$, may give a reasonably good value for ϵ_k. In view of (32e), one may argue that the frequency ϵ_k determined by the solution of the equation

$$\epsilon_k^2 - \omega_k^2 - P_1(\mathbf{k}, N_q(\epsilon_q);\ \omega = \epsilon_k) - 2\omega_k P^{(0)}(k,\epsilon_k) = 0 \quad \text{(34b)}$$

is a better approximation to Ω_k than that obtained by the solution of (34a). In fact, this is generally true; the only disadvantage of (34b) is that much more effort is required for the computation of ϵ_k than that for the corresponding solution of (34a). Although the last term in (34b) is only an approximation to the corresponding term in (32e), it will be improved in the next approximation. The solutions of (34) corresponding to the frequencies ϵ_k imply that the bare polariton is dressed by the anharmonic interaction of the others and the resultant dressed quasiparticle with energy ϵ_k may be called "physical polariton." The excitation spectrum described by (33) results from an equivalent renormalized Hamiltonian which is correct in the first approximation, i.e.,

$$\mathcal{H}_{\text{ren}}^{(1)} = \text{const} + \tfrac{1}{4} \sum_k \left[\left(\frac{\epsilon_k^2}{\omega_k} \right) A_k^\dagger A_k + \omega_k B_k^\dagger B_k \right]. \quad \text{(35)}$$

Therefore, the polariton Green's function in the second approximation turns out to be

$$G^{(2)}(k,\omega) = (\omega_k/\pi)\delta_{kk'}[\omega^2 - \epsilon_k^2 - 2\omega_k P^{(1)}(k,\omega)]^{-1}, \quad \text{(36)}$$

and the polarization operator $P^{(1)}(k,\omega)$ has to be evaluated via the first-order Hamiltonian (35). A comparison between (31) and (35) shows that the expression for $P^{(1)}(k,\omega)$ can be derived from that of $P^{(0)}(k,\omega)$ [Eq. (32)] by replacing the renormalized frequencies correct to the lowest order, viz., $\tilde{\omega}_{k_1}$, $\tilde{\omega}_{k_2}$, and $\tilde{\omega}_{k_3}$, by ϵ_{k_1}, ϵ_{k_2}, and ϵ_{k_3}, respectively, where the energies of excitation ϵ_{k_1}, ϵ_{k_2}, and ϵ_{k_3} are obtained from the solutions of the Eq. (34) for each particular mode. Then the expression for

$P^{(1)}(k,\omega)$ is found to be

$$\begin{aligned}P^{(1)}(k,\omega)=2\sum_{k_1,k_2}\{&[\tilde{Q}_3^{(+)}(k_1,\,k_2,\,-k;\,\omega)(\epsilon_{k_1}+\epsilon_{k_2})-2\omega\hat{Q}_3^{(+)}(k_1,\,k_2,\,-k;\,\omega)](\eta_{k_1}+\eta_{k_2})[\omega^2-(\epsilon_{k_1}+\epsilon_{k_2})^2]^{-1}\\&+[\tilde{Q}_3^{(-)}(k_1,\,k_2,\,-k;\,\omega)(\epsilon_{k_1}-\epsilon_{k_2})-2\omega\hat{Q}_3^{(-)}(k_1,\,k_2,\,-k;\,\omega)](\eta_{k_2}-\eta_{k_1})[\omega^2-(\epsilon_{k_1}-\epsilon_{k_2})^2]^{-1}\}\\&+2\sum_{k_1,k_2,k_3}\{[\tilde{Q}_4^{(+)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3})-2\omega\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)]\\&\times(1+\eta_{k_1}\eta_{k_2}+\eta_{k_2}\eta_{k_3}+\eta_{k_1}\eta_{k_3})[\omega^2-(\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3})^2]^{-1}+[\tilde{Q}_4^{(-)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\epsilon_{k_1}-\epsilon_{k_2}-\epsilon_{k_3})\\&-2\omega\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)](1+\eta_{k_2}\eta_{k_3}-\eta_{k_1}\eta_{k_3}-\eta_{k_1}\eta_{k_2})[\omega^2-(\epsilon_{k_1}-\epsilon_{k_2}-\epsilon_{k_3})^2]^{-1}\\&+(\epsilon_{k_2}\leftrightarrow-\epsilon_{k_2})+(\epsilon_{k_3}\leftrightarrow-\epsilon_{k_3})\}+(\text{terms with } n>4)\,,\end{aligned}\tag{37a}$$

where $\eta_{k_1}=\coth\frac{1}{2}\beta\epsilon_{k_1}$, the coupling functions are given by the expressions

$$\begin{aligned}\tilde{Q}_3^{(\pm)}(k_1,\,k_2,\,-k;\,\omega)=\tfrac{1}{2}\sum_{k_1',k_2'}\Big[&Q_3(k_1,\,k_2,\,-k;\,\omega)\\&\times Q_3^*(k_1',\,k_2',\,-k;\,\omega)(\delta_{k_1'k_1}\delta_{k_2'k_2}+\delta_{k_1'k_2}\delta_{k_2'k_1})\\&+4\left(\frac{\epsilon_{k_1}}{\omega_{k_1}}\right)\tilde{\phi}_3(k_1,\,k_2,\,-k)\tilde{\phi}_3^*(k_1',\,k_2',\,-k)\\&\times\left(\frac{\epsilon_{k_1}}{\omega_{k_1}}\delta_{k_1'k_1}\delta_{k_2'k_2}\pm\frac{\epsilon_{k_2}}{\omega_{k_2}}\delta_{k_1'k_2}\delta_{k_2'k_1}\right)\Big]\left(\frac{\omega_{k_1}\omega_{k_2}}{\epsilon_{k_1}\epsilon_{k_2}}\right),\end{aligned}\tag{37b}$$

$$\begin{aligned}&\hat{Q}_3^{(\pm)}(k_1,\,k_2,\,-k;\,\omega)\\&\quad=2\sum_{k_1',k_2'}Q_3(k_1,\,k_2,\,-k;\,\omega)\tilde{\phi}_3^*(k_1',\,k_2',\,-k)\\&\qquad\times\left(\frac{\epsilon_{k_1}}{\omega_{k_1}}\delta_{k_1'k_1}\delta_{k_2'k_2}\pm\frac{\epsilon_{k_2}}{\omega_{k_2}}\delta_{k_1'k_2}\delta_{k_2'k_1}\right)\left(\frac{\omega_{k_1}\omega_{k_2}}{\epsilon_{k_1}\epsilon_{k_2}}\right),\end{aligned}\tag{37c}$$

$$\begin{aligned}&\tilde{Q}_4^{(\pm)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)\\&\quad=\tfrac{1}{4}\sum_{k_1',k_2',k_3'}\Big[Q_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)\\&\qquad\times Q_4^*(k_1',\,k_2',\,k_3',\,-k;\,\omega)\delta\\&\qquad+9\left(\frac{\epsilon_{k_1}}{\omega_{k_1}}\right)\tilde{\phi}_4(k_1,\,k_2,\,k_3,\,-k)\tilde{\phi}_4^*(k_1',\,k_2',\,k_3',\,-k)\\&\qquad\times\left(\frac{\epsilon_{k_1}}{\omega_{k_1}}\delta_{123}\pm\frac{\epsilon_{k_2}}{\omega_{k_2}}\delta_{213}\pm\frac{\epsilon_{k_3}}{\omega_{k_3}}\delta_{321}\right)\Big]\left(\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\epsilon_{k_1}\epsilon_{k_2}\epsilon_{k_3}}\right),\end{aligned}\tag{37d}$$

$$\begin{aligned}\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)=\tfrac{3}{4}\sum_{k_1',k_2',k_3'}&\tilde{\phi}_4(k_1,\,k_2,\,k_3,\,-k)\\&\times Q_4^*(k_1',\,k_2',\,k_3',\,-k;\,\omega)\left(\frac{\omega_{k_2}\omega_{k_3}}{\epsilon_{k_2}\epsilon_{k_3}}\right)\delta\,,\end{aligned}\tag{37e}$$

and the Kronecker symbols δ, δ_{123}, δ_{213}, and δ_{321} have been defined by Eq. (A9d). The expression (37) for the polarization operator $P^{(1)}(k,\omega)$ is a function of the frequencies of the dressed polariton modes (physical polaritons), and therefore the Green's function $G^{(2)}(k,\omega)$ describes the excitation spectrum of dressed interacting polariton modes. We observed that in (37), and similarly in (32), the square of the anharmonic coupling functions Q_n and $\tilde{\phi}_n$ as well as their products $Q_n\tilde{\phi}_n^*$ are multiplied by factors having the general forms

$$(\omega_{k_1}\omega_{k_2}\cdots\omega_{k_{n-1}}/\epsilon_{k_1}\epsilon_{k_2}\cdots\epsilon_{k_{n-1}})$$

and

$$(\epsilon_{k_1}\omega_{k_2}\omega_{k_3}\cdots\omega_{k_{n-1}}/\omega_{k_1}\epsilon_{k_2}\epsilon_{k_3}\cdots\epsilon_{k_{n-1}})\,,$$

respectively, where n is the number of modes contained in each particular term. They result from the evaluation of the Green's functions having the forms

$$\begin{gathered}\langle\langle A_{k_1}A_{k_2}\cdots A_{k_{n-1}};\,A_{k_1'}^{\dagger}A_{k_2'}^{\dagger}\cdots A_{k'_{n-1}}^{\dagger}\rangle\rangle\,,\\\langle\langle B_{k_1}A_{k_2}A_{k_3}\cdots A_{k_{n-1}};\,A_{k'_{n-1}}^{\dagger}\cdots A_{k_3'}^{\dagger}A_{k_2'}^{\dagger}B_{k_1'}^{\dagger}\rangle\rangle\,,\\\langle\langle B_{k_1}A_{k_2}A_{k_3}\cdots A_{k_{n-1}};\,A_{k_1'}^{\dagger}A_{k_2'}^{\dagger}\cdots A_{k_{n-1}'}^{\dagger}\rangle\rangle\,,\end{gathered}$$

and they give an account of the nondiagonal contributions arising from the renormalized first-order Hamiltonian (35). Considering that the ratio (ω_k/ϵ_k) is either greater than or less than unity, depending on whether the energy shift is negative or positive, respectively, we conclude that both factors result in increasing or in reducing the square of the amplitudes of the anharmonic coupling functions that appear in the expression for the polarization operator. Another important effect arising from the aforementioned factors is that they are temperature-dependent. We remark that the expression (36) for $G^{(2)}(k,\omega)$ can be obtained directly from (32b) if use is made of the same approximations that have been done for the derivation of (36). The poles of the Green's function $G^{(2)}(k,\omega)$ give the energies of excitation for the polariton spectrum correct in the second approximation. The results obtained can be improved by going into higher-order approximations but, as far as our problem is concerned, the second approximation is sufficient to describe the polariton excitation spectrum because the interactions appearing in the expression (14) for $\mathcal{H}_{\text{int}}$ are weak.

It should be pointed out that in our calculation for $P(k,\omega)$ given by (27) terms with $n\neq n'$ vanish; this is due to the Hamiltonian representation employed at each successive approximation. The derived results can be improved if use is made of the complete expression for the polarization operator as given by (23) at each successive step. For example, we may write $G^{(2)}(k,\omega)$ as

$$G^{(2)}(k,\omega)=(\omega_k/\pi)\delta_{kk'}[\omega^2-\epsilon_k^2-2\omega_k\Pi^{(1)}(k,\omega)]^{-1} \quad (38)$$

with

$$\Pi^{(1)}(k,\omega)\approx P^{(1)}(k,\omega)[1-G_{00}(k,\omega)P^{(1)}(k,\omega)+\cdots], \quad (39)$$

and $P^{(1)}(k,\omega)$ is expressed by (37). The second, third, $\cdots$, terms in the expansion (39) will contribute small corrections to the dominant first term. The small corrections obtained by this procedure at each successive step will compensate the terms appearing in (27) with $n'\neq n$ because both corrections are of the same order of magnitude.

In the range of wave vectors where retardation effects are not important and may be neglected, the expressions (36) and (37) can be reduced to those corresponding to the bare phonon spectrum by taking the proper limits when $\omega_k\rightarrow\omega_k{}^0$ and $\tilde{\epsilon}(k,\omega_k)\rightarrow 1$ then $\tilde{\phi}_n(k_1,k_2,\cdots,k_n)\rightarrow 0$ and $\tilde{V}_n(k_1,k_2,\cdots,k_n)\rightarrow V_n(k_1,k_2,\cdots,k_n)$. In this case for the bare phonon spectrum we have

$$G_b{}^{(2)}(k,\omega)=(\omega_k{}^0/\pi)\delta_{kk'}[\omega^2-(\epsilon_k{}^0)^2 -2\omega_k{}^0P_b{}^{(1)}(k,\omega)]^{-1}, \quad (40a)$$

where

$$P_b{}^{(1)}(k,\omega)=18\sum_{k_1,k_2}|V_3(k_1,\,k_2,\,-k)|^2\left(\frac{\omega_{k_1}{}^0\omega_{k_2}{}^0}{\epsilon_{k_1}{}^0\epsilon_{k_2}{}^0}\right)$$
$$\times\left\{(\eta_{k_1}{}^0+\eta_{k_2}{}^0)\left[\frac{(\epsilon_{k_1}{}^0+\epsilon_{k_2}{}^0)}{\omega^2-(\epsilon_{k_1}{}^0+\epsilon_{k_2}{}^0)^2}\right]+(\eta_{k_2}{}^0-\eta_{k_1}{}^0)\left[\frac{(\epsilon_{k_1}{}^0-\epsilon_{k_2}{}^0)}{\omega^2-(\epsilon_{k_1}{}^0-\epsilon_{k_2}{}^0)^2}\right]\right\}+48\sum_{k_1,k_2,k_3}|V_4(k_1,\,k_2,\,k_3,\,-k)|^2$$
$$\times\left(\frac{\omega_{k_1}{}^0\omega_{k_2}{}^0\omega_{k_3}{}^0}{\epsilon_{k_1}{}^0\epsilon_{k_2}{}^0\epsilon_{k_3}{}^0}\right)\left\{(1+\eta_{k_1}{}^0\eta_{k_2}{}^0+\eta_{k_2}{}^0\eta_{k_3}{}^0+\eta_{k_1}{}^0\eta_{k_3}{}^0)\left[\frac{(\epsilon_{k_1}{}^0+\epsilon_{k_2}{}^0+\epsilon_{k_3}{}^0)}{\omega^2-(\epsilon_{k_1}{}^0+\epsilon_{k_2}{}^0+\epsilon_{k_3}{}^0)^2}\right]\right.$$
$$\left.+3(1+\eta_{k_2}{}^0\eta_{k_3}{}^0-\eta_{k_1}{}^0\eta_{k_3}{}^0-\eta_{k_1}{}^0\eta_{k_2}{}^0)\left[\frac{(\epsilon_{k_1}{}^0-\epsilon_{k_2}{}^0-\epsilon_{k_3}{}^0)}{\omega^2-(\epsilon_{k_1}{}^0-\epsilon_{k_2}{}^0-\epsilon_{k_3}{}^0)^2}\right]\right\}+(\text{terms with } n>4), \quad (40b)$$

$\eta_{k_1}{}^0=\coth\frac{1}{2}\beta\epsilon_{k_1}{}^0$ and $k\equiv\mathbf{k}j$. The energies of excitation, $\epsilon_k{}^0$, are determined from the solutions of the equation

$$(\epsilon_k{}^0)^2-(\tilde{\omega}_k{}^0)^2-2\omega_k{}^0P_b{}^{(0)}(k,\epsilon_k{}^0)=0, \quad (40c)$$

and the expression for $P_b{}^{(0)}(k,\epsilon_k{}^0)$ is obtained from (32) with $\omega=\epsilon_k{}^0$, $\tilde{\phi}_n(k_1,k_2,\cdots,k_n)=0$, $\tilde{V}_n(k_1,k_2,\cdots,k_n)=V_n(k_1,k_2,\cdots,k_n)$ and the $\tilde{\omega}_k$'s are replaced by the $\tilde{\omega}_k{}^0$'s where

$$(\tilde{\omega}_k{}^0)^2=(\omega_k{}^0)^2+\omega_k{}^0\sum_{n=3}^{\infty}n\sum_{k_1,k_2,\cdots,k_{n-1}}V_n(k_1,\,k_2,\,\cdots,\,k_{n-1},\,-k)\times\langle[A_{k_1}A_{k_2}\cdots A_{k_{n-1}},B_k{}^\dagger]_-\rangle_{t=t',\omega=\tilde{\omega}_k{}^0}. \quad (40d)$$

The expression (40b) for $P_b{}^{(1)}(k,\omega)$ consists of terms which are proportional to two-, three-, and many-phonon Green's functions having the form of

$$\langle\langle A_{k_1}A_{k_2}\cdots A_{k_{n-1}};\,A_{k_1'}{}^\dagger A_{k_2'}{}^\dagger\cdots A_{k_{n-1}'}{}^\dagger\rangle\rangle.$$

Wehner[9] and more recently Kwok[4] have developed methods for calculating the various many-phonon Green's functions by employing the functional derivative technique of Martin and Schwinger.[13] Although their expressions for the many-phonon Green's functions have a form similar to those appearing in (40b), they differ with respect to the expressions for the renormalized frequencies $\epsilon_k{}^0$. Complete agreement with the results of Wehner[9] and Kwok[4] is achieved only if the Eq. (40c) is replaced by

$$(\epsilon_k{}^0)^2\sim(\tilde{\omega}_k{}^0)^2+2\omega_k{}^0P_b{}^{(0)}(k,\omega_k{}^0), \quad (41)$$

also in the expression for $P_b{}^{(0)}(k,\omega_k{}^0)$ all the frequencies $\tilde{\omega}_k{}^0$ have been replaced by $\omega_k{}^0$ which are correct in the harmonic approximation. Having these approximations in mind, the one phonon Green's function (33) with $\epsilon_k\rightarrow\epsilon_k{}^0$ as well as the two- and three-phonon Green's functions appearing in (40b), which are correct in the first approximation, become identical to the corresponding ones derived by Wehner,[9] but the expression (40a) for $G_b{}^{(2)}(k,\omega)$ is correct in the second approximation. In conclusion, the developed formalism based on successive approximations, apart from its simplicity, succeeds in the renormalization of the frequencies for the phonon modes.

In discussing the polariton spectrum we have dealt only with the diagonal part of the polariton Green's function with respect to the polariton branch index ρ $(=\rho')$. To include nondiagonal contributions one can easily derive the following equation:

$$G_{\rho\rho'}(k,\omega)=G_{\rho\rho}(k,\omega)\times[\delta_{\rho\rho'}+\pi\sum_{\rho''\neq\rho'}\Pi_{\rho'\rho''}(k,\omega)G_{\rho''\rho'}(k,\omega)], \quad (42)$$

which can be solved by iteration.

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[13] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

IV. EXCITATION SPECTRUM

To study the excitation spectrum, we make use of the spectral function $J_k(\omega)$ given by the relation[11]

$$J_k(\omega)=2(1-e^{\beta\omega})^{-1}\,\mathrm{Im}G(k,\,\omega+i\eta)\,, \tag{43}$$

where Im stands for the imaginary part and η is a small positive quantity, $\eta\rightarrow 0+$. Substituting the imaginary part of (37) into (43), we obtain

$$J_k{}^{(2)}(\omega)=\left(\frac{2\omega_k}{\pi}\right)\frac{2\omega_k\Gamma_k{}^{(1)}(\omega)(e^{\beta\omega}-1)^{-1}}{[\omega^2-\nu_k{}^2]^2+4\omega_k{}^2(\Gamma_k{}^{(1)}(\omega))^2}\,, \tag{44}$$

where ν_k are the energies of excitation determined by the solutions of the equation

$$\nu_k{}^2-\epsilon_k{}^2-2\omega_k\Delta_k(\nu_k)=0\,; \tag{45}$$

$\Delta_k(\omega)=\mathrm{Re}P_k{}^{(1)}(\omega)$ is the real part of the polarization operator given by the expression (37), but now the principal value over the summations must be taken. In (44), $\Gamma_k{}^{(1)}(\omega)=\mathrm{Im}P^{(1)}(k,\omega)$ is the imaginary part of the polarization operator in the first approximation and is equal to

$$\begin{aligned}\Gamma^{(1)}(k,\omega)=\pi\sum_{k_1,k_2}\Big\llbracket&\{\tilde{Q}_3{}^{(+)}(k_1,\,k_2,\,-k;\,\omega)[\delta(\omega+\epsilon_{k_1}+\epsilon_{k_2})-\delta(\omega-\epsilon_{k_1}-\epsilon_{k_2})]\\&-2\hat{Q}_3{}^{(+)}(k_1,\,k_2,\,-k;\,\omega)[\delta(\omega+\epsilon_{k_1}+\epsilon_{k_2})+\delta(\omega-\epsilon_{k_1}-\epsilon_{k_2})]\}(\eta_{k_1}+\eta_{k_2})\\&+[\tilde{Q}_3{}^{(-)}(k_1,\,k_2,\,-k;\,\omega)(\delta(\omega+\epsilon_{k_1}-\epsilon_{k_2})-\delta(\omega-\epsilon_{k_1}+\epsilon_{k_2}))\\&-2\hat{Q}_3{}^{(-)}(k_1,\,k_2,\,-k;\,\omega)(\delta(\omega+\epsilon_{k_1}-\epsilon_{k_2})+\delta(\omega-\epsilon_{k_1}+\epsilon_{k_2}))](\eta_{k_1}-\eta_{k_2})\Big\rrbracket\\&+\pi\sum_{k_1,k_2,k_3}\{[\tilde{Q}_4{}^{(+)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\delta(\omega+\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3})-\delta(\omega-\epsilon_{k_1}-\epsilon_{k_2}-\epsilon_{k_3}))\\&-2\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\delta(\omega+\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3})+\delta(\omega-\epsilon_{k_1}-\epsilon_{k_2}-\epsilon_{k_3}))](1+\eta_{k_1}\eta_{k_2}+\eta_{k_2}\eta_{k_3}+\eta_{k_1}\eta_{k_3})\\&+[\tilde{Q}_4{}^{(-)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\delta(\omega+\epsilon_{k_1}-\epsilon_{k_2}-\epsilon_{k_3})-\delta(\omega-\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3}))\\&-2\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)(\delta(\omega+\epsilon_{k_1}-\epsilon_{k_2}-\epsilon_{k_3})+\delta(\omega-\epsilon_{k_1}+\epsilon_{k_2}+\epsilon_{k_3}))](1+\eta_{k_2}\eta_{k_3}-\eta_{k_1}\eta_{k_3}-\eta_{k_1}\eta_{k_2})\\&+(\epsilon_{k_2}\leftrightarrow-\epsilon_{k_2})+(\epsilon_{k_3}\leftrightarrow-\epsilon_{k_3})\}+(\text{terms with }n>4)\,.\end{aligned} \tag{46}$$

The spectral function (44) describes the polariton excitation spectrum in the whole range of frequencies ω.

As $\Gamma^{(1)}(k,\omega)$ goes to zero, the spectral function $J_k{}^{(2)}(\omega)$ tends to a delta-shape distribution, i.e.,

$$J_k{}^{(2)}(\omega)\approx 2\omega_k(e^{\beta\omega}-1)^{-1}\delta(\omega^2-\nu_k{}^2)\,, \tag{47}$$

where ν_k are the energies of the elementary excitations determined by the solutions of (45) with $\Delta_k(\nu_k)=P^{(1)}(k,\nu_k)$. The excitation spectrum given by (47) corresponds to the transparent range of frequencies of the crystal and the expression for $P^{(1)}(k,\nu_k)$, as shown by (37) with $\omega=\nu_k$, is the scattering amplitude in energy units describing the scattering processes that occur among the dressed polariton modes far from resonances. Integration of (47) over ω at $t=t'$ leads to the expression for the polariton distribution function correct in the second approximation as

$$\langle A_k{}^\dagger A_k\rangle^{(2)}=(\omega_k/\nu_k)\coth\tfrac{1}{2}\beta\nu_k\,.$$

In the limiting case where $\Gamma_k{}^{(1)}(\omega)$ may be considered to be very small but finite, $\Gamma_k{}^{(1)}(\omega)\ll\omega_k$, the spectral function (44) has a steep maximum at the frequencies $\omega^2=\nu_k{}^2$, provided that $\partial\Gamma_k{}^{(1)}(\omega)/\partial\omega\ll 1$ and $(\partial/\partial\omega)\Delta_k(\omega)\ll 1$. If it is further assumed that in the neighborhood of $\omega^2\sim\nu_k{}^2$ the function $\Gamma_k{}^{(1)}(\omega)$ varies slowly with ω, i.e., $\Gamma_k{}^{(1)}(\omega)\approx\Gamma_k{}^{(1)}(\nu_k)$, then (44) reduces to that describing the spectrum of the fundamental absoprtion band

$$J_k{}^{(2)}(\omega)\approx\left(\frac{2\omega_k}{\pi}\right)\frac{2\omega_k\Gamma_k{}^{(1)}(\nu_k)(e^{\beta\omega}-1)^{-1}}{(\omega^2-\nu_k{}^2)^2+4\omega_k{}^2(\Gamma_k{}^{(1)}(\nu_k))^2}\,. \tag{48}$$

The function (48) is a Lorentzian line with a maximum at $\omega^2=\nu_k{}^2$, the energy shift is equal to $(\nu_k{}^2-\omega_k{}^2)^{1/2}$ and the width is of the order of $\Gamma_k{}^{(1)}(\nu_k)$ in energy units, provided that the frequency ν_k satisfies at least one of the arguments of the delta function appearing in (46). It should be pointed out that in evaluating (48) from (44) the ω dependence of the functions $\Gamma_k{}^{(1)}(\omega)$ and $\Delta_k(\omega)$ has been neglected. If the variation of $\Gamma_k{}^{(1)}(\omega)$ and $\Delta_k(\omega)$ with respect to ω is taken into consideration then, apart from the appearance of the combination bands which arise from the derivatives of the delta functions with respect to ω, there will appear new peaks and possibly the shape of the absorption band may change as a result of the ω-dependent terms in the coupling functions of (46) and $\Delta_k(\omega)$. Therefore, for an accurate calculation of the excitation spectrum (44) for a specific crystal the ω-dependence of $\Gamma_k{}^{(1)}(\omega)$ and $\Delta_k(\omega)$ must be examined with care. Further, the possibility of observing these new peaks depends on the numerical value of the quantity $(\tilde{\phi}_n/\omega_k)$.

For values of frequencies ω not near ν_k, that is, in the vicinity of the edges of the polariton absorption bands, we may discard $(\Gamma_k{}^{(1)}(\omega))^2$ from the denominator of (44) with the result

$$J_k{}^{(2)}(\omega)\approx\left(\frac{2\omega_k}{\pi}\right)\frac{2\omega_k\Gamma_k{}^{(1)}(\omega)(e^{\beta\omega}-1)^{-1}}{[\omega^2-\epsilon_k{}^2-2\omega_k\Delta_k(\omega)]^2}\,. \tag{49}$$

If now the expression $\Gamma_k{}^{(1)}(\omega)$ given by (46) is written as

$$\Gamma_k^{(1)}(\omega)=\gamma_1(k,\omega)+\omega^2\gamma_2(k,\omega)+\omega\gamma_3(k,\omega)\,, \tag{50}$$

where the functions $\gamma_1(k,\omega)$, $\gamma_2(k,\omega)$, and $\gamma_3(k,\omega)$ depend on ω only through the delta functions that appear in (46), then substitution of (50) into (49) leads to

$$J_k^{(2)}(\omega)\approx\left(\frac{2\omega_k}{\pi}\right)\times\frac{2\omega_k[\gamma_1(k,\omega)+\omega^2\gamma_2(k,\omega)+\omega\gamma_3(k,\omega)](e^{\beta\omega}-1)^{-1}}{[\omega^2-\epsilon_k^2-2\omega_k\Delta_k(\omega)]^2}. \tag{51a}$$

For large ω the expression (51a) may be written as

$$J_k^{(2)}(\omega)\sim\left(\frac{4\omega_k^2}{\pi}\right)(e^{\beta\omega}-1)^{-1}\times[\omega^{-2}\gamma_2(k,\omega)+\omega^{-3}\gamma_3(k,\omega)+\omega^{-4}\gamma_1(k,\omega)]\,, \tag{51b}$$

where the functions $\gamma_2(k,\omega)$, $\gamma_3(k,\omega)$, and $\gamma_1(k,\omega)$ consist of the anharmonic coupling functions of the general form $|\tilde{\phi}_n|^2$, $\tilde{V}_n\tilde{\phi}_n$, and $|\tilde{V}_n|^2$, respectively. Therefore, $\omega^{-2}\gamma_2(k,\omega)$ is the dominant term in the neighborhood of the edges of the polariton fundamental absorption bands, where $\omega^2-\epsilon_k^2\gg 2\omega_k\Delta_k(\omega)$, indicating the importance of the function $|\tilde{\phi}_n|^2$; such behavior could be observed for large values of ω.

For the renormalized bare phonon spectrum, the spectral function (44) becomes

$$J_b^{(2)}(k,\omega)=\left(\frac{2\omega_k^0}{\pi}\right)\frac{2\omega_k^0\Gamma_b^{(1)}(k,\omega)(e^{\beta\omega}-1)^{-1}}{[\omega^2-(\nu_k^0)^2]^2+4(\omega_k^0)^2(\Gamma_b^{(1)}(k,\omega))^2}\,, \tag{52}$$

where the energies of excitation ν_k^0 are given by the solutions of the equation

$$(\nu_k^0)^2-(\epsilon_k^0)^2-2\omega_k^0\Delta_k^0(\nu_k^0)=0\,, \tag{53}$$

with $\Delta_k^0(\omega)=\mathrm{Re}P_b^{(1)}(k,\omega)$ and the imaginary part of $P_b^{(1)}(k,\omega)=\Gamma_b^{(1)}(k,\omega)$ is given by

$$\begin{aligned}\Gamma_b^{(1)}(k,\omega)=9\pi\sum_{k_1,k_2}|V_3(k_1,\,k_2,\,-k)|^2\left(\frac{\omega_{k_1}^0\omega_{k_2}^0}{\epsilon_{k_1}^0\epsilon_{k_2}^0}\right)\\ \times\{(\eta_{k_1}^0+\eta_{k_2}^0)[\delta(\omega+\epsilon_{k_1}^0+\epsilon_{k_2}^0)-\delta(\omega-\epsilon_{k_1}^0-\epsilon_{k_2}^0)]+(\eta_{k_2}^0-\eta_{k_1}^0)[\delta(\omega+\epsilon_{k_1}^0-\epsilon_{k_2}^0)-\delta(\omega-\epsilon_k^0+\epsilon_{k_2}^0)]\}\\ +24\pi\sum_{k_1,k_2,k_3}|V_4(k_1,\,k_2,\,k_3,\,-k)|^2\left(\frac{\omega_{k_1}^0\omega_{k_2}^0\omega_{k_3}^0}{\epsilon_{k_1}^0\epsilon_{k_2}^0\epsilon_{k_3}^0}\right)\{(1+\eta_{k_1}^0\eta_{k_2}^0+\eta_{k_2}^0\eta_{k_3}^0+\eta_{k_1}^0\eta_{k_3}^0)\\ \times[\delta(\omega+\epsilon_{k_1}^0+\epsilon_{k_2}^0+\epsilon_{k_3}^0)-\delta(\omega-\epsilon_{k_1}^0-\epsilon_{k_2}^0-\epsilon_{k_3}^0)]+3(1+\eta_{k_2}^0\eta_{k_3}^0-\eta_{k_1}^0\eta_{k_3}^0-\eta_{k_1}^0\eta_{k_2}^0)\\ \times[\delta(\omega+\epsilon_{k_1}^0-\epsilon_{k_2}^0-\epsilon_{k_3}^0)-\delta(\omega-\epsilon_{k_1}^0+\epsilon_{k_2}^0+\epsilon_{k_3}^0)]\}+(\text{terms with } n>4)\,.\end{aligned} \tag{54}$$

The renormalized phonon spectrum described by (52) is completely different from that derived by means of diagram techniques.[10] The main difference is due to the appearance of the complete renormalization of the frequencies for each particular mode in the expression (52). Agreement with the results of previous studies[10,14] is achieved only when all the renormalized effects are ignored, i.e., all the ϵ_k^0's in the expressions appearing in (52) have to be replaced by the ω_k^0's. Formulas (52)–(54) are reduced to those derived by Kashcheev[15] if the factors

$$(\omega_{k_1}^0\omega_{k_2}^0/\epsilon_{k_1}^0\epsilon_{k_2}^0)$$

and

$$(\omega_{k_1}^0\omega_{k_2}^0\omega_{k_3}^0/\epsilon_{k_1}^0\epsilon_{k_2}^0\epsilon_{k_3}^0)$$

are taken equal to unity and the energies of excitation ϵ_k^0's are replaced by $\tilde{\omega}_k^0$'s with the expression for $\tilde{\omega}_k^0$ including only quartic anharmonic contributions for each particular frequency mode.

As far as the temperature dependence for the excitation spectrum (44) or (52) is concerned, the renormalization effects are twofold: firstly, the renormalized frequencies for the polariton (or the bare phonon) modes are temperature dependent and, secondly, the factors of the general form

$$(\omega_{k_1}\omega_{k_2}\cdots\omega_{k_n}/\epsilon_{k_1}\epsilon_{k_2}\cdots\epsilon_{k_n})$$

and

$$(\epsilon_{k_1}\omega_{k_2}\omega_{k_3}\cdots\omega_{k_n}/\omega_{k_1}\epsilon_{k_2}\epsilon_{k_3}\cdots\epsilon_{k_n})$$

that appear in the expressions for the real and imaginary parts of the polarization operator change the temperature dependence of the frequency shift and spectral width of the absorption bands. Therefore, it is evident that the renormalization effects are important in connection with the temperature variations as well as the quantitative calculations[16] of the frequency shift and spectral width of the fundamental infrared absorption spectra of ionic crystals.

It is easy to see from (16) that one of the effects of taking into account the intrinsic coupling between the radiation field and the transverse optical phonons, when $k\sim10^3$ cm^{-1}, is to reduce the magnitudes of the anharmonic coupling functions $V_n(k_1,k_2,\cdots,k_n)$. A

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[14] V. N. Kashcheev, Fiz. Tverd. Tela 5, 1358 (1963) [English transl.: Soviet Phys.—Solid State 5, 988 (1963)].

[15] V. N. Kashcheev, Fiz. Tverd. Tela 5, 2339 (1963) [English transl.: Soviet Phys.—Solid State 5, 1700 (1964)].

[16] I. P. Ipatova, A. A. Maradudin, and R. F. Wallis, Phys. Rev. **155**, 882 (1967).

rough estimate, for the ratio of the square of the cubic anharmonic coefficient with and without retardation is of the order of

$$|\tilde{V}_3/V_3|^2 \sim \left(\frac{\omega_T\omega_k\omega_p^2}{(\omega_T^2-\omega_k^2)^2+\omega_T^2\omega_p^2}\right)^3, \tag{55}$$

where $\omega_T \sim \omega_k^0$ is the frequency for the transverse optical phonons. In the absence of retardation $\omega_k \sim \omega_T$ the right-hand side of (55) is equal to unity. However, in the long wavelength region $k \sim 10^3$ cm^{-1}, the frequency ω_k for the two polariton branches may be taken to be of the order of $\frac{1}{2}\omega_T$ and ω_L, respectively, where ω_L is the longitudinal frequency for optical phonons. Moreover, if we consider that for NaCl $\omega_L^2 \sim 2\omega_T^2$, then the right-hand side of (55) is roughly of the order of 0.12, that is, the square of the magnitude of the cubic anharmonic coefficient, $|V_3|^2$, is decreased by about 12% due to retardation. Similarly, the square of the quartic coefficient is decreased roughly by 6%. Of course, these are only rough estimates; the computation of the results obtained in the present study concerning the polariton as well as the phonon excitation spectrum shall be reported later.

V. CONCLUSION

The present study is concerned with the excitation spectrum of interacting polaritons in the infrared range of frequencies of dielectric crystals. The development of Dyson's equation describing the polariton spectrum has made possible the evaluation of the polarization operator and the polariton Green's function in successive and well-defined approximations. The spectral function for the polariton spectrum has been calculated in the second approximation and expressed in terms of the renormalized polariton frequencies. The temperature-dependent effects on the excitation spectrum arising from the renormalization of the frequencies for the polariton modes have been pointed out. The importance of the retardation effects have been discussed in detail. In the case where retardation effects may be neglected the resulting expressions for the phonon excitation spectrum have been compared with those appearing in the literature.

It is hoped that this work will stimulate an interest in measuring the polariton lifetime by Raman scattering experiments.

APPENDIX

We wish to carry out the evaluation of the two- and three-particle Green's functions by means of the zeroth-order renormalized Hamiltonian (31). If we introduce the operator which is a four-component row vector

$$\tilde{A}^\dagger(k_1',k_2') \equiv (A_{k_1'}{}^\dagger A_{k_2'}{}^\dagger \quad A_{k_1'}{}^\dagger B_{k_2'}{}^\dagger \quad B_{k_1'}{}^\dagger A_{k_2'}{}^\dagger \quad B_{k_1'}{}^\dagger B_{k_2}{}^\dagger), \tag{A1}$$

then using (31) we derive the equation of motion for the Green's function $\langle\langle \tilde{A}(k_1,k_2); \tilde{A}^\dagger(k_1',k_2')\rangle\rangle$, which is in a matrix form, as

$$L(k_1,k_2;\omega)\langle\langle \tilde{A}(k_1,k_2); \tilde{A}^\dagger(k_1',k_2')\rangle\rangle = (1/2\pi)\langle[\tilde{A}(k_1,k_2),\tilde{A}^\dagger(k_1',k_2')]_-\rangle_{t=t'}, \tag{A2}$$

where $L(k_1,k_2;\omega)$ is a four-by-four matrix whose nonzero matrix elements are given by

$$\begin{aligned} &L_{11}=L_{22}=L_{33}=L_{44}=\omega; \quad L_{12}=L_{34}=-\omega_{k_2}; \\ &L_{13}=L_{24}=-\omega_{k_1}; \quad L_{21}=L_{43}=-\tilde{\omega}_{k_2}{}^2/\omega_{k_2}; \\ &L_{31}=L_{42}=-\tilde{\omega}_{k_1}{}^2/\omega_{k_1}. \end{aligned} \tag{A3}$$

The determinant of the matrix $L(k_1,k_2;\omega)$ is found to be

$$\det L(k_1,k_2;\omega) = [\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2] \times [\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2], \tag{A4}$$

which gives the poles of the Green's function

$$\langle\langle \tilde{A}(k_1,k_2); \tilde{A}^\dagger(k_1',k_2')\rangle\rangle.$$

Solving Eqs. (A2) we obtain the following expression for the various two-particle Green's functions:

$$\begin{aligned} \langle\langle A_{k_1}A_{k_2}; A_{k_1'}{}^\dagger A_{k_2'}{}^\dagger\rangle\rangle = \frac{1}{2\pi}\left(\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\right)\Bigg[(\tilde{\eta}_{k_1}+\tilde{\eta}_{k_2})\frac{(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2} \\ +(\tilde{\eta}_{k_2}-\tilde{\eta}_{k_1})\frac{(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})}{\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2}\Bigg](\delta_{k_1k_1'}\delta_{k_2k_2'}+\delta_{k_1k_2'}\delta_{k_2k_1'}), \end{aligned} \tag{A5a}$$

$$\begin{aligned} \langle\langle B_{k_1}A_{k_2}; A_{k_2'}{}^\dagger B_{k_1'}{}^\dagger\rangle\rangle = \frac{1}{2\pi}\left(\frac{\tilde{\omega}_{k_1}\omega_{k_2}}{\omega_{k_1}\tilde{\omega}_{k_2}}\right)\left\{(\tilde{\eta}_{k_1}+\tilde{\eta}_{k_2})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2}+(\tilde{\eta}_{k_2}-\tilde{\eta}_{k_1})\frac{\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2}\right\}\delta_{k_1k_1'}\delta_{k_2k_2'} \\ +\frac{1}{2\pi}\left\{(\tilde{\eta}_{k_1}+\tilde{\eta}_{k_2})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2}-(\tilde{\eta}_{k_2}-\tilde{\eta}_{k_1})\frac{\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2}\right\}\delta_{k_2'k_1}\delta_{k_1'k_2}, \end{aligned} \tag{A5b}$$

$$\begin{aligned} \langle\langle A_{k_1}A_{k_2}; A_{k_2'}{}^\dagger B_{k_1'}{}^\dagger\rangle\rangle = \frac{1}{2\pi}\left(\frac{\omega_{k_2}\omega}{\tilde{\omega}_{k_2}}\right)\left[\frac{(\tilde{\eta}_{k_1}+\tilde{\eta}_{k_2})}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2}+\frac{(\tilde{\eta}_{k_2}-\tilde{\eta}_{k_1})}{\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2}\right]\delta_{k_1'}\delta_{k_1}\delta_{k_2'k_2} \\ +\frac{1}{2\pi}\left(\frac{\omega_{k_1}\omega}{\tilde{\omega}_{k_1}}\right)\left[\frac{\tilde{\eta}_{k_1}+\tilde{\eta}_{k_2}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2})^2}-\frac{\tilde{\eta}_{k_2}-\tilde{\eta}_{k_1}}{\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2})^2}\right]\delta_{k_1'k_2}\delta_{k_2'k_1}, \end{aligned} \tag{A5c}$$

where $\tilde{\eta}_{k_1}=\coth\frac{1}{2}\beta\tilde{\omega}_{k_1}$ and $\beta=(\kappa_B T)^{-1}$, κ_B being the Boltzmann constant and T the absolute temperature. In evaluating (A5) from (A2) we have made use of

$$\langle A_{k_1}{}^\dagger A_{k_1}\rangle^{(0)}=(\omega_{k_1}/\tilde{\omega}_{k_1})\coth\tfrac{1}{2}\beta\tilde{\omega}_{k_1},\quad \langle B_{k_1}{}^\dagger B_{k_1}\rangle^{(0)}=(\tilde{\omega}_{k_1}/\omega_{k_1})\coth\tfrac{1}{2}\beta\tilde{\omega}_{k_1},$$

and

$$\langle A_{k_2}{}^\dagger A_{k_2}\rangle^{(0)}=(\omega_{k_2}/\tilde{\omega}_{k_2})\coth\tfrac{1}{2}\beta\tilde{\omega}_{k_2}$$

for the distribution functions in the lowest approximation.

Similarly, if the operator $\tilde{A}^\dagger(k_1',k_2',k_3')$ is defined as the row vector

$$\begin{aligned}\tilde{A}^\dagger(k_1',k_2',k_3')\equiv(&A_{k_1'}{}^\dagger A_{k_2'}{}^\dagger A_{k_3'}{}^\dagger \quad B_{k_1'}{}^\dagger A_{k_2'}{}^\dagger A_{k_3'}{}^\dagger \quad A_{k_1'}{}^\dagger B_{k_2'}{}^\dagger A_{k_3'}{}^\dagger \quad A_{k_1'}{}^\dagger A_{k_2'}{}^\dagger B_{k_3'}{}^\dagger\\ &B_{k_1'}{}^\dagger B_{k_2'}{}^\dagger A_{k_3'}{}^\dagger \quad A_{k_1'}{}^\dagger B_{k_2'}{}^\dagger B_{k_3'}{}^\dagger \quad B_{k_1'}{}^\dagger A_{k_2'}{}^\dagger B_{k_3'}{}^\dagger \quad B_{k_1'}{}^\dagger B_{k_2'}{}^\dagger B_{k_3'}{}^\dagger),\end{aligned}\tag{A6}$$

then by means of (31) we derive the equation of motion

$$L(k_1,k_2,k_3;\,)\langle\langle\tilde{A}(k_1,k_2,k_3);\tilde{A}^\dagger(k_1',k_2',k_3')\rangle\rangle=1/2\pi\langle[\tilde{A}(k_1,k_2,k_3),\tilde{A}^\dagger(k_1',k_2',k_3')]_-\rangle_{t=t'},\tag{A7}$$

where $L(k_1,k_2,k_3;\omega)$ is an eight-by-eight matrix having all diagonal elements equal to ω while the nonzero off-diagonal elements are given by

$$L_{12}=L_{35}=L_{47}=L_{68}=-\omega_{k_1};\quad L_{13}=L_{25}=L_{46}=L_{78}=-\omega_{k_2};\quad L_{14}=L_{27}=L_{36}=L_{58}=-\omega_{k_3};$$

$$L_{21}=L_{53}=L_{74}=L_{86}=-\tilde{\omega}_{k_1}{}^2/\omega_{k_1};\quad L_{31}=L_{52}=L_{64}=L_{87}=-\tilde{\omega}_{k_2}{}^2/\omega_{k_2};\quad L_{41}=L_{63}=L_{72}=L_{85}=-\tilde{\omega}_{k_3}{}^2/\omega_{k_3}.$$

The determinant of the matrix $L(k_1,k_2,k_3;\omega)$ factorizes into

$$\begin{aligned}\det L(k_1,k_2,k_3;\omega)=&[\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2][\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})^2]\\ &\times[\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2][\omega^2-(\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3}-\tilde{\omega}_{k_1})^2],\end{aligned}\tag{A8}$$

and describes the poles of the Green's function $\langle\langle\tilde{A}(k_1,k_2,k_3);\tilde{A}^\dagger(k_1',k_2',k_3')\rangle\rangle$. Solving the system of equations (A7) and after some lengthy algebra, we derive the following expressions for the three-particle Green's functions:

$$\begin{aligned}\langle\langle A_{k_1}A_{k_2}A_{k_3};A_{k_1'}{}^\dagger A_{k_2'}{}^\dagger A_{k_3'}{}^\dagger\rangle\rangle=&\left(\frac{\delta}{4\pi}\right)\left(\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}\right)\{(1+\tilde{\eta}_{k_1}\tilde{\eta}_{k_2}+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}+\tilde{\eta}_{k_1}\tilde{\eta}_{k_3})\\ &\times(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})[\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2]^{-1}+(1+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_3}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_2})\\ &\times(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})[\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})^2]^{-1}+(\tilde{\omega}_{k_2}\leftrightarrow-\tilde{\omega}_{k_2})+(\tilde{\omega}_{k_3}\leftrightarrow-\tilde{\omega}_{k_3})\},\end{aligned}\tag{A9a}$$

$$\begin{aligned}\langle\langle B_{k_1}A_{k_2}A_{k_3};A_{k_1'}{}^\dagger A_{k_2'}{}^\dagger A_{k_3'}{}^\dagger\rangle\rangle=&\left(\frac{\omega\delta}{4\pi}\right)\left(\frac{\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}\right)\{(1+\tilde{\eta}_{k_1}\tilde{\eta}_{k_2}+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}+\tilde{\eta}_{k_1}\tilde{\eta}_{k_3})[\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2]^{-1}\\ &+(1+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_2}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_3})[\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})^2]^{-1}+(\tilde{\omega}_{k_2}\leftrightarrow-\tilde{\omega}_{k_2})+(\tilde{\omega}_{k_3}\leftrightarrow-\tilde{\omega}_{k_3})\},\end{aligned}\tag{A9b}$$

$$\begin{aligned}\langle\langle B_{k_1}A_{k_2}A_{k_3};A_{k_3'}{}^\dagger A_{k_2'}{}^\dagger B_{k_1'}{}^\dagger\rangle\rangle=&\frac{1}{4\pi}\left(\frac{\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}\right)\{(1+\tilde{\eta}_{k_1}\tilde{\eta}_{k_2}+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}+\tilde{\eta}_{k_3}\tilde{\eta}_{k_1})\\ &\times\left(\frac{\tilde{\omega}_{k_1}}{\omega_{k_1}}\delta_{123}+\frac{\tilde{\omega}_{k_2}}{\omega_{k_2}}\delta_{213}+\frac{\tilde{\omega}_{k_3}}{\omega_{k_3}}\delta_{321}\right)(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})[\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2]^{-1}\\ &+(1+\tilde{\eta}_{k_2}\tilde{\eta}_{k_3}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_3}-\tilde{\eta}_{k_1}\tilde{\eta}_{k_2})\left(\frac{\tilde{\omega}_{k_1}}{\omega_{k_1}}\delta_{123}-\frac{\tilde{\omega}_{k_2}}{\omega_{k_2}}\delta_{213}-\frac{\tilde{\omega}_{k_3}}{\omega_{k_3}}\delta_{321}\right)(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})\\ &\times[\omega^2-(\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})^2]^{-1}+(\tilde{\omega}_{k_2}\leftrightarrow-\tilde{\omega}_{k_2})+(\tilde{\omega}_{k_3}\leftrightarrow-\tilde{\omega}_{k_3})\},\end{aligned}\tag{A9c}$$

where

$$\delta\equiv\delta_{123}+\delta_{213}+\delta_{321},\quad \delta_{123}\equiv\delta_{k_1'k_1}\delta_{k_2'k_2}\delta_{k_3'k_3}+\delta_{k_3'k_2}\delta_{k_1'k_1}\delta_{k_2'k_3},\tag{A9d}$$

δ_{213} and δ_{321} are obtained from δ_{123} by interchanging k_1 and k_2 and k_1 and k_3, respectively. In (A9) we have indicated by $(\tilde{\omega}_{k_2}\leftrightarrow-\tilde{\omega}_{k_2})$ and $(\tilde{\omega}_{k_3}\leftrightarrow-\tilde{\omega}_{k_3})$ that there are two further terms obtained by interchanging $\tilde{\omega}_{k_2}$ and $-\tilde{\omega}_{k_2}$, $\tilde{\omega}_{k_3}$, and $-\tilde{\omega}_{k_3}$ in the first term, respectively.

If we substitute the two- and three-polariton Green's functions given by (A5) and (A9) into (27) we obtain the expression (32) for the polarization operator $P^{(0)}(k,\omega)$, where the coupling functions

$$\tilde{Q}_3^{(\pm)}(k_1,\,k_2,\,-k;\,\omega),\quad \hat{Q}_3^{(\pm)}(k_1,\,k_2,\,-k;\,\omega),\quad \hat{Q}_4^{(\pm)}(k_1,\,k_2,\,k_3,\,-k;\,\omega),\quad \text{and}\quad \hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)$$

have been defined as follows:

$$\begin{aligned}\tilde{Q}_3^{(\pm)}(k_1,\,k_2,\,-k;\,\omega)=\tfrac{1}{2}\sum_{k_1',k_2'}\Big[&Q_3(k_1,\,k_2,\,-k;\,\omega)Q_3^*(k_1',\,k_2',\,-k;\,\omega)(\delta_{k_1'k_1}\delta_{k_2'k_2}+\delta_{k_1'k_2}\delta_{k_2'k_1})\\&+4\left(\frac{\tilde{\omega}_{k_1}}{\omega_{k_1}}\right)\tilde{\phi}_3(k_1,\,k_2,\,-k)\tilde{\phi}_3^*(k_1',\,k_2',\,-k)\left(\frac{\tilde{\omega}_{k_1}}{\omega_{k_1}}\delta_{k_1'k_1}\delta_{k_2'k_2}\pm\frac{\tilde{\omega}_{k_2}}{\omega_{k_2}}\delta_{k_1'k_2}\delta_{k_2'k_1}\right)\Big]\left(\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\right),\end{aligned}\tag{A10a}$$

$$\hat{Q}_3^{(\pm)}(k_1,\,k_2,\,-k;\,\omega)=2\sum_{k_1',k_2'}Q_3(k_1,\,k_2,\,-k;\,\omega)\tilde{\phi}_3^*(k_1',\,k_2',\,-k)\left(\frac{\tilde{\omega}_{k_1}}{\omega_{k_1}}\delta_{k_1'k_1}\delta_{k_2'k_2}\pm\frac{\tilde{\omega}_{k_2}}{\omega_{k_2}}\delta_{k_1'k_2}\delta_{k_2'k_1}\right)\left(\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\right),\tag{A10b}$$

$$\begin{aligned}\tilde{Q}_4^{(\pm)}(k_1,\,k_2,\,k_3,\,-k;\,\omega)=\tfrac{1}{4}\sum_{k_1',k_2',k_3'}\Big[&Q_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)Q_4^*(k_1',\,k_2',\,k_3',\,-k;\,\omega)\delta\\&+9\left(\frac{\tilde{\omega}_{k_1}}{\omega_{k_1}}\right)\tilde{\phi}_4(k_1,\,k_2,\,k_3,\,-k)\tilde{\phi}_4^*(k_1',\,k_2',\,k_3',\,-k)\left(\frac{\tilde{\omega}_{k_1}}{\omega_{k_1}}\delta_{123}\pm\frac{\tilde{\omega}_{k_2}}{\omega_{k_2}}\delta_{213}\pm\frac{\tilde{\omega}_{k_3}}{\omega_{k_3}}\delta_{321}\right)\Big]\left(\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}\right),\end{aligned}\tag{A10c}$$

$$\hat{Q}_4(k_1,\,k_2,\,k_3,\,-k;\,\omega)=\tfrac{3}{4}\sum_{k_1',k_2',k_3'}\tilde{\phi}_4(k_1,\,k_2,\,k_3,\,-k)Q_4^*(k_1',\,k_2',\,k_3',\,-k;\,\omega)\left(\frac{\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}\right)\delta.\tag{A10d}$$

In general, using the Hamiltonian (31) or (35) one can derive the equation of motion

$$\begin{aligned}L(k_1,k_2,k_3,\cdots,k_n;\,\omega)\langle\langle\tilde{A}(k_1,k_2,k_3,\cdots,k_n);\,\tilde{A}_k^\dagger(k_1',k_2',k_3',\cdots,k_n')\rangle\rangle\\=(1/2\pi)\langle[\tilde{A}(k_1,k_2,k_3,\cdots,k_n),\tilde{A}^\dagger(k_1',k_2',k_3',\cdots,k_n')]_-\rangle_{t=t'},\end{aligned}\tag{A11}$$

where the operator $\tilde{A}^\dagger(k_1,k_2,k_3,\cdots,k_n)$ is now a row vector having 2^n components of the form of

$$\begin{aligned}\tilde{A}_k^\dagger(k_1,k_2,k_2,k_3,\cdots,k_n)\equiv(A_{k_1}^\dagger A_{k_2}^\dagger\cdots A_{k_n}^\dagger\quad B_{k_1}^\dagger A_{k_2}^\dagger\cdots A_{k_n}^\dagger\quad A_{k_1}^\dagger B_{k_2}^\dagger A_{k_3}^\dagger\cdots A_{k_n}^\dagger\quad\cdots\cdots\\B_{k_1}^\dagger B_{k_2}^\dagger\cdots B_{k_{n-1}}^\dagger A_{k_n}^\dagger\quad B_{k_1}^\dagger B_{k_2}^\dagger\cdots B_{k_{n-1}}^\dagger B_{k_n}^\dagger)\end{aligned}\tag{A12}$$

and $L(k_1,k_2,k_3,\cdots,k_n;\,\omega)$ is a $2^n\times 2^n$ matrix with all diagonal elements equal to ω while the nonzero off-diagonal elements are easily established, but they shall not be given here. Solving the system of Eqs. (A10) it is possible, in principle, to calculate polariton Green's functions for any desired value of n. In practice for n greater than three, though the calculation of the corresponding Green's functions is straightforward, the algebra is tedious.