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# Optical Excitation Spectrum of Interacting Polariton Waves in Molecular Crystals*

C. Mavroyannis
*Division of Pure Chemistry, National Research Council, Ottawa, Canada*

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In the optical region of frequencies, the excitation spectrum of interacting polariton waves in molecular crystals has been studied by means of the polariton Hamiltonian, which includes both cubic and quartic anharmonic terms with respect to the polariton operators. A general expression for Dyson's equation is developed which describes the system of interacting polariton fields and the polarization operator is a function of two-, three-, and mixed-polariton Green's functions. The polarization operator and, therefore, the polariton Green's function is then evaluated in successive approximations. In the zero approximation, the quartic anharmonic terms in the polariton Hamiltonian renormalize the frequencies of each polariton mode. The polarization operator is calculated in the lowest order via a zeroth-order renormalized Hamiltonian; the derived expression contains terms arising from the cubic and quartic anharmonicity and is a function of the renormalized frequencies of the polariton modes. In this approximation, the spectral function for the polariton spectrum is found to have a shape of an asymmetric Lorentzian line when the frequency dependence of the energy shift and spectral width is neglected. Resonances occur (i) when either two renormalized polaritons are created or one is created and the other is absorbed (two-polariton process), and (ii) when three renormalized polaritons are created or two are created and one is absorbed (three-polariton process) by a single incident renormalized polariton and vice versa. Formulas are derived for the probability amplitudes corresponding to the third- and fourth-order nonlinear scattering processes in the transparent range of frequencies of the crystal; an expression for the energy of excitation is developed where the frequency of the polariton mode is dressed by the field of all the others in the first approximation and propagates in the crystal without damping. A discussion is given on how the derived results can be improved by calculating the polarization operator in the next order in such a self-consistent manner as to become a function of the frequencies of the polariton modes, which are correct in the first approximation.

## I. INTRODUCTION

In general, polariton waves in crystals consist of quasiparticles, which propagate in the medium with definite energy and momentum that satisfy the linear Maxwell equations. In the optical region of frequencies of molecular crystals, polaritons are defined in the lowest approximation[1] as tightly bound electron-hole pairs dressed by photons of the electromagnetic field. In mathematical language, the exact diagonalization of the bare exciton Hamiltonian of the crystal plus the interaction with the transverse electromagnetic field in the lowest approximation, i.e., when the anharmonic part of the total Hamiltonian due to scattering processes is neglected, leads to normal electromagnetic (polariton) waves in the crystal which satisfy the microscopic Maxwell equations. The diagonalization can be achieved either by means of Bogoliubov's canonical transformation[1,2] or the Green's-function method.[3]

The propagation of polariton waves in the medium is damped. In pure crystals and at finite temperatures, the damping is mainly caused by the interaction of polaritons with the acoustic phonon field of the crystal[4]; this process governs the optical absorption bands in molecular crystals.[4] At zero temperature, polaritons are either scattered by bare excitons[5] or interact with each other, and both processes lead to the appearance of nonlinear optical effects. Scattering by impurities and defects are possible mechanisms as well. The kinematic interaction of the bare exciton waves in molecular crystals leading to an energy spectrum which has acoustic dispersion and the possible appearance of Bose-Einstein exciton condensation has been recently studied by Agranovich and Toshich.[6]

The purpose of the present work is to formulate a general theory concerning the optical excitation spectrum of molecular crystals arising from the interaction of polariton waves with each other at zero temperature. In Sec. II, the equations of motion for the polariton Green's function, which is in a matrix form, are derived with respect to both time arguments; use has been made of the polariton Hamiltonian consisting of the unperperturbed part plus the interaction Hamiltonian that includes both cubic and quartic anharmonic terms with respect to the polariton operators. Then, Dyson's equation for the polariton spectrum is developed and the polarization operator is a function of two-, three-, and mixed-polariton Green's functions.

A general formula for the polariton Green's function is derived in Sec. III and then is evaluated in successive approximations. In the zero approximation, the unperturbed polariton energy is renormalized and the renormalization is caused by the quartic anharmonic terms of the interaction Hamiltonian. A renormalized zeroth-order Hamiltonian is constructed and is used to calcu-

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[1] V. M. Agranovich, Zh. Eksperim. i Teor. Fiz. **37**, 430 (1959) [English transl.: Soviet Phys.—JETP **10**, 307 (1960)].

[2] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

[3] C. Mavroyannis, J. Math. Phys. **8**, 1515 (1967).

[4] C. Mavroyannis, J. Math. Phys. **11**, 491 (1970).

[5] C. Mavroyannis, J. Math. Phys. **8**, 1522 (1967).

[6] V. M. Agranovich and B. S. Toshich, Zh. Eksperim. i Teor. Fiz. **53**, 149 (1967) [English transl.: Soviet Phys.—JETP **26**, 104 (1968)].

late the polarization operator in the lowest order. In this approximation, the expression for the polarization operator contains terms due to the cubic and quartic anharmonicity whose energy denominators give rise to poles which are equal to $\tilde{\omega}_{\rho_1}(\mathbf{q})\pm\tilde{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$ and $\tilde{\omega}_{\rho_1}(\mathbf{k}_1)\pm\tilde{\omega}_{\rho_2}(\mathbf{q})\pm\tilde{\omega}_{\rho_3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)$, respectively, where $\tilde{\omega}_{\rho_1}(\mathbf{q})$ is the renormalized frequency of the $\rho_1$th polariton mode with wave vector $\mathbf{q}$. The poles at the frequencies $\tilde{\omega}_{\rho_1}(\mathbf{q})-\tilde{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$ and $\tilde{\omega}_{\rho_1}(\mathbf{k}_1)-\tilde{\omega}_{\rho_2}(\mathbf{q})+\tilde{\omega}_{\rho}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)$ arise entirely from the renormalization procedure.

The spectral function for the polariton spectrum is calculated in Sec. IV by considering the imaginary part of the polariton Green's function in the first approximation. The spectral function is found to have the shape of an asymmetric Lorentzian line in the region of frequencies where both the real part of the polarization operator and the damping function vary slowly with respect to frequency. Formulas are developed for the energy shift and the width of the resonance line. Resonances occur when frequencies equal to either $\tilde{\omega}_{\rho_1}(\mathbf{q})\pm\tilde{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$ or $\tilde{\omega}_{\rho_1}(\mathbf{k}_1)\pm\tilde{\omega}_{\rho_2}(\mathbf{q})\pm\tilde{\omega}_{\rho_3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)$ are created or annihilated by a single renormalized polariton and vice versa. Far from resonance, the form of the spectral function has been considered.

In the transparent region of frequencies of the crystal an expression is obtained for the energy of the polariton mode in the first approximation which represents an elementary excitation (physical polariton), where the polariton mode is dressed by the field of all the others and propagates in the medium without damping. In this case, the obtained expressions for the probability amplitudes corresponding to the third- and fourth-order nonlinear optical processes can be reduced, after making some approximations, to describe the specific problems studied by Toshich.[7] Finally, the derived results are improved by considering the polariton Green's function in the second approximation. The Green's functions, that contained in the expression for the polarization operator, are calculated by means of an equivalent first-order Hamiltonian in such self-consistent manner so that in the final result the polarization operator is expressed as a function of the polariton frequencies, which are correct in the first approximation.

## II. DYSON'S EQUATION FOR POLARITON SPECTRUM

The Hamiltonian describing the polariton spectrum for a molecular crystal in an undisplaced lattice including cubic and quartic anharmonic interactions is taken as

$$\mathcal{H}=\mathcal{H}^{(0)}+\mathcal{H}^{\text{III}}+\mathcal{H}^{\text{IV}}, \tag{1}$$

where $\mathcal{H}^{(0)}$ is the Hamiltonian for the unperturbed polariton spectrum

$$\mathcal{H}^{(0)}=\langle\mathcal{H}^{(0)}\rangle+\sum_{\mathbf{k},\rho}\omega_\rho(\mathbf{k})\xi_\rho{}^\dagger(\mathbf{k})\xi_\rho(\mathbf{k}). \tag{2}$$

The excitation energy of the polariton spectrum in the zero approximation, $\omega_\rho(\mathbf{k})$, with wave vector $\mathbf{k}$ of the $\rho$th band satisfies the linear Maxwell equation

$$c^2k^2=\omega_\rho{}^2(\mathbf{k})\hat{\eta}_\lambda{}^2[\mathbf{k},\omega_\rho(\mathbf{k})], \tag{3}$$

where $ck$ is the energy of the electromagnetic field and $\hat{\eta}_\lambda[\mathbf{k},\omega_\rho(\mathbf{k})]$ is the real index of refraction of polariton waves in the medium with energy $\omega_\rho(\mathbf{k})$ and polarization $\lambda$. The quantity $\langle\mathcal{H}^{(0)}\rangle$ is the average energy of interaction of the electron-hole pairs (dressed by the electromagnetic field) that are tightly bound at the lattice sites of the crystal. Explicit expressions for $\hat{\eta}_\lambda{}^2[\mathbf{k},\omega_\rho(\mathbf{k})]$ and $\langle\mathcal{H}^{(0)}\rangle$ have been given elsewhere.[3] The creation and annihilation operators for the polariton field are denoted by $\xi_\rho{}^\dagger(\mathbf{k})$ and $\xi_\rho(\mathbf{k})$, respectively, and satisfy Bose statistics. The system of units where $\hbar=1$ is used throughout.

In (1), $\mathcal{H}^{\text{III}}$ and $\mathcal{H}^{\text{IV}}$ are the cubic and quartic anharmonic terms with respect to polariton operators, respectively, describing the scattering of the polariton waves and they are equal to

$$\begin{aligned}\mathcal{H}^{\text{III}}=\sum_{\mathbf{k}_1,\mathbf{k}_2,\rho_1,\rho_2,\rho_3}&[\alpha(\mathbf{k}_1,\rho_1;\,\mathbf{k}_2,\rho_2;\,\mathbf{k}_1+\mathbf{k}_2,\,\rho_3)\xi_{\rho1}(\mathbf{k}_1)\xi_{\rho2}(\mathbf{k}_2)\xi_{\rho3}{}^\dagger(\mathbf{k}_1+\mathbf{k}_2)\\&+\beta(\mathbf{k}_1,\rho_1;\,\mathbf{k}_2,\rho_2;\,-\mathbf{k}_1-\mathbf{k}_2,\,\rho_3)\xi_{\rho1}(\mathbf{k}_1)\xi_{\rho2}(\mathbf{k}_2)\xi_{\rho3}(-\mathbf{k}_1-\mathbf{k}_3)+\text{H.c.}],\end{aligned} \tag{4}$$

$$\begin{aligned}\mathcal{H}^{\text{IV}}=\sum_{\substack{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3\\ \rho_1,\rho_2,\rho_3,\rho_4}}&[Q_1(\mathbf{k}_1,\rho_1;\,\mathbf{k}_2,\rho_2;\,\mathbf{k}_3,\rho_3;\,-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3,\,\rho_4)\xi_{\rho1}(\mathbf{k}_1)\xi_{\rho2}(\mathbf{k}_2)\xi_{\rho3}(\mathbf{k}_3)\xi_{\rho4}(-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3)\\&+Q_2(\mathbf{k}_1,\rho_1;\,\mathbf{k}_2\rho_2;\,\mathbf{k}_3,\rho_3;\,\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,\,\rho_4)\xi_{\rho1}(\mathbf{k}_1)\xi_{\rho2}(\mathbf{k}_2)\xi_{\rho3}(\mathbf{k}_3)\xi_{\rho4}{}^\dagger(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\\&+Q_3(\mathbf{k}_1\rho_1;\,\mathbf{k}_2,\rho_2;\,\mathbf{k}_3,\rho_3;\,\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3,\,\rho_4)\xi_{\rho1}(\mathbf{k}_1)\xi_{\rho2}(\mathbf{k}_2)\xi_{\rho3}{}^\dagger(\mathbf{k}_3)\xi_{\rho4}{}^\dagger(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3)+\text{H.c.}].\end{aligned} \tag{5}$$

The coupling functions in the expression for the Hamiltonian $\mathcal{H}^{\text{III}}$ include terms corresponding to the interaction between the charges in the crystal as well as the interaction between the charges and the electromagnetic field and they have been discussed in detail by Ovander[8]; we refer to his review paper for details. The Hamiltonian $\mathcal{H}^{\text{III}}$ describes the interaction of three

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[7] B. S. Toshich, Fiz. Tverd. Tela **9**, 1713 (1967) [English transl.: Soviet Phys.—Solid State **9**, 1346 (1967)].

[8] L. N. Ovander, Usp. Fiz. Nauk **86**, 3 (1965) [English transl.: Soviet Phys.—Usp. **8**, 337 (1965)].

polaritons with each other and has been used by Agranovich *et al.*[9] to calculate the expression for the third-order nonlinear polarizability tensor corresponding to the optical spectrum of anharmonic crystals.

The quartic anharmonic Hamiltonian $\mathcal{H}^{\mathrm{IV}}$ gives an account of the interaction of four polaritons. The coupling functions $Q_1$, $Q_2$, and $Q_3$ contain terms which are due not only to the Coulomb interaction between the charges but also terms arising from the fact that the original bare-exciton operators are not exact Bose operators. For a multilevel system, the bare-exciton operators are not even exactly Pauli operators as it is the case for a two-level system. Following the Holstein-Primakoff transformation for the spin-wave operators, Toshich[7] and Agranovich and Toshich[6] have developed a similar representation where the bare-exciton operators are transformed into Bose operators. The bare-exciton Hamiltonian in the new representation contains terms arising from both kinematic as well as dynamic exciton-exciton interactions in complete analogy with the spin-wave theory. Unlike the spin-wave spectrum, the kinematic exciton-exciton interaction leads to new phenomena like the possibility of exciton condensation.[6] Therefore, the coupling functions $Q_1$, $Q_2$, $Q_3$ include all the fourth-order anharmonic interactions as described in the paper by Toshich[7]; we refer to his paper for details. In view of the complexity of the expressions for the coupling functions that appear in the expressions for $\mathcal{H}^{\mathrm{III}}$ and $\mathcal{H}^{\mathrm{IV}}$, their explicit expressions shall not be given here but they can be obtained by the procedure discussed by Ovander[8] and Toshich,[7] respectively. Our main interest is based on how the unperturbed spectrum of $\mathcal{H}^{(0)}$ is modified due to the presence of $\mathcal{H}^{\mathrm{III}}$ and $\mathcal{H}^{\mathrm{IV}}$ in the range of frequencies near and far from resonances. On the other hand, the explicit expressions for the coupling functions appearing in (4) and (5) shall be needed only when application of the final results is made to specific crystals.

To study the polariton spectrum, we introduce the Fourier transform of the retarded double-time polariton Green's function in the matrix form

$$G_\rho(\mathbf{k},\omega)\equiv\langle\langle A_\rho(\mathbf{k});\,A_\rho^\dagger(\mathbf{k})\rangle\rangle$$

$$=\left\langle\left\langle\begin{pmatrix}\xi_\rho(\mathbf{k})\\ \xi_\rho^\dagger(-\mathbf{k})\end{pmatrix};\,(\xi_\rho^\dagger(\mathbf{k})\xi_\rho(-\mathbf{k}))\right\rangle\right\rangle,\quad(6)$$

where the Green's function is defined in the usual way,[10] the operators $\xi_\rho(\mathbf{k})$ and $\xi_\rho^\dagger(\mathbf{k})$ are in the Heisenberg representation, and their time arguments have been suppressed for convenience. In (6), the average is over a canonical ensemble appropriate to the Hamiltonian $\mathcal{H}$ and the Green's function $G_\rho(\mathbf{k},\omega)$ satisfy the following equation of motion:

$$\omega G_\rho(\mathbf{k},\omega)=(1/2\pi)\langle[A_\rho(\mathbf{k}),A_\rho^\dagger(\mathbf{k})]_-\rangle\delta_{tt'}$$
$$+\langle\langle[A_\rho(\mathbf{k}),\mathcal{H}]_-;\,A_\rho^\dagger(\mathbf{k})\rangle\rangle,\quad(7)$$

where the last term in (7) represents also the Fourier transform of the corresponding Green's function and $\mathcal{H}$ is the total Hamiltonian of the system. Using the Hamiltonian (1) and (7), we derive the equation of motion for the Green's function $G_\rho(\mathbf{k},\omega)$:

$$G_\rho^{(00)-1}(\mathbf{k},\omega)G_\rho(\mathbf{k},\omega)=I$$
$$+\langle\langle\tilde{B}(\mathbf{k},\rho)+\tilde{F}(\mathbf{k},\rho);\,A_\rho^\dagger(\mathbf{k})\rangle\rangle,\quad(8)$$

where we have made use of the following notation:

$$I=\begin{pmatrix}1&0\\0&1\end{pmatrix}(2\pi)^{-1},\quad G^{(00)-1}(\mathbf{k},\omega)=[\hat{\alpha}\omega-\omega_\rho(\mathbf{k})],\quad\hat{\alpha}=\begin{pmatrix}1&0\\0&-1\end{pmatrix},\quad(9)$$

$$\tilde{B}(\mathbf{k},\rho)=\sum_{\mathbf{q},\rho_1,\rho_2}\begin{pmatrix}B_{\mathbf{k}\rho}(\mathbf{q},\rho_1;\,\mathbf{k}-\mathbf{q},\,\rho_2)\\ B_{-\mathbf{k}\rho}^\dagger(-\mathbf{q},\,\rho_1;\,\mathbf{q}-\mathbf{k},\,\rho_2)\end{pmatrix},\quad(10)$$

$$\tilde{F}(\mathbf{k},\rho)=\sum_{\substack{\mathbf{q},\mathbf{k}_1\\ \rho_1,\rho_2,\rho_3}}\begin{pmatrix}F_{\mathbf{k}\rho}(\mathbf{k}_1,\rho_1;\,\mathbf{q},\rho_2;\,\mathbf{k}-\mathbf{k}_1\mp\mathbf{q},\,\rho_3)\\ F_{-\mathbf{k}\rho}^\dagger(-\mathbf{k}_1,\,\rho_1;\,-\mathbf{q},\,\rho_2;\,\pm\mathbf{q}+\mathbf{k}_1-\mathbf{k},\,\rho_3)\end{pmatrix},\quad(11)$$

$$B_{\mathbf{k}\rho}(\mathbf{q},\rho_1;\,\mathbf{k}-\mathbf{q},\,\rho_2)$$
$$\equiv\alpha(\mathbf{q},\rho_1;\,\mathbf{k}-\mathbf{q},\,\rho_2;\,\mathbf{k},\rho)\xi_{\rho1}(\mathbf{q})\xi_{\rho2}(\mathbf{k}-\mathbf{q})+3\beta^*(-\mathbf{k},\,\rho;\,\mathbf{q},\rho_1;\,\mathbf{k}-\mathbf{q},\,\rho_2)\xi_{\rho1}^\dagger(-\mathbf{q})\xi_{\rho2}^\dagger(\mathbf{q}-\mathbf{k})$$
$$+2\alpha^*(-\mathbf{k},\,\rho;\,\mathbf{q},\rho_1;\,\mathbf{q}-\mathbf{k},\,\rho_2)\xi_{\rho2}(\mathbf{k}-\mathbf{q})\xi_{\rho1}^\dagger(-\mathbf{q}),\quad(12)$$

$$F_{\mathbf{k}\rho}(\mathbf{k}_1,\rho_1;\,\mathbf{q},\rho_2;\,\mathbf{k}-\mathbf{k}_1\mp\mathbf{q},\,\rho_3)$$
$$\equiv Q_2(\mathbf{k}_1,\rho_1;\,\mathbf{q},\rho_2;\,\mathbf{k}-\mathbf{k}_1-\mathbf{q},\,\rho_3;\,\mathbf{k},\rho)\xi_{\rho1}(\mathbf{k}_1)\xi_{\rho2}(\mathbf{q})\xi_{\rho3}(\mathbf{k}-\mathbf{k}_1-\mathbf{q})+4Q_1^*(-\mathbf{k}_1,\,\rho_1;\,-\mathbf{q},\,\rho_2;\,-\mathbf{k}+\mathbf{k}_1+\mathbf{q},\,\rho_3;\,\mathbf{k},\rho)$$
$$\times\xi_{\rho3}^\dagger(\mathbf{k}_1+\mathbf{q}-\mathbf{k})\xi_{\rho2}^\dagger(-\mathbf{q})\xi_{\rho1}^\dagger(-\mathbf{k}_1)+4Q_3(\mathbf{k}_1,\rho_1;\,\mathbf{q},\rho_2;\,\mathbf{k},\rho;\,\mathbf{k}_1+\mathbf{q}-\mathbf{k},\,\rho_3)\xi_{\rho1}(\mathbf{k}_1)\xi_{\rho2}(\mathbf{q})\xi_{\rho3}^\dagger(\mathbf{k}_1+\mathbf{q}-\mathbf{k})$$
$$+3Q_2^*(-\mathbf{k}_1,\,\rho_1;\,-\mathbf{q},\,\rho_2;\,\mathbf{k},\rho;\,\mathbf{k}_1-\mathbf{q}-\mathbf{k},\,\rho_3)\xi_{\rho3}(\mathbf{k}-\mathbf{k}_1-\mathbf{q})\xi_{\rho2}^\dagger(-\mathbf{q})\xi_{\rho1}^\dagger(-\mathbf{k}_1).\quad(13)$$

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[9] V. M. Agranovich, L. N. Ovander, and B. S. Toshich, Zh. Eksperim. i Teor. Fiz. **50**, 1332 (1966) [English transl.: Soviet Phys.—JETP **23**, 885 (1966)].

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

The equation of motion for the Green's function that appears on the right-hand side of (8) is equal to

$$
\begin{aligned}
&\langle\langle \widetilde{B}(\mathbf{k},\rho)+\widetilde{F}(\mathbf{k},\rho); A_\rho^\dagger(\mathbf{k})\rangle_\sigma G\rangle^{(00)-1}(\mathbf{k},\omega)\\
&\quad=(1/2\pi)\langle[\widetilde{B}(\mathbf{k},\rho)+\widetilde{F}(\mathbf{k},\rho), A_\rho^\dagger(\mathbf{k})]_-\hat{\alpha}\rangle_{t=t'}\\
&\qquad+\langle\langle \widetilde{B}(\mathbf{k},\rho)+\widetilde{F}(\mathbf{k},\rho); \widetilde{B}^\dagger(\mathbf{k},\rho)+\widetilde{F}^\dagger(\mathbf{k},\rho)\rangle\rangle. \qquad (14)
\end{aligned}
$$

Substituting (14) into (8), we derive Dyson's equation:

$$
\begin{aligned}
G_\rho(\mathbf{k},\omega)&=G_\rho^{(00)}(\mathbf{k},\omega)+G_\rho^{(00)}(\mathbf{k},\omega)\Pi_\rho(\mathbf{k},\omega)G_\rho^{(00)}(\mathbf{k},\omega)\\
&=G_\rho^{(00)}(\mathbf{k},\omega)+G_\rho^{(00)}(\mathbf{k},\omega)\tilde{\Pi}_\rho(\mathbf{k},\omega)G_\rho(\mathbf{k},\omega), \qquad (15)
\end{aligned}
$$

where

$$
\begin{aligned}
\Pi_\rho(\mathbf{k},\omega)=(2\pi)&([\widetilde{B}(\mathbf{k},\rho)+\widetilde{F}(\mathbf{k},\rho), A_\rho^\dagger(\mathbf{k})]_-\hat{\alpha}\rangle_{t=t'}\\
&+(2\pi)^2\langle\langle \widetilde{B}(\mathbf{k},\rho)+\widetilde{F}(\mathbf{k},\rho);\\
&\qquad\widetilde{B}^\dagger(\mathbf{k},\rho)+\widetilde{F}^\dagger(\mathbf{k},\rho)\rangle\rangle, \qquad (16)
\end{aligned}
$$

and the polarization operator $\tilde{\Pi}_\rho(\mathbf{k},\omega)$ is given by

$$\tilde{\Pi}_\rho(\mathbf{k},\omega)=\Pi_\rho(\mathbf{k},\omega)[I+G_\rho^{(00)}(\mathbf{k},\omega)\Pi_\rho(\mathbf{k},\omega)]^{-1}, \qquad (17)$$

then (15) becomes

$$[G_\rho^{(00)-1}(\mathbf{k},\omega)-\tilde{\Pi}_\rho(\mathbf{k},\omega)]G_\rho(\mathbf{k},\omega)=I. \qquad (18)$$

The frequencies, where the localized or trapped polariton spectrum occurs, satisfy the dispersion relation

$$I+G_\rho^{(00)}(\mathbf{k},\omega)\ \mathrm{Re}\Pi_\rho(\mathbf{k},\omega)=0, \qquad (19)$$

where $\mathrm{Re}\Pi_\rho(\mathbf{k},\omega)$ is given by the real part of the expression (16). The energy spectrum determined by the solutions of (19) corresponds to the strong coupling case and in this region of frequencies $\omega$, satisfying Eq. (19), the real part of the Green's function $G_\rho(\mathbf{k},\omega)$ goes to zero while the imaginary part of $G_\rho(\mathbf{k},\omega)$ is proportional to the imaginary part of $\Pi_\rho(\mathbf{k},\omega)$ which determines the shape of the localized polariton bands. On the other hand, the energy spectrum of propagating polariton waves occurs at frequencies $\omega$ which are outside the region of the solutions of (19), i.e., when

$$I+G_\rho^{(00)}(\mathbf{k},\omega)\ \mathrm{Re}\Pi_\rho(\mathbf{k},\omega)\neq 0. \qquad (20a)$$

In this case, we may neglect the second term appearing in the denominator of (17) in comparison with unity; then the expression (18) may be written as

$$[G_\rho^{(0)-1}(\mathbf{k},\omega)-P(\mathbf{k},\rho;\omega)]G_\rho(\mathbf{k},\omega)=I, \qquad (20b)$$

where the renormalized unperturbed Green's function $G_\rho^{(0)-1}(\mathbf{k},\omega)$ is equal to

$$
\begin{aligned}
G_\rho^{(0)-1}(\mathbf{k},\omega)&=G_\rho^{(00)-1}(\mathbf{k},\omega)\\
&\quad-\langle[\widetilde{B}(\mathbf{k},\rho)+\widetilde{F}(\mathbf{k},\rho), A_\rho^\dagger(\mathbf{k})\hat{\alpha}\rangle_{t=t'}, \qquad (21)
\end{aligned}
$$

and $P(\mathbf{k},\rho;\omega)$ is the polarization operator arising from the anharmonic polariton-polariton interactions in the crystal in the region of frequencies $\omega$ which satisfy the requirements of (20a) and is given by the expression

$$
\begin{aligned}
P(\mathbf{k},\rho;\omega)=(2\pi)&\langle\langle \widetilde{B}(\mathbf{k},\rho)+\widetilde{F}(\mathbf{k},\rho);\\
&\widetilde{B}^\dagger(\mathbf{k},\rho)+\widetilde{F}^\dagger(\mathbf{k},\rho)\rangle\rangle. \qquad (22)
\end{aligned}
$$

In the following sections we shall study the polariton Green's function and the energy spectrum determined by the solutions of (20b).

## III. POLARITON GREEN'S FUNCTION

If we introduce the Green's function

$$D_\rho(\mathbf{k},\omega)\equiv\langle\langle \xi_\rho(\mathbf{k})+\xi_\rho^\dagger(-\mathbf{k}); \xi_\rho^\dagger(\mathbf{k})+\xi_\rho(-\mathbf{k})\rangle\rangle, \qquad (23)$$

then considering the diagonal and nondiagonal elements of (20b) and taking into account that in the complex $\omega$ plane the components of the polarization operator $P(\mathbf{k},\rho;\omega)$ satisfy the relations

$$P_{22}(\mathbf{k},\rho;\omega)=P_{11}(\mathbf{k},\rho;-\omega)=P_{11}(\mathbf{k},\rho;\omega)$$

and

$$P_{21}(\mathbf{k},\rho;\omega)=P_{12}(\mathbf{k},\rho;-\omega)=P_{12}(\mathbf{k},\rho;\omega),$$

the expression for $D_\rho(\mathbf{k},\omega)$ is found to be

$$
\begin{aligned}
D_\rho(\mathbf{k},\omega)=(1/\pi)&\Omega_{\mathbf{k}\rho}^{(-)}(\omega)\\
&\times\{\omega^2-\Omega_{\mathbf{k}\rho}^{(+)}(\omega)\Omega_{\mathbf{k}\rho}^{(-)}(\omega)\}^{-1}, \qquad (24)
\end{aligned}
$$

where

$$\Omega_{\mathbf{k}\rho}^{(\pm)}(\omega)=\bar{\omega}_\rho(\mathbf{k})\pm\hat{\omega}_\rho(\mathbf{k})+\tfrac{1}{2}[P_{11}(\mathbf{k},\rho;\omega)+P_{11}(\mathbf{k},\rho;-\omega)\pm P_{12}(\mathbf{k},\rho;\omega)\pm P_{12}(\mathbf{k},\rho,;-\omega)], \qquad (25)$$

$$
\begin{aligned}
\bar{\omega}_\rho(\mathbf{k})\equiv\omega_\rho(\mathbf{k})&+8\sum_{\mathbf{q},\rho'}Q_3(\mathbf{k},\rho;\mathbf{q},\rho';\mathbf{k},\rho;\mathbf{q},\rho')\langle\xi_{\rho'}(\mathbf{q})\xi_{\rho'}^\dagger(\mathbf{q})\rangle+6\sum_{\mathbf{q},\rho'}Q_2(-\mathbf{q},\rho';\mathbf{q},\rho';\mathbf{k},\rho;\mathbf{k},\rho)\\
&\times\langle\xi_{\rho'}(\mathbf{q})\xi_{\rho'}(-\mathbf{q})\rangle, \qquad (26)
\end{aligned}
$$

$$
\begin{aligned}
\hat{\omega}_\rho(\mathbf{k})\equiv 6\sum_{\mathbf{q},\rho'}Q_2(\mathbf{k},\rho;\mathbf{q},\rho';-\mathbf{k},\rho;\mathbf{q},\rho')&\langle\xi_{\rho'}(\mathbf{q})\xi_{\rho'}^\dagger(\mathbf{q})\rangle+4\sum_{\mathbf{q},\rho'}[Q_3(-\mathbf{q},\rho';\mathbf{q},\rho';-\mathbf{k},\rho;\mathbf{k},\rho)\\
&+3Q_1(-\mathbf{q},\rho';\mathbf{q},\rho';-\mathbf{q},\rho;\mathbf{q},\rho)]\langle\xi_{\rho'}(\mathbf{q})\xi_{\rho'}(-\mathbf{q})\rangle. \qquad (27)
\end{aligned}
$$

In (25), the quantities $P_{11}(\mathbf{k},\rho;\omega)$ and $P_{12}(\mathbf{k},\rho;\omega)$ represent the diagonal and nondiagonal elements of (22), respectively, while the last two terms of (26) as well as the expression for $\hat{\omega}_\rho(\mathbf{k})$ result from the evaluation of the commutator that appears on the right-hand side of (21).

In the zero approximation, i.e., when all the elements of $P(\mathbf{k},\rho;\omega)$ are taken equal to zero, we have

$$D_\rho^{(0)}(\mathbf{k},\omega)=(1/\pi)[\bar{\omega}_\rho(\mathbf{k})-\hat{\omega}_\rho(\mathbf{k})][\omega^2-\tilde{\omega}_\rho^2(\mathbf{k})]^{-1}, \qquad (28)$$

where the energy of excitation is determined from the equation

$$\tilde{\omega}_\rho^2(\mathbf{k})=\bar{\omega}_\rho^2(\mathbf{k})-\hat{\omega}_\rho^2(\mathbf{k}), \qquad (29a)$$

with the expressions for $\bar{\omega}_\rho(\mathbf{k})$ and $\hat{\omega}_\rho(\mathbf{k})$ given by (26) and (27), respectively. The distribution functions appearing in (26) and (27) are calculated in the zero approximation from the corresponding Green's functions in the usual way and they are equal to

$$\langle \xi_{\rho'}(\mathbf{q})\xi_{\rho'}^\dagger(\mathbf{q})\rangle = \frac{1}{2}\left[1+\frac{\bar{\omega}_{\rho'}(\mathbf{q})}{\tilde{\omega}_{\rho'}(\mathbf{q})}\coth\tfrac{1}{2}\beta\tilde{\omega}_{\rho'}(\mathbf{q})\right],$$

$$\langle \xi_{\rho'}^\dagger(\mathbf{q})\xi_{\rho'}(\mathbf{q})\rangle = \frac{1}{2}\left[-1+\frac{\bar{\omega}_{\rho'}(\mathbf{q})}{\tilde{\omega}_{\rho'}(\mathbf{q})}\coth\tfrac{1}{2}\beta\tilde{\omega}_{\rho'}(\mathbf{q})\right],$$

$$\langle \xi_{\rho'}(\mathbf{q})\xi_{\rho'}(-\mathbf{q})\rangle = \langle \xi_{\rho'}^\dagger(\mathbf{q})\xi_{\rho'}^\dagger(-\mathbf{q})\rangle = -\frac{1}{2}\frac{\hat{\omega}_{\rho'}(\mathbf{q})}{\tilde{\omega}_{\rho'}(\mathbf{q})}\coth\tfrac{1}{2}\beta\tilde{\omega}_{\rho'}(\mathbf{q}), \quad (29\text{b})$$

with $\beta=(k_BT)^{-1}$, where $k_B$ is Boltzmann's constant and $T$ the absolute temperature. In the limit when $\beta\rightarrow\infty$, $\coth\frac{1}{2}\beta\tilde{\omega}_{\rho'}(\mathbf{q})\rightarrow 1$, the distribution functions (29b) are reduced to those at zero temperature.

The poles of the unperturbed Green's function (28) occur at frequencies $\omega^2=\tilde{\omega}_\rho^2(\mathbf{k})$, where $\tilde{\omega}_\rho^2(\mathbf{k})$ is given by (29a), which indicates that even in the zero approximation the polariton optical spectrum is renormalized and the renormalization is caused by the quartic anharmonic interactions. We note that in deriving (26) and (27) we have neglected contributions arising from the cubic anharmonic terms when $\mathbf{k}=\mathbf{q}$ and $\mathbf{q}=0$. A typical term of this kind has the form $\alpha(0,\rho;0\rho;\mathbf{k},\rho)\times\langle\xi_\rho(0)\rangle$ and, therefore, all of them have been taken equal to zero as should be the case for a crystal having a center of symmetry.

In the first approximation the Green's function, $D_\rho^{(1)}(\mathbf{k},\omega)$ is given by (24) but the expression for $\Omega_{\mathbf{k}\rho}^{(\pm)}(\omega)$ is now equal to

$$\Omega_{\mathbf{k}\rho}^{(\pm)}(\omega) = \bar{\omega}_\rho(\mathbf{k})\pm\hat{\omega}_\rho(\mathbf{k})+\tfrac{1}{2}\big[P_{11}^{(0)}(\mathbf{k},\rho,\omega)+P_{11}^{(0)}(\mathbf{k},\rho,-\omega)\pm P_{12}^{(0)}(\mathbf{k},\rho,\omega)\pm P_{12}^{(0)}(\mathbf{k},\rho,-\omega)\big], \quad (30)$$

where the superscript (0) indicates that the Green's functions involved in the diagonal and nondiagonal elements of $P(\mathbf{k},\rho;\omega)$ given by (22) must be calculated in the zero approximation, i.e., in the approximation which corresponds to the excitation spectrum determined by the poles of the Green's function (21) or (28). The renormalized zeroth-order Hamiltonian which gives rise to the spectrum of (21) or (28) is given by

$$\mathcal{H}_{\text{ren}}^{(0)} = \text{const}+\sum_{\mathbf{k},\rho}\bar{\omega}_\rho(\mathbf{k})\xi_\rho^\dagger(\mathbf{k})\xi_\rho(\mathbf{k})+\tfrac{1}{2}\sum_{\mathbf{k},\rho}\hat{\omega}_\rho(\mathbf{k})\times\big[\xi_\rho(\mathbf{k})\xi_\rho(-\mathbf{k})+\xi_\rho^\dagger(\mathbf{k})\xi_\rho^\dagger(-\mathbf{k})\big]. \quad (31)$$

The expression for $\Omega_{\mathbf{k}\rho}^{(\pm)}(\omega)$ has been calculated in the Appendix by making use of the renormalized zeroth-order Hamiltonian (31) and, in the limit of zero temperature, is found to be equal to

$$\Omega_{\mathbf{k}\rho}^{(\pm)}(\omega) = \tilde{\Omega}_{\mathbf{k}\rho}^{(\pm)}(\omega)+R_{\mathbf{k}\rho}^{(\pm)}(\omega), \quad (32)$$

where

$$\tilde{\Omega}_{\mathbf{k}\rho}^{(\pm)}(\omega) = \bar{\omega}_\rho(\mathbf{k})\pm\hat{\omega}_\rho(\mathbf{k})+\big[\omega_\rho(\mathbf{k})-\bar{\omega}_\rho(\mathbf{k})\pm\hat{\omega}_\rho(\mathbf{k})\big]^2\tilde{\omega}_\rho(\mathbf{k})\big[\omega^2-\tilde{\omega}_\rho^2(\mathbf{k})\big]^{-1}, \quad (33)$$

$$\begin{aligned} R_{\mathbf{k}\rho}^{(\pm)}(\omega) = {} & 2\sum_{\mathbf{q},\rho_1,\rho_2} V_3^{(\pm)}(\mathbf{k},\mathbf{q})\frac{[\tilde{\omega}_{\rho1}(\mathbf{q})+\tilde{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\tilde{\omega}_{\rho1}(\mathbf{q})+\tilde{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})]^2}+2\sum_{\mathbf{q},\rho_1,\rho_2}\hat{V}_3^{(\pm)}(\mathbf{k},\mathbf{q})\frac{[\tilde{\omega}_{\rho1}(\mathbf{q})-\tilde{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\tilde{\omega}_{\rho1}(\mathbf{q})-\tilde{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})]^2} \\ & +2\sum_{\substack{\mathbf{q},\mathbf{k}_1\\ \rho_1,\rho_2,\rho_3}} V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)\frac{[\tilde{\omega}_{\rho1}(\mathbf{k}_1)+\tilde{\omega}_{\rho2}(\mathbf{q})+\tilde{\omega}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]}{\omega^2-[\tilde{\omega}_{\rho1}(\mathbf{k}_1)+\tilde{\omega}_{\rho2}(\mathbf{q})+\tilde{\omega}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]^2} \\ & +2\sum_{\substack{\mathbf{q},\mathbf{k}_1\\ \rho_1,\rho_2,\rho_3}} \hat{V}_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)\frac{[\tilde{\omega}_{\rho1}(\mathbf{k}_1)-\tilde{\omega}_{\rho2}(\mathbf{q})+\tilde{\omega}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]}{\omega^2-[\tilde{\omega}_{\rho1}(\mathbf{k}_1)-\tilde{\omega}_{\rho2}(\mathbf{q})+\tilde{\omega}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]^2}. \end{aligned} \quad (34)$$

The last term on the right-hand side of (33) gives a small correction to the energy of excitation arising from the renormalization of the $(\mathbf{k},\rho)$ polariton mode in the lowest approximation. The function $R_{\mathbf{k}\rho}^{(\pm)}(\omega)$ gives an account of the scattering processes occurring among the renormalized polariton modes. The first two terms on the right-hand side of (34) describe the scattering arising from the interaction between two polaritons with energies $\tilde{\omega}_{\rho_1}(\mathbf{q})$ and $\tilde{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$ and their energy denominators correspond to energies of excitation which are equal to $\tilde{\omega}_{\rho_1}(\mathbf{q})+\tilde{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$ and $\tilde{\omega}_{\rho_1}(\mathbf{q})-\tilde{\omega}_{\rho_2}(\mathbf{q})$, respectively. The coupling functions $V_3^{(\pm)}(\mathbf{k},\mathbf{q})$ and $\hat{V}_3^{(\pm)}(\mathbf{k},\mathbf{q})$ are given by the expressions (A6)–(A9) in the Appendix. Taking into account the relations $u_+\gg u_-$, $u_\pm\gg v_\pm$, and $\alpha>\beta$, it is easily shown that $V_3^{(\pm)}(\mathbf{k},\mathbf{q})\gg\hat{V}_3^{(\pm)}(\mathbf{k},\mathbf{q})$, $V_3^{(+)}(\mathbf{k},\mathbf{q})\gtrsim V_3^{(-)}(\mathbf{k},\mathbf{q})$, $\hat{V}_3^{(+)}(\mathbf{k},\mathbf{q})\gtrsim V_3^{(-)}(\mathbf{k},\mathbf{q})$, and, in particular, $\hat{V}_3^{(+)}(\mathbf{k},\mathbf{q})/V_3^{(+)}(\mathbf{k},\mathbf{q})\sim(u_-/u_+)$, where the functions $u_\pm$ and $v_\pm$ are given by (A10). The expressions for $\hat{V}_3^{(\pm)}(\mathbf{k},\mathbf{q})$ depend entirely on the numerical values of the quantities $\hat{\omega}_{\rho_1}(\mathbf{q})$ and $\hat{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$, which are much smaller than the unperturbed energies, $\hat{\omega}_{\rho_1}(\mathbf{q})\ll\bar{\omega}_{\rho_1}(\mathbf{q})$, $\hat{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})\ll\bar{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$. In the limiting case where both $\hat{\omega}_{\rho_1}(\mathbf{q})$ and $\hat{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})$ are equal to zero, then $\hat{V}_3^{(\pm)}(\mathbf{k},\mathbf{q})=0$ and $V_3^{(\pm)}(\mathbf{k},\mathbf{q})=|\tilde{\alpha}_\pm(\mathbf{k},\mathbf{q})|^2$. On the other hand, if only one of them is equal to zero, i.e., either $\hat{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})=0$ and $\hat{\omega}_{\rho_1}(\mathbf{q})\neq 0$ or vice versa, then $\hat{V}_3^{(\pm)}(\mathbf{k},\mathbf{q})\neq 0$.

Therefore, the chance that the second term on the right-hand side of (34) will be observed experimentally at very low temperatures depends on the numerical values of both quantities $u_-$ and $v_\pm$.

The last two terms on the right-hand side of (34) represent the quartic anharmonic contributions to the polarization operator arising from interaction of three polaritons with each other with energies $\tilde{\omega}_{\rho 1}(\mathbf{k}_1)$, $\tilde{\omega}_{\rho 2}(\mathbf{q})$, and $\tilde{\omega}_{\rho 3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)$, respectively, and their energy denominators have poles in the region of frequencies $\tilde{\omega}_{\rho 1}(\mathbf{k})\pm\tilde{\omega}_{\rho 2}(\mathbf{q})+\tilde{\omega}_{\rho 3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)$. Let us examine the three-polariton scattering amplitudes $V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ and $\hat{V}_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ as given by the expressions (A16) and (A17), respectively. The first term on the right-hand side of (A16) consists of the amplitude $3|Q_2\pm4Q_1|^2$ multiplied by a factor which is of the order of unity, while the amplitudes of the remaining two terms are multiplied by factors which are much smaller than unity. Hence, it is evident that the first term in (A16) gives the main contribution to $V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$. The last two terms in (A16) disappear in the limit when $\hat{\omega}_1$, $\hat{\omega}_2$, and $\hat{\omega}_3$ tend to zero simultaneously, but they become appreciable only as the quantities $\hat{\omega}_1/\tilde{\omega}_1$, $\hat{\omega}_2/\tilde{\omega}_2$, and $\hat{\omega}_3/\tilde{\omega}_3$ approach unity. In fact, the ratios $\hat{\omega}_1/\tilde{\omega}_1$, $\hat{\omega}_2/\tilde{\omega}_2$, and $\hat{\omega}_3/\tilde{\omega}_3$ always are much smaller than unity; therefore, both terms make up a small correction to the first term. Taking into account that $Q_2>Q_1$, it follows that $V_4^{(+)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)\gtrsim V_4^{(-)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$.

The expression for $\hat{V}_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ shown by (A17) as well as the last two terms in (A16) are the outcome of the renormalization procedure. The importance of the scattering amplitude $\hat{V}^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ is due to the fact that it is responsible for the appearance of the pole in the frequency region of $\tilde{\omega}_1-\tilde{\omega}_2+\tilde{\omega}_3$ at zero temperature. Though $\hat{V}_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ is smaller than $V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ by at least one order of magnitude, it is, in general, a finite quantity different than zero unless the quantities $\hat{\omega}_1/\tilde{\omega}_1$, $\hat{\omega}_2/\tilde{\omega}_2$, and $\hat{\omega}_3/\tilde{\omega}_3$ are negligibly small simultaneously, which is rather a rare possibility. Hence, it is quite possible that one or more than one of the $(\hat{\omega}/\tilde{\omega})$'s may take such a value as to make the pole at the frequency $\tilde{\omega}_1-\tilde{\omega}_2+\tilde{\omega}_3$ observable experimentally. Of course, the described process may be of importance only at very low temperatures because at finite temperatures the corresponding process arising from the polariton-phonon interaction is predominant. In (A17), $\hat{V}_4^{(+)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)\gtrsim\hat{V}_4^{(-)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$.

We remark that the form of the expression for $R_{\mathbf{k}\rho}^{(\pm)}(\omega)$ given by (34) as a function of the renormalized polariton frequencies is similar, apart from the specific expressions for the $V_3$'s, $V_4$'s, and those for the renormalized frequencies, to that derived for the polarization operator corresponding to the polariton spectrum in the infrared region of frequencies of anharmonic crystals at finite temperatures.[11] In this particular case, infrared polaritons consist of low-energy photons dressed by the optical-phonon field in dielectric crystals.

In general, the expression for $R_{\mathbf{k}\rho}^{(\pm)}(\omega)$ is a complex quantity and may be written as

$$R_{\mathbf{k}\rho}^{(\pm)}(\omega+i\epsilon)=\mathrm{Re}R_{\mathbf{k}\rho}^{(\pm)}(\omega)-i\,\mathrm{Im}R_{\mathbf{k}\rho}^{(\pm)}(\omega)\,,\quad \lim\epsilon\to+0 \tag{35}$$

where $\mathrm{Re}R_{\mathbf{k}\rho}^{(\pm)}(\omega)$ is the real part of $R_{\mathbf{k}\rho}^{(\pm)}(\omega)$ which is obtained from the expression (34) when the principal value over the summations or integrations is taken. The imaginary part of $R_{\mathbf{k}\rho}^{(\pm)}(\omega)$ is equal to

$$\begin{aligned}\mathrm{Im}R_{\mathbf{k}\rho}^{(\pm)}(\omega)=\pi\sum_{\mathbf{q},\rho_1,\rho_2}\{&V_3^{(\pm)}(\mathbf{k},\mathbf{q})[\delta(\omega-\tilde{\omega}_{\rho 1}(\mathbf{q})-\tilde{\omega}_{\rho 2}(\mathbf{k}-\mathbf{q}))-\delta(\omega+\tilde{\omega}_{\rho 1}(\mathbf{q})+\tilde{\omega}_{\rho 2}(\mathbf{q}))]\\&+\hat{V}_3^{(\pm)}(\mathbf{k},\mathbf{q})[\delta(\omega-\tilde{\omega}_{\rho 1}(\mathbf{q})+\tilde{\omega}_{\rho 2}(\mathbf{k}-\mathbf{q}))-\delta(\omega+\tilde{\omega}_{\rho 1}(\mathbf{q})-\tilde{\omega}_{\rho}(\mathbf{k}-\mathbf{q}))]\}\\&+\pi\sum_{\substack{\mathbf{q},\mathbf{k}_1\\ \rho_1,\rho_2,\rho_3}}\{V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)[\delta(\omega-\tilde{\omega}_{\rho 1}(\mathbf{k}_1)-\tilde{\omega}_{\rho 2}(\mathbf{q})-\tilde{\omega}_{\rho 3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1))\\&-\delta(\omega+\tilde{\omega}_{\rho 1}(\mathbf{k}_1)+\tilde{\omega}_{\rho 2}(\mathbf{q})+\tilde{\omega}_{\rho 3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1))]+\hat{V}_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)\\&+[\delta(\omega-\tilde{\omega}_{\rho 1}(\mathbf{k}_1)-\tilde{\omega}_{\rho 2}(\mathbf{q})+\tilde{\omega}_{\rho 3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1))-\delta(\omega+\tilde{\omega}_{\rho 1}(\mathbf{k}_1)+\tilde{\omega}_{\rho 2}(\mathbf{q})-\tilde{\omega}_{\rho 3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1))]\}\,.\end{aligned} \tag{36}$$

Substituting (35) into (24), we derive the expression for the polariton Green's function in the first approximation as

$$D_\rho^{(1)}(\mathbf{k},\omega)-\frac{1}{\pi}\tilde{\Omega}_{\mathbf{k}\rho}^{(-)}(\omega)\times\frac{1+\Delta_{\mathbf{k}\rho}^{(-)}(\omega)-i\gamma_{\mathbf{k}\rho}^{(-)}(\omega)}{\omega^2-\Omega_{\mathbf{k}\rho}^2(\omega)[\Delta_{\mathbf{k}\rho}(\omega)-i\gamma_{\mathbf{k}\rho}(\omega)]}, \tag{37}$$

where we have introduced the notation

$$\Omega_{\mathbf{k}\rho}^2(\omega)\equiv\tilde{\Omega}_{\mathbf{k}\rho}^{(+)}(\omega)\tilde{\Omega}_{\mathbf{k}\rho}^{(-)}(\omega)\,, \tag{38}$$

$$\begin{aligned}\Delta_{\mathbf{k}\rho}(\omega)\equiv1+\Delta_{\mathbf{k}\rho}^{(+)}(\omega)+\Delta_{\mathbf{k}\rho}^{(-)}(\omega)&\\+[\Delta_{\mathbf{k}\rho}^{(+)}(\omega)\Delta_{\mathbf{k}\rho}^{(-)}(\omega)&\\-\gamma_{\mathbf{k}\rho}^{(+)}(\omega)\gamma_{\mathbf{k}\rho}^{(-)}(\omega)],&\end{aligned} \tag{39}$$

$$\begin{aligned}\Delta_{\mathbf{k}\rho}^{(\pm)}(\omega)&\equiv\mathrm{Re}R_{\mathbf{k}\rho}^{(\pm)}(\omega)/\tilde{\Omega}_{\mathbf{k}\rho}^{(\pm)}(\omega)\,,\\ \gamma_{\mathbf{k}\rho}^{(\pm)}(\omega)&\equiv\mathrm{Im}R_{\mathbf{k}\rho}^{(\pm)}(\omega)/\tilde{\Omega}_{\mathbf{k}\rho}^{(\pm)}(\omega)\,,\end{aligned} \tag{40}$$

$$\gamma_{\mathbf{k}\rho}(\omega)\equiv\gamma_{\mathbf{k}\rho}^{(+)}(\omega)+\gamma_{\mathbf{k}\rho}^{(-)}(\omega)\,. \tag{41}$$

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[11] C. Mavroyannis and K. N. Pathak, Phys. Rev. **182**, 872 (1969).

The expression (37) shall be used in the next section to study the excitation spectrum of polariton waves in molecular crystals.

## IV. EXCITATION SPECTRUM

### A. First Approximation

Using the well-known relation for the spectral function

$$J_{\mathbf{k}\rho}(\omega) = -2\,\mathrm{Im}D_\rho(\mathbf{k},\omega)(e^{\beta\omega}-1)^{-1}, \tag{42}$$

and substituting the imaginary part of (37) into (42), we obtain the spectral function in the first approximation

$$J_{\mathbf{k}\rho}{}^{(1)}(\omega) = (e^{\beta\omega}-1)^{-1}\left(\frac{2}{\pi}\right)\tilde{\Omega}_{\mathbf{k}\rho}{}^{(-)}(\omega) \times \frac{\Omega_{\mathbf{k}\rho}{}^2(\omega)\gamma_{\mathbf{k}\rho}(\omega) + [\omega^2 - \Omega_{\mathbf{k}\rho}{}^2(\omega)]\gamma_{\mathbf{k}\rho}{}^{(-)}(\omega)}{[\omega^2 - \Omega_{\mathbf{k}\rho}{}^2(\omega)\Delta_{\mathbf{k}\rho}(\omega)]^2 + [\Omega_{\mathbf{k}\rho}{}^2(\omega)\gamma_{\mathbf{k}\rho}(\omega)]^2}. \tag{43}$$

The spectral function (43) describes the behavior of the polariton excitation spectrum in the whole range of frequencies $\omega$ and it is an asymmetric Lorentzian line even when the $\omega$ dependence in the expressions for $\Omega_{\mathbf{k}\rho}{}^2(\omega)$, $\Delta_{\mathbf{k}\rho}{}^2(\omega)$, and $\gamma_{\mathbf{k}\rho}{}^{(\pm)}(\omega)$ is neglected. The asymmetry of the absorption line is caused by the damping function $\gamma_{\mathbf{k}\rho}{}^{(-)}(\omega)$ which is, in general, different than zero, $\gamma_{\mathbf{k}\rho}{}^{(-)}(\omega) \lesssim \gamma_{\mathbf{k}\rho}{}^{(+)}(\omega)$.

To study the excitation spectrum of (43) it is sufficient to examine the solutions of the equation

$$\frac{\partial}{\partial\omega}\,\mathrm{Im}D_\rho{}^{(1)}(\mathbf{k},\omega) = 0. \tag{44}$$

Using the assumption that the functions $\Omega_{\mathbf{k}\rho}{}^2(\omega)$, $\Delta_{\mathbf{k}\rho}(\omega)$, and $\gamma_{\mathbf{k}\rho}(\omega)$ vary slowly with $\omega$ and may be considered as constants in the neighborhood of frequencies $\omega^2 \sim \epsilon_{\mathbf{k}\rho}{}^2$, where $\epsilon_{\mathbf{k}\rho}{}^2$ is the square of the energy of excitation obtained from the positive solutions of (44) and is equal to

$$\epsilon_{\mathbf{k}\rho}{}^2 = \Omega_{\mathbf{k}\rho}{}^2\{-\gamma_{\mathbf{k}\rho}{}^{(+)}/\gamma_{\mathbf{k}\rho}{}^{(-)} + [(\Delta_{\mathbf{k}\rho} + \gamma_{\mathbf{k}\rho}{}^{(+)}/\gamma_{\mathbf{k}\rho}{}^{(-)})^2 + \gamma_{\mathbf{k}\rho}{}^2]^{1/2}\}, \tag{45}$$

where $\Omega_{\mathbf{k}\rho}{}^2 \equiv \Omega_{\mathbf{k}\rho}{}^2(\epsilon_{\mathbf{k}\rho})$, $\gamma_{\mathbf{k}\rho}{}^{(\pm)} \equiv \gamma_{\mathbf{k}\rho}{}^{(\pm)}(\epsilon_{\mathbf{k}\rho})$, and $\Delta_{\mathbf{k}\rho} \equiv \Delta_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})$. Considering that $\gamma_{\mathbf{k}\rho}{}^{(+)}/\gamma_{\mathbf{k}\rho}{}^{(-)} \gtrsim 1$, $\Delta_{\mathbf{k}\rho} \gtrsim 1$, and using (45) we find that the energy shift from the maximum frequency corresponding to a symmetric Lorentzian line is equal to

$$\epsilon_{\mathbf{k}\rho}{}^2 - \Omega_{\mathbf{k}\rho}{}^2\Delta_{\mathbf{k}\rho} = \Omega_{\mathbf{k}\rho}{}^2\{-(\Delta_{\mathbf{k}\rho} + \gamma_{\mathbf{k}\rho}{}^{(+)}/\gamma_{\mathbf{k}\rho}{}^{(-)}) + [(\Delta_{\mathbf{k}\rho} + \gamma_{\mathbf{k}\rho}{}^{(+)}/\gamma_{\mathbf{k}\rho}{}^{(-)})^2 + \gamma_{\mathbf{k}\rho}{}^2]^{1/2}\}. \tag{46}$$

The expression (46) indicates that the energy shift from the maximum frequency of the symmetric Lorentzian line depends entirely on the value of the damping function $\gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})$. In the case of resonance at frequencies $\omega^2 \sim \epsilon_{\mathbf{k}\rho}{}^2$, the damping function $\gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})$ cannot be disregarded in (46), for the same reason that it must be retained in the denominator of (43). Therefore, in the neighborhood of frequencies $\omega^2 \sim \epsilon_{\mathbf{k}\rho}{}^2$ the spectral function (43) may be written as

$$J_{\mathbf{k}\rho}{}^{(1)}(\omega) \approx (e^{\beta\omega}-1)^{-1}\left(\frac{2}{\pi}\right)\tilde{\Omega}_{\mathbf{k}\rho}{}^{(-)}(\epsilon_{\mathbf{k}\rho}) \times \frac{\Omega_{\mathbf{k}\rho}{}^2(\epsilon_{\mathbf{k}\rho})\gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho}) + [\omega^2 - \Omega_{\mathbf{k}\rho}{}^2(\epsilon_{\mathbf{k}\rho})]\gamma_{\mathbf{k}\rho}{}^{(-)}(\epsilon_{\mathbf{k}\rho})}{[\omega^2 - \Omega_{\mathbf{k}\rho}{}^2(\epsilon_{\mathbf{k}\rho})\Delta_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})]^2 + [\Omega_{\mathbf{k}\rho}{}^2(\epsilon_{\mathbf{k}\rho})\gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})]^2}, \tag{47}$$

provided that $\epsilon_{\mathbf{k}\rho}{}^2$, given by (45), satisfies at least one of the following relations:

$$\epsilon_{\mathbf{k}\rho}{}^2 - [\tilde{\omega}_{\rho_1}(\mathbf{q}) \pm \tilde{\omega}_{\rho_2}(\mathbf{k}-\mathbf{q})]^2 = 0, \tag{48}$$

$$\epsilon_{\mathbf{k}\rho}{}^2 - [\tilde{\omega}_{\rho_1}(\mathbf{k}_1) + \tilde{\omega}_{\rho_2}(\mathbf{q}) \pm \tilde{\omega}_{\rho_3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]^2 = 0, \tag{49}$$

a condition that is required so that the damping functions $\gamma_{\mathbf{k}\rho}{}^{(\pm)}(\epsilon_{\mathbf{k}\rho})$ are different than zero. The relations (48) and (49) are derived from the arguments of the $\delta$ functions appearing in the expression (36).

In the limit when the damping functions $\gamma_{\mathbf{k}\rho}{}^{(\pm)}(\epsilon_{\mathbf{k}\rho})$ may be considered to be very small but finite, $\gamma_{\mathbf{k}\rho}{}^{(\pm)}(\epsilon_{\mathbf{k}\rho}) \ll 1$, the resonance band described by the function (47) is an asymmetric Lorentzian line with maximum at frequencies $\omega^2 \sim \epsilon_{\mathbf{k}\rho}{}^2$. In the case of exact resonance, when $\omega^2 = \epsilon_{\mathbf{k}\rho}{}^2$ the function (47) becomes

$$J_{\mathbf{k}\rho}{}^{(1)}(\epsilon_{\mathbf{k}\rho}) \approx (2/\pi)(e^{\beta\epsilon_{\mathbf{k}\rho}}-1)^{-1}\Gamma_{\mathbf{k}\rho}{}^{-1}(\epsilon_{\mathbf{k}\rho}), \tag{50}$$

where $\Gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})$ and $\Gamma_{\mathbf{k}\rho}{}^{-1}(\epsilon_{\mathbf{k}\rho})$ are the width and the height of the resonance band in energy units, respectively, with

$$\Gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho}) = 2\tilde{\Omega}_{\mathbf{k}\rho}{}^{(+)}\gamma_{\mathbf{k}\rho}{}^{(+)} \times [(1 + \Delta_{\mathbf{k}\rho}\gamma_{\mathbf{k}\rho}{}^{(-)}/\gamma_{\mathbf{k}\rho}{}^{(+)})^2 + \gamma_{\mathbf{k}\rho}{}^2(\gamma_{\mathbf{k}\rho}{}^{(-)}/\gamma_{\mathbf{k}\rho}{}^{(+)})^2]^{1/2} - (1 + \Delta_{\mathbf{k}\rho}\gamma_{\mathbf{k}\rho}{}^{(-)}/\gamma_{\mathbf{k}\rho}{}^{(+)})\}\gamma_{\mathbf{k}\rho}{}^{(-)-2}. \tag{51}$$

It is easily seen from (51) that the expression for $\Gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})$ is made up of the product of two factors: The first one, $\tilde{\Omega}_{\mathbf{k}\rho}{}^{(+)}\gamma_{\mathbf{k}\rho}{}^{(+)}$, represents the bandwidth in energy units of a symmetric Lorentzian line, while the remaining factor indicates the deviation from the symmetric line caused by the existence of the damping function $\gamma_{\mathbf{k}\rho}{}^{(-)}$.

With reference to our discussion in the preceding section regarding the coupling functions appearing in the expressions (A6)–(A9), (A16), and (A17) as well as from (36) and the definition of the functions $\gamma_{\mathbf{k}\rho}{}^{(\pm)}$, Eq. (40), it follows that $\gamma_{\mathbf{k}\rho}{}^{(+)}$ and $\gamma_{\mathbf{k}\rho}{}^{(-)}$ are of the same order of magnitude; therefore, both functions are either finite or go to zero simultaneously. Thus the spectrum described by the function (47) for $\gamma_{\mathbf{k}\rho}{}^{(\pm)} \ll 1$ resonates at maximum frequencies $\omega^2 \sim \epsilon_{\mathbf{k}\rho}{}^2$ obtained from the solutions of (45) and has an asymmetric Lorentzian line shape with a bandwidth of the order of $\Gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})$ shown by the expression (51). Since $\gamma_{\mathbf{k}\rho}{}^{(-)}(\epsilon_{\mathbf{k}\rho})/\gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho}) \lesssim \frac{1}{2}$, the deviation from the symmetric Lorentzian line depends entirely on the value of the damping function $\gamma_{\mathbf{k}\rho}(\epsilon_{\mathbf{k}\rho})$. In discussing the excitation spectrum of (43), we have neglected the $\omega$ dependence of the damping functions $\gamma_{\mathbf{k}}^{(\pm)}(\omega)$. This assumption is justifiable because we are concerned with the polariton excitation spectrum at zero temperature and in most physical problems the nature of the real final states is such that the relation $(\partial/\partial\omega)\gamma_{\mathbf{k}\rho}^{(\pm)}(\omega)\ll 1$ is applicable.

For values of $\omega$ not near $\Omega_{\mathbf{k}\rho}^{2}(\omega)\Delta_{\mathbf{k}\rho}(\omega)$, that is, in the vicinity of the edges of the polariton absorption band the spectral function (43) can be approximated by

$$J_{\mathbf{k}\rho}^{(1)}(\omega)\approx\left(\frac{2}{\pi}\right)(e^{\beta\omega}-1)^{-1}\tilde{\Omega}_{\mathbf{k}\rho}^{(-)}(\omega)\times\frac{\Omega_{\mathbf{k}\rho}^{2}(\omega)\gamma_{\mathbf{k}\rho}^{(+)}(\omega)+\omega^{2}\gamma_{\mathbf{k}\rho}^{(-)}(\omega)}{[\omega^{2}-\Omega_{\mathbf{k}\rho}^{2}(\omega)\Delta_{\mathbf{k}\rho}(\omega)]^{2}}. \tag{52}$$

We remark that the two terms in (52) behave differently with respect to $\omega$. For example, for large values of $\omega$ considering only the leading terms in (52) the functions $\gamma_{\mathbf{k}\rho}^{(+)}(\omega)$ and $\gamma_{\mathbf{k}\rho}^{(-)}(\omega)$ are proportional to $\omega^{-4}$ and $\omega^{-2}$, respectively. Therefore, for very large values of $\omega$ such behavior should be observed experimentally in the vicinity of the edges of the polariton absorption band.

In the limiting case when both damping functions $\gamma_{\mathbf{k}\rho}^{(\pm)}(\omega)$ go to zero simultaneously, the spectral function (43) tends to a $\delta$ shape distribution, i.e.,

$$J_{\mathbf{k}\rho}^{(1)}(\omega)\approx 2(e^{\beta\omega}-1)^{-1}\tilde{\Omega}_{\mathbf{k}\rho}^{(-)}(\omega)\times\delta(\omega^{2}-\Omega_{\mathbf{k}\rho}^{(+)}(\omega)\Omega_{\mathbf{k}\rho}^{(-)}(\omega)),\quad\text{for}\quad\gamma_{\mathbf{k}\rho}^{(\pm)}(\omega)\to 0 \tag{53}$$

where the functions $\Omega_{\mathbf{k}\rho}^{(\pm)}(\omega)$ are given by (32) with the scattering function $R_{\mathbf{k}\rho}^{(\pm)}(\omega)$, which is now a real quantity, determined by the expression (34). The spectral function (53) corresponds to the transparent region of frequencies of the crystal and has a $\delta$-function distribution peaked at frequencies $\tilde{\epsilon}_{\mathbf{k}\rho}$ determined by the real solutions of the equation

$$\tilde{\epsilon}_{\mathbf{k}\rho}^{2}-\Omega_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})\Omega_{\mathbf{k}\rho}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})=0, \tag{54}$$

where $\Omega_{\mathbf{k}\rho}^{(\pm)}(\tilde{\epsilon}_{\mathbf{k}\rho})$ are obtained from the expressions (32)–(34) by replacing $\omega$ by $\tilde{\epsilon}_{\mathbf{k}\rho}$. Then (53) becomes

$$J_{\mathbf{k}\rho}^{(1)}(\omega)\approx 2(e^{\beta\omega}-1)^{-1}\tilde{\Omega}_{\mathbf{k}\rho}^{(-)}(\omega)\delta(\omega^{2}-\tilde{\epsilon}_{\mathbf{k}\rho}^{2}). \tag{55}$$

In this case, the polariton waves propagate in the medium without damping with frequencies $\tilde{\epsilon}_{\mathbf{k}\rho}$ derived from the solutions of (54), which indicates that the crystal is transparent in the range of frequencies $\tilde{\epsilon}_{\mathbf{k}\rho}$. Rewriting (32) as

$$\Omega_{\mathbf{k}\rho}^{(\pm)}(\tilde{\epsilon}_{\mathbf{k}\rho})=\tilde{\Omega}_{\mathbf{k}\rho}^{(\pm)}(\tilde{\epsilon}_{\mathbf{k}\rho})+R_{\mathbf{k}\rho}^{(\pm)}(\tilde{\epsilon}_{\mathbf{k}\rho}) \tag{56}$$

and if we make some drastic approximations which are correct only as far as the order of magnitude is concerned, i.e., take $R_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})\sim R_{\mathbf{k}\rho}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})\equiv R_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})$, $\tilde{\Omega}_{\mathbf{k}\rho}^{(\pm)}(\tilde{\epsilon}_{\mathbf{k}\rho})\sim\tilde{\Omega}_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})$ then the expression (54) is reduced to the approximate form

$$\tilde{\epsilon}_{\mathbf{k}\rho}-\omega_{\rho}(\mathbf{k})\approx[\bar{\omega}_{\rho}(\mathbf{k})-\omega_{\rho}(\mathbf{k})+\hat{\omega}_{\rho}(\mathbf{k})]+[\omega_{\rho}(\mathbf{k})-\bar{\omega}_{\rho}(\mathbf{k})+\hat{\omega}_{\rho}(\mathbf{k})]^{2}\tilde{\omega}_{\rho}(\mathbf{k})\times[\tilde{\epsilon}_{\mathbf{k}\rho}^{2}-\tilde{\omega}_{\rho}^{2}(\mathbf{k})]^{-1}+R_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho}). \tag{57}$$

The expression (57) represents the equivalent result obtained by applying a power series expansion in (54) and retaining only the first nonvanishing term. If in the first term on the right-hand side of (57), that is defined by (26) and (27), we take $\langle\xi_{\rho'}^{\dagger}(\mathbf{q})\xi_{\rho'}(\mathbf{q})\rangle\approx 0$ and $\langle\xi_{\rho'}(\mathbf{q})\xi_{\rho'}(-\mathbf{q})\rangle\approx 0$, then the resulting expression for $\hat{\omega}_{\rho}(\mathbf{k})$ can be employed to describe the probability amplitude in energy units for the three-photon absorption process far from resonance, which has been considered by Toshich[7] via first-order perturbation theory. Similar contributions arise from the amplitude $Q_3$ contained in the expression for $\bar{\omega}_{\rho}(\mathbf{k})$. If $\tilde{\epsilon}_{\mathbf{k}\rho}$ as well as the $\bar{\omega}_{\rho}(\mathbf{k})$'s are replaced by the corresponding unperturbed frequencies, $\omega_{\rho}(\mathbf{k})$'s, in the expression for the cubic anharmonic terms that appear in $R_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})$, the resultant expression can be reduced to that derived by Toshich[7] by means of second-order perturbation theory.

### B. Second Approximation

In the limiting case when the imaginary part of the polarization operator in the lowest approximation tends to zero, i.e., $\gamma_{\mathbf{k}\rho}^{(\pm)}(\epsilon_{\mathbf{k}\rho})\to 0$, the polariton Green's function (24) in the first approximation becomes

$$D_{\mathbf{k}\rho}^{(1)}(\omega)=(1/\pi)\Omega_{\mathbf{k}\rho}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})[\omega^{2}-\tilde{\epsilon}_{\mathbf{k}\rho}^{2}]^{-1}, \tag{58}$$

where the frequencies $\tilde{\epsilon}_{\mathbf{k}\rho}$ are determined by the solutions of (54). Mathematically, this situation means that the frequencies $\tilde{\epsilon}_{\mathbf{k}\rho}$ do not satisfy the requirements of the Eqs. (48) and (49) corresponding to the arguments of the $\delta$ functions appearing in the expression for the imaginary part of the polarization operator in the lowest approximation, while the physical implications are that the bare polariton is dressed by the anharmonic field of the others and the resulting quasiparticle with energy $\tilde{\epsilon}_{\mathbf{k}\rho}$ may be called the "physical polariton." It is easily shown that the excitation spectrum described by (58) results from an equivalent Hamiltonian, that is correct in the first approximation, had has the form

$$\mathcal{H}^{(1)}=\text{const}+\tfrac{1}{2}\sum_{\mathbf{k},\rho}[\Omega_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})+\Omega_{\mathbf{k}\rho}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})]\xi_{\rho}^{\dagger}(\mathbf{k})\xi_{\rho}(\mathbf{k})+\tfrac{1}{4}\sum_{\mathbf{k},\rho}[\Omega_{\mathbf{k}\rho}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})-\Omega_{\mathbf{k}\rho}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})]\times[\xi_{\rho}(\mathbf{k})\xi_{\rho}(-\mathbf{k})+\xi_{\rho}^{\dagger}(\mathbf{k})\xi_{\rho}^{\dagger}(-\mathbf{k})]. \tag{59}$$

In the second approximation, the polariton Green's function (24) may be written as

$$D_{\mathbf{k}\rho}^{(2)}(\omega)=(1/\pi)\,{}^{1}\Omega_{\mathbf{k}\rho}^{(-)}(\omega)\times[\omega^{2}-{}^{1}\Omega_{\mathbf{k}\rho}^{(+)}(\omega)\,{}^{1}\Omega_{\mathbf{k}\rho}^{(-)}(\omega)]^{-1}, \tag{60}$$

where

$${}^{1}\Omega_{\mathbf{k}\rho}^{(\pm)}(\omega)=\Omega_{\mathbf{k}\rho}^{(\pm)}(\tilde{\epsilon}_{\mathbf{k}\rho})+\tfrac{1}{2}[P_{11}^{(1)}(\mathbf{k},\rho;\omega)+P_{11}^{(1)}(\mathbf{k},\rho;-\omega)\pm P_{12}^{(1)}(\mathbf{k},\rho;\omega)\pm P_{12}^{(1)}(\mathbf{k},\rho;-\omega)], \tag{61}$$

and the superscript (1) indicates that the quantities in question have to be evaluated by means of the Hamiltonian (59). Performing the calculation we find that the derived expression for $D_{\mathbf{k}\rho}{}^{(2)}(\omega)$ has similar form with that of (37) but now all the expressions appearing in (37) are correct in the first approximation, i.e.,

$$D_{\mathbf{k}\rho}{}^{(2)}(\omega)=\frac{1}{\pi}{}^1\tilde{\Omega}_{\mathbf{k}\rho}{}^{(-)}(\omega)\times\frac{1+{}^1\Delta_{\mathbf{k}\rho}{}^{(-)}(\omega)-i{}^1\gamma_{\mathbf{k}\rho}{}^{(-)}(\omega)}{\omega^2-\Omega_{\mathbf{k}\rho}{}^{(1)2}(\omega)[\Delta_{\mathbf{k}\rho}{}^{(1)}(\omega)-i\gamma_{\mathbf{k}\rho}{}^{(1)}(\omega)]},\quad(62)$$

where the expressions for $\Delta_{\mathbf{k}\rho}{}^{(1)}(\omega)$, $\gamma_{\mathbf{k}\rho}{}^{(1)}(\omega)$, ${}^1\gamma_{\mathbf{k}\rho}{}^{(\pm)}(\omega)$, and $\Omega_{\mathbf{k}\rho}{}^{(1)}(\omega)$ are obtained from the corresponding ones for $\Delta_{\mathbf{k}\rho}(\omega)$, $\gamma_{\mathbf{k}\rho}(\omega)$, $\gamma_{\mathbf{k}\rho}{}^{(\pm)}(\omega)$, and $\Omega_{\mathbf{k}\rho}(\omega)$, respectively, by making the following replacements:

$$\tilde{\omega}_\rho(\mathbf{k})\rightarrow\tilde{\epsilon}_{\mathbf{k}\rho},\quad\bar{\omega}_\rho(\mathbf{k})\rightarrow\tfrac{1}{2}[\Omega_{\mathbf{k}\rho}{}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})+\Omega_{\mathbf{k}\rho}{}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})],$$
$$\hat{\omega}_\rho(\mathbf{k})\rightarrow\tfrac{1}{2}[\Omega_{\mathbf{k}\rho}{}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})-\Omega_{\mathbf{k}\rho}{}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})],\quad(63)$$

for each particular frequency mode. The relations (63) become obvious when a comparison between the Hamiltonians (31) and (59) is made. As an example, we give the expressions (32)–(35) in the new representation:

$${}^1\Omega_{\mathbf{k}\rho}{}^{(\pm)}(\omega)={}^1\tilde{\Omega}_{\mathbf{k}\rho}{}^{(\pm)}(\omega)+{}^1R_{\mathbf{k}\rho}{}^{(\pm)}(\omega),\quad(64\text{a})$$

$${}^1\tilde{\Omega}_{\mathbf{k}\rho}{}^{(+)}(\omega)=\Omega_{\mathbf{k}\rho}{}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})+[\omega_\rho(\mathbf{k})-\Omega_{\mathbf{k}\rho}{}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})]^2\tilde{\epsilon}_{\mathbf{k}\rho}[\omega^2-\tilde{\epsilon}_{\mathbf{k}\rho}{}^2]^{-1},\quad(64\text{b})$$

$${}^1\tilde{\Omega}_{\mathbf{k}\rho}{}^{(-)}(\omega)=\Omega_{\mathbf{k}\rho}{}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})+[\omega_\rho(\mathbf{k})-\Omega_{\mathbf{k}\rho}{}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})]^2\tilde{\epsilon}_{\mathbf{k}\rho}[\omega^2-\tilde{\epsilon}_{\mathbf{k}\rho}{}^2]^{-1},\quad(64\text{c})$$

$$\begin{aligned}{}^1R_{\mathbf{k}\rho}{}^{(\pm)}(\omega)={}&2\sum_{\mathbf{q},\rho1,\rho2}{}^1V_3{}^{(\pm)}(\mathbf{k},\mathbf{q})\frac{[\tilde{\epsilon}_{\rho1}(\mathbf{q})+\tilde{\epsilon}_{\rho2}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\tilde{\epsilon}_{\rho1}(\mathbf{q})+\tilde{\epsilon}_{\rho2}(\mathbf{k}-\mathbf{q})]^2}+2\sum_{\mathbf{q},\rho1,\rho2}{}^1\hat{V}_3{}^{(\pm)}(\mathbf{k},\mathbf{q})\frac{[\tilde{\epsilon}_{\rho1}(\mathbf{q})-\tilde{\epsilon}_{\rho2}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\tilde{\epsilon}_{\rho1}(\mathbf{q})-\tilde{\epsilon}_{\rho2}(\mathbf{k}-\mathbf{q})]^2}\\&+2\sum_{\substack{\mathbf{q},\mathbf{k}_1\\\rho1,\rho2,\rho3}}{}^1V_4{}^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)\frac{[\tilde{\epsilon}_{\rho1}(\mathbf{k}_1)+\tilde{\epsilon}_{\rho2}(\mathbf{q})+\tilde{\epsilon}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]}{\omega^2-[\tilde{\epsilon}_{\rho1}(\mathbf{k}_1)+\tilde{\epsilon}_{\rho2}(\mathbf{q})+\tilde{\epsilon}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]^2}\\&+2\sum_{\substack{\mathbf{q},\mathbf{k}_1\\\rho1,\rho2,\rho3}}{}^1\hat{V}_4{}^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)\frac{[\tilde{\epsilon}_{\rho1}(\mathbf{k}_1)-\tilde{\epsilon}_{\rho2}(\mathbf{q})+\tilde{\epsilon}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]}{\omega^2-[\tilde{\epsilon}_{\rho1}(\mathbf{k}_1)-\tilde{\epsilon}_{\rho2}(\mathbf{q})+\tilde{\epsilon}_{\rho3}(\mathbf{k}-\mathbf{q}-\mathbf{k}_1)]^2},\end{aligned}\quad(65)$$

where the coupling functions ${}^1V_3{}^{(\pm)}(\mathbf{k},\mathbf{q})$, ${}^1\hat{V}_3{}^{(\pm)}(\mathbf{k},\mathbf{q})$, ${}^1V_4{}^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$, and ${}^1\hat{V}_4{}^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ are given by (A7)–(A9), A(16), and (A17), respectively, after the replacements (63) have been made. In this approximation, the coupling functions ${}^1\hat{V}_3{}^{(\pm)}(\mathbf{k},\mathbf{q})$ and ${}^1\hat{V}_4{}^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ depend entirely on the numerical value of the quantity $\Omega_{\mathbf{k}\rho}{}^{(+)}(\tilde{\epsilon}_{\mathbf{k}\rho})-\Omega_{\mathbf{k}\rho}{}^{(-)}(\tilde{\epsilon}_{\mathbf{k}\rho})$, which is taken equal to zero when conventional perturbation methods are used for the calculation. The renormalization of the frequencies for the polariton modes that has been achieved in this approximation is the outcome of the self-consistent manner in which the calculation has been conducted. The excitation spectrum described by (60), which is now due to the interaction among the physical polariton modes, can be discussed in the same manner that has been employed in the first part of this section regarding the polariton Green's function in the first approximation. Therefore, there is no need for repetition.

## V. SUMMARY

We have presented an accurate microscopic approach for the calculation of the optical anharmonic excitation spectrum of molecular crystals by means of the Green's-function method. The development of a general expression for Dyson's equation describing the system of interacting polariton fields has made possible the evaluation of the polarization operator and consequently the polariton Green's function in successive and well-defined approximations. The important effects on the frequency of the polariton modes arising from the renormalization procedure in the sequence of approximations have been pointed out. Physical phenomena occurring when the system of interacting polaritons is either near or far from resonances or in the transparent range of frequencies of the crystal have been considered. Application of the results developed in the present study to specific crystals shall be reported later.

## APPENDIX

The components of the polarization operator that appear in the expression (30) consist of linear combinations of two- and three-polariton Green's functions which are calculated here by means of the renormalized zeroth-order Hamiltonian (31). If we introduce the operator

$$\begin{aligned}\tilde{A}^\dagger(\mathbf{q},\mathbf{k}-\mathbf{q})\equiv(&\xi_{\rho_1}{}^\dagger(\mathbf{q})\xi_{\rho_2}{}^\dagger(\mathbf{k}-\mathbf{q})\ \ \xi_{\rho_1}(-\mathbf{q})\xi_{\rho_2}(\mathbf{q}-\mathbf{k})\\&\xi_{\rho_2}{}^\dagger(\mathbf{k}-\mathbf{q})\xi_{\rho_1}(-q)\ \ \xi_{\rho_1}{}^\dagger(\mathbf{q})\xi_{\rho_2}(\mathbf{q}-\mathbf{k})),\end{aligned}\quad(\text{A1})$$

then using (31) we derive the equation of motion for the Green's function $\langle\langle\tilde{A}(\mathbf{q},\mathbf{k}-\mathbf{q});\tilde{A}^\dagger(\mathbf{q},\mathbf{k}-\mathbf{q})\rangle\rangle$ in the form

$$\begin{aligned}L(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)\langle\langle\tilde{A}(\mathbf{q},\mathbf{k}-\mathbf{q});\tilde{A}^\dagger(\mathbf{q},\mathbf{k}-\mathbf{q})\rangle\rangle&=(1/2\pi)\\&\times\langle[\tilde{A}(\mathbf{q},\mathbf{k}-\mathbf{q}),\tilde{A}^\dagger(\mathbf{q},\mathbf{k}-\mathbf{q})]_{-\beta}\rangle_{t=t'},\end{aligned}\quad(\text{A2})$$

where $L(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)$ is a four-by-four matrix having the following nonzero matrix elements:

$$\begin{aligned}
&L_{11}(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)=\omega-\bar{\omega}_{\rho1}(\mathbf{q})-\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q}),\\
&L_{22}(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)=L_{11}(\mathbf{q},\mathbf{k}-\mathbf{q};-\omega),\\
&L_{33}(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)=\omega-\bar{\omega}_{\rho2}(\mathbf{q}-\mathbf{k})+\bar{\omega}_{\rho1}(\mathbf{q}),\\
&L_{44}(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)=L_{33}(\mathbf{q},\mathbf{k}-\mathbf{q};-\omega),\\
&L_{13}=L_{24}=-L_{31}=-L_{42}=-\hat{\omega}_{\rho1}(\mathbf{q}),\\
&L_{14}=L_{23}=L_{32}=L_{41}=-\hat{\omega}_{\rho2}(\mathbf{k}-\mathbf{q}),\\
&\qquad\hat{\beta}=\begin{pmatrix}\hat{\alpha} & \\ & \hat{\alpha}\end{pmatrix}.
\end{aligned}\tag{A3}$$

The determinant of the matrix $L(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)$ factorizes into

$$\begin{aligned}\det L(\mathbf{q},\mathbf{k}-\mathbf{q};\omega)=&\{\omega^2-[\bar{\omega}_{\rho1}(\mathbf{q})+\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})]^2\}\\&\times\{\omega^2-[\bar{\omega}_{\rho1}(\mathbf{q})-\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})]^2\},\end{aligned}\tag{A4}$$

which shows that the poles of the Green's function $\langle\langle\tilde{A}(\mathbf{q},\mathbf{k}-\mathbf{q});\tilde{A}^+(\mathbf{q},\mathbf{k}-\mathbf{q})\rangle\rangle$ determined by the zeros of (A4) are equal to

$$\omega^2=[\bar{\omega}_{\rho1}(\mathbf{q})\pm\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})]^2,\tag{A5}$$

indicating the existence of frequencies that are equal not only of the sum but also of the difference between the two renormalized polariton modes $\bar{\omega}_{\rho1}(\mathbf{q})$ and $\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})$, respectively.

Solving the set of equations (A2) and then substituting the calculated expressions for the different combinations of the two-polariton Green's functions into (30), we derive the two first terms that appear on the right-hand side of (34) with the two-particle scattering amplitudes $V_3^{(\pm)}(\mathbf{k},\mathbf{q})$ given by

$$V_3^{(+)}(\mathbf{k},\mathbf{q})=|\tilde{\alpha}_+|^2(u_+^2+v_-^2)-|2\alpha|^2(u_-^2+v_+^2),\tag{A6}$$

$$\begin{aligned}V_3^{(-)}(\mathbf{k},\mathbf{q})=&|\tilde{\alpha}_-|^2(u_+^2+v_+^2)\\&+2\alpha\tilde{\alpha}_-(u_+v_-+u_-v_+),\end{aligned}\tag{A7}$$

$$\begin{aligned}\hat{V}_3^{(+)}(\mathbf{k},\mathbf{q})=&2[|\tilde{\alpha}_+|^2-|2\alpha|^2]u_+u_-\\&+4\tilde{\alpha}_+\alpha(u_+v_--u_-v_+),\end{aligned}\tag{A8}$$

$$\hat{V}_3^{(-)}(\mathbf{k},\mathbf{q})=2|\tilde{\alpha}_-|^2u_+u_-+4\tilde{\alpha}_-\alpha u_+v_+,\tag{A9}$$

where we have made use of the following notation:

$$\begin{aligned}
&u_\pm\equiv\frac{1}{2}\left[\frac{\bar{\omega}_{\rho1}(\mathbf{q})}{\bar{\omega}_{\rho1}(\mathbf{q})}\pm\frac{\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})}{\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})}\right],\\
&v_\pm\equiv\frac{1}{2}\left[\frac{\hat{\omega}_{\rho1}(\mathbf{q})}{\hat{\omega}_{\rho1}(\mathbf{q})}\pm\frac{\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})}{\bar{\omega}_{\rho2}(\mathbf{k}-\mathbf{q})}\right],
\end{aligned}\tag{A10}$$

$$\begin{aligned}
&\tilde{\alpha}_\pm\equiv\alpha\pm3\beta,\\
&\alpha\equiv\alpha(\mathbf{q},\rho_1;\mathbf{k}-\mathbf{q},\rho_2;\mathbf{k},\rho),\\
&\beta\equiv\beta(-\mathbf{k},\rho;\mathbf{q},\rho_1;\mathbf{k}-\mathbf{q},\rho_2).
\end{aligned}\tag{A11}$$

In deriving (A6)–(A9), we have made use of the expressions (29b) in the limit of zero temperature for the distribution functions that result when the average value of the commutator appearing on the right-hand side of (A2) is taken.

The three-polariton Green's functions can be calculated in the same way. For example, if we define the operator $\tilde{A}_{123}$

$$\begin{aligned}\tilde{A}_{123}{}^\dagger\equiv\big(&\xi_3{}^\dagger\xi_2{}^\dagger\xi_1{}^\dagger\ \xi_{-3}\xi_{-2}\xi_{-1}\ \xi_3{}^\dagger\xi_2\xi_{-1}\ \xi_1{}^\dagger\xi_{-3}\xi_{-2}\ \xi_3{}^\dagger\xi_{-2}\xi_1{}^\dagger\\&\xi_{-1}\xi_2{}^\dagger\xi_{-3}\ \xi_{-3}\xi_2{}^\dagger\xi_1{}^\dagger\ \xi_{-1}\xi_{-2}\xi_3{}^\dagger\big),\end{aligned}\tag{A12}$$

where $1\equiv(\mathbf{k}_1,\rho_1)$, $2\equiv(\mathbf{q},\rho_2)$ ,and $3\equiv(\mathbf{k}-\mathbf{q}-\mathbf{k}_1,\rho_3)$, then the equation of motion for the Green's function $\langle\langle\tilde{A}_{123};\tilde{A}_{123}{}^\dagger\rangle\rangle$ is determined by making use of (31) as

$$\begin{aligned}&\tilde{L}(1,2,3;\omega)\langle\langle\tilde{A}_{123};\tilde{A}_{123}{}^\dagger\rangle\rangle\\&\qquad=(1/2\pi)\langle[\tilde{A}_{123},\tilde{A}_{123}{}^\dagger]_-\hat{\gamma}\rangle_{t=t'}.\end{aligned}\tag{A13}$$

The function $\tilde{L}(1,2,3;\omega)$ is now an 8×8 matrix whose nonzero matrix elements are equal to

$$\begin{aligned}
&\tilde{L}_{11}(\omega)=\tilde{L}_{22}(-\omega)=\omega-\bar{\omega}_1-\bar{\omega}_2-\bar{\omega}_3,\\
&\tilde{L}_{33}(\omega)=\tilde{L}_{44}(-\omega)=\omega+\bar{\omega}_1-\bar{\omega}_2-\bar{\omega}_3;\\
&\tilde{L}_{55}(\omega)=\tilde{L}_{66}(-\omega)=\omega-\bar{\omega}_1+\bar{\omega}_2-\bar{\omega}_3,\\
&\tilde{L}_{77}(\omega)=\tilde{L}_{88}(-\omega)=\omega-\bar{\omega}_1-\bar{\omega}_2+\bar{\omega}_3;\\
&\tilde{L}_{13}=\tilde{L}_{24}=-\tilde{L}_{31}=-\tilde{L}_{42}=\tilde{L}_{58}=\tilde{L}_{67}=\tilde{L}_{76}=\tilde{L}_{85}=-\hat{\omega}_1,\\
&\tilde{L}_{15}=\tilde{L}_{26}=\tilde{L}_{38}=\tilde{L}_{47}=-\tilde{L}_{62}=\tilde{L}_{74}=\tilde{L}_{82}=-\hat{\omega}_2,\\
&\tilde{L}_{17}=\tilde{L}_{28}=\tilde{L}_{36}=\tilde{L}_{45}=\tilde{L}_{54}=\tilde{L}_{63}\\
&\qquad=-\tilde{L}_{71}=-\tilde{L}_{82}=-\hat{\omega}_3.
\end{aligned}\tag{A14}$$

In (A13) $\hat{\gamma}$ is an 8×8 unit matrix with all the off-diagonal elements equal to zero while the diagonal ones consist of a sequence of $+1$ to $-1$. The determinant of $\tilde{L}(1,2,3;\omega)$ is equal to

$$\begin{aligned}\det\tilde{L}(1,2,3;\omega)=&[\omega^2-(\bar{\omega}_1+\bar{\omega}_2+\bar{\omega}_3)^2]\\&\times[\omega^2-(\bar{\omega}_1+\bar{\omega}_2-\bar{\omega}_3)^2][\omega^2-(\bar{\omega}_1-\bar{\omega}_2+\bar{\omega}_3)^2]\\&\times[\omega^2-(\bar{\omega}_2+\bar{\omega}_3-\bar{\omega}_1)^2].\end{aligned}\tag{A15}$$

The zeros of (A15) determine the poles of the Green's function $\langle\langle\tilde{A}_{123};\tilde{A}_{123}{}^\dagger\rangle\rangle$, indicating the existence of frequencies of all possible combinations among the three renormalized polariton modes.

Solving the system of equations (A13), substituting the results into (30), and using (29b) in the limit of zero temperature, we obtain, after some lengthy algebra, the last two terms appearing on the right-hand side of (34) where the three-polariton scattering amplitudes

$V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)$ are found to be

$$V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)=3|Q_2\pm 4Q_1|^2\frac{\bar\omega_1\bar\omega_2}{\tilde\omega_1\tilde\omega_2}\mu+\tfrac{1}{4}|4Q_3\pm 3Q_2|^2\frac{\bar\omega_2(\bar\omega_3\mp\hat\omega_3)}{\tilde\omega_2\tilde\omega_3}\left[\frac{\bar\omega_1}{\tilde\omega_1}\left(1-\frac{\bar\omega_1\bar\omega_2+\hat\omega_1\hat\omega_2}{\tilde\omega_1\tilde\omega_2}\right)\pm\frac{\hat\omega_1{}^2\hat\omega_2}{\tilde\omega_1{}^2\tilde\omega_2}\right]$$

$$\pm\tfrac{3}{4}(4Q_3\pm 3Q_2)(Q_2\pm 4Q_1)\frac{\bar\omega_2\hat\omega_2}{\tilde\omega_1\tilde\omega_2}\left[\frac{(\bar\omega_1\bar\omega_2-\hat\omega_1\hat\omega_2)\tilde\omega_3}{\tilde\omega_1\tilde\omega_2\tilde\omega_3}-\frac{\hat\omega_2}{\tilde\omega_2}\right], \tag{A16}$$

$$\hat V_4^{(\pm)}(\mathbf{k},\mathbf{q},\mathbf{k}_1)=3|Q_2\pm 4Q_1|^2\mu\hat\mu_{123}+(Q_2\pm 4Q_1)(4Q_3\pm 3Q_2)$$

$$\times\left\{\frac{6\hat\omega_1}{\tilde\alpha_1}\left(\bar\mu\pm\frac{\hat\omega_3}{\tilde\omega_3}\mu\right)-(6\mu+\tfrac{1}{4}\hat\mu_{123})\left[\frac{2\hat\omega_1}{\tilde\omega_1}\left(\frac{\bar\omega_2}{\tilde\omega_2}+\frac{\bar\omega_3}{\tilde\omega_3}\right)+\frac{2\bar\omega_1\hat\omega_2}{\tilde\omega_1\tilde\omega_2}\mp\frac{3\hat\omega_1\hat\omega_2}{\tilde\omega_1\tilde\omega_2}\right]\right\}$$

$$+|4Q_3\mp 3Q_2|^2\left\{\left[\frac{2\bar\omega_1\bar\omega_2}{\tilde\omega_1\tilde\omega_2}-2\bar\mu+\frac{\hat\omega_1\hat\omega_2}{\tilde\omega_1\tilde\omega_2}\mp\frac{\hat\omega_1}{\tilde\omega_1}\left(\frac{\bar\omega_2}{\tilde\omega_2}-\frac{\bar\omega_3}{\tilde\omega_3}\right)\right]\mu+\frac{1}{8}\left[\frac{4\hat\omega_2}{\tilde\omega_2}\bar\mu-\frac{2\bar\omega_1\bar\omega_2}{\tilde\omega_1\tilde\omega_2}\left(\frac{\hat\omega_2}{\tilde\omega_2}-\frac{\hat\omega_3}{\tilde\omega_3}\right)\mp\frac{\bar\omega_2\hat\omega_1\hat\omega_3}{\tilde\omega_1\tilde\omega_2\tilde\omega_3}\right.\right.$$

$$\left.\left.-\frac{2\hat\omega_1}{\tilde\omega_1}\left(1\pm\frac{\hat\omega_2\bar\omega_3}{\tilde\omega_2\tilde\omega_3}\right)\right]\left[\frac{\hat\omega_1}{\tilde\omega_1}\left(\frac{\bar\omega_2}{\tilde\omega_2}+\frac{\bar\omega_3}{\tilde\omega_3}\mp\frac{\hat\omega_2}{\tilde\omega_2}\right)+\frac{\hat\omega_2}{\tilde\omega_2}\left(\frac{\bar\omega_1}{\tilde\omega_1}+\frac{\bar\omega_3}{\tilde\omega_3}\mp\frac{\hat\omega_3}{\tilde\omega_3}\right)+\frac{\hat\omega_3}{\tilde\omega_3}\left(\frac{\bar\omega_1}{\tilde\omega_1}+\frac{\bar\omega_2}{\tilde\omega_2}\mp\frac{\hat\omega_1}{\tilde\omega_1}\right)\right]\right\}, \tag{A17}$$

where

$$\mu\equiv\frac{1}{4}\left(\frac{\bar\omega_1}{\tilde\omega_1}+\frac{\bar\omega_2}{\tilde\omega_2}+\frac{\bar\omega_3}{\tilde\omega_3}+\frac{\bar\omega_1\bar\omega_2\bar\omega_3\mp\hat\omega_1\hat\omega_2\hat\omega_3}{\tilde\omega_1\tilde\omega_2\tilde\omega_3}\right), \tag{A18}$$

$$\bar\mu\equiv\frac{1}{4}\left(1+\frac{\bar\omega_1\bar\omega_2}{\tilde\omega_1\tilde\omega_2}+\frac{\bar\omega_2\bar\omega_3}{\tilde\omega_2\tilde\omega_3}+\frac{\bar\omega_1\bar\omega_3}{\tilde\omega_1\tilde\omega_3}\right), \tag{A19}$$

$$\hat\mu_{123}\equiv\left(\frac{\bar\omega_1}{\tilde\omega_1}-\frac{\bar\omega_1\bar\omega_2\bar\omega_3\mp\hat\omega_1\hat\omega_2\hat\omega_3}{\tilde\omega_1\tilde\omega_2\tilde\omega_3}\right), \tag{A20}$$

$$Q_1\equiv Q_1(\mathbf{k}_1,\rho_1;\,\mathbf{q},\rho_2;\,\mathbf{k}-\mathbf{k}_1-\mathbf{q},\,\rho_3;\,-\mathbf{k},\,\rho),\quad Q_2\equiv Q_2(\mathbf{k}_1,\rho_1;\,\mathbf{q},\rho_2;\,\mathbf{k}-\mathbf{k}_1-\mathbf{q},\,\rho_3;\,\mathbf{k},\rho),$$

$$Q_3\equiv Q_3(\mathbf{k}_1,\rho_1;\,\mathbf{q},\rho_2;\,-\mathbf{k},\,\rho;\,\mathbf{k}-\mathbf{k}_1-\mathbf{q},\,\rho_3). \tag{A21}$$

We remark that in the approximation used here there is no coupling between the two- and three-polariton Green's functions.