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Quantum theory of polariton absorption

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In honor of Emanuel Mooser's 60th birthday

Abstract. The quantum theory of light absorption in crystals is formulated taking into account spatial dispersion in the treatment of the mixed exciton-photon states. The imaginary part of the dielectric function is computed for the case of CuCl using different additional boundary conditions. The resulting lineshape is shown to differ from the perturbative Lorentzian lineshape. The role of dispersive polaritons in non linear processes is also described.

I. Introduction

Polaritons are the modes of the crystal which result from elementary excitations, like optical phonons and excitons, coupled to the radiation. The anomalous behaviour of the electromagnetic radiation at frequencies near those of the elementary excitation had been recognized for a long-time as responsible for the total reflection (Reststrahl) of the infrared radiation at the optical phonon frequencies in polar materials [1]. Classical theories of this phenomenon, based on the solution of Maxwell equations in a medium, lead to an anomalous dispersion in correspondence to peaks in the imaginary part of the dielectric function [2]. The quantum theory of polaritons was given by Hopfield [3], who diagonalized the Hamiltonian describing excitons coupled to photons and found the eigenmodes as superposition of excitons and photons, obtaining the same dispersion law as given by the classical theory.

The $\vec{k}$-dependence of the exciton states, not considered explicitly in the Hopfield treatment, is however important for all optical processes; it gives rise to two degenerate modes at frequencies higher than ω_L (longitudinal exciton frequency at $\vec{k} = 0$). This requires the introduction of additional boundary conditions (*abc*) [4] to decide the modes' relative occupancy, which cannot be obtained from the ordinary boundary conditions of Maxwell equations.

The classical analysis of the optical absorption and reflection, including the spatial dispersion ($\vec{k}$-dependence of the dielectric function) and different types of additional boundary conditions, have been considered by various authors [5], who have obtained spectral absorption and reflection profiles essentially different from Lorentzian lineshapes.

We here present a quantum approach to polariton absorption which takes into account the $\vec{k}$-dependence of the exciton states. We also propose a new additional condition and compare the resulting lineshapes.

II. Description of polariton states

The method of Hopfield for the diagonalization of coupled exciton-photon systems has been extended [6] to take into account the $\vec{k}$-dependence of the exciton state. The basic Hamiltonian is the same as that of Hopfield [3], but contains a quadratic $\vec{k}$-dependence of the exciton energy, which reads in the effective mass approximation

$$E_{ex}(\vec{k}) \equiv \hbar\omega_{ex}(\vec{k}) = \hbar\omega_T + \hbar^2 k^2/2(m_e + m_h). \tag{1}$$

The diagonalization of the Hamiltonian gives the polariton energies $E_{Pol}(l, \vec{k}) = \hbar\Omega_l(\vec{k})$, $l = 1, 2$, as the solution of the eigenvalue equation

$$[\omega_{ex}^2(\vec{k}) - \Omega^2][\Omega^2 - (vk)^2] + \beta\Omega^2\omega_T^2 = 0. \tag{2a}$$

In (2a) $vk = ck/\sqrt{\varepsilon_\infty}$ denotes the photon frequency, while the coupling parameter is given by

$$\beta = |\langle\psi_{ex}| x |\phi_0\rangle|^2 \, 8\pi e/V_0\hbar\omega_T, \tag{2b}$$

where V_0 is the volume of the lattice cell, and the dipole matrix element between the electronic ground state $|\phi_0\rangle$ and the exciton state $|\psi_{ex}\rangle$ depends on the band structure of the crystal [7]. The one-polariton states result to be of the form

$$|P^l, \vec{k}\rangle = B_R^{(l)}(\vec{k}) A_1^+(\vec{k}) |0\rangle + B_E^{(l)}(\vec{k}) A_2^+(\vec{k}) |0\rangle, \tag{3}$$

where $|0\rangle$ denotes the exciton and photon vacuum, $A_1^+(\vec{k})(A_2^+(\vec{k}))$ are the photon (exciton) creation operators, and $B_R^{(l)}(\vec{k})$ and $B_E^{(l)}(\vec{k})$, with $|B_R^{(l)}(\vec{k})|^2 + |B_E^{(l)}(\vec{k})|^2 = 1$, give the relative amplitude of photon and exciton in each polariton state. The superscripts $l = 1, 2$ denote the two polariton branches. For $\Omega < \omega_L$ only the lower polariton branch $l = 2$ exists, the frequency corresponding to the $l = 1$ solution being imaginary. The amplitudes $B_R^{(l)}(\vec{k})$ and $B_E^{(l)}(\vec{k})$ are given by complicated expressions [6] which involve all the material constants and the interaction parameter β defined in (2b). In terms of the exciton static polarizability α_0 and of the higher frequency dielectric constant ε_∞, we also have

$$\beta = 4\pi\alpha_0/\varepsilon_\infty. \tag{4}$$

The numerical values of the amplitudes $B^{(l)}(\vec{k})$ used in the following discussion, have been computed for the case of CuCl, for which extensive experimental studies [8] have been performed.

III. Quantum theory of the optical constants

As pointed out by Hopfield [3], absorption is due to the dissipation of energy through states, like phonons or impurities, that are coupled to the excitons. These processes in the end give rise to a finite polariton lifetime. As a consequence the

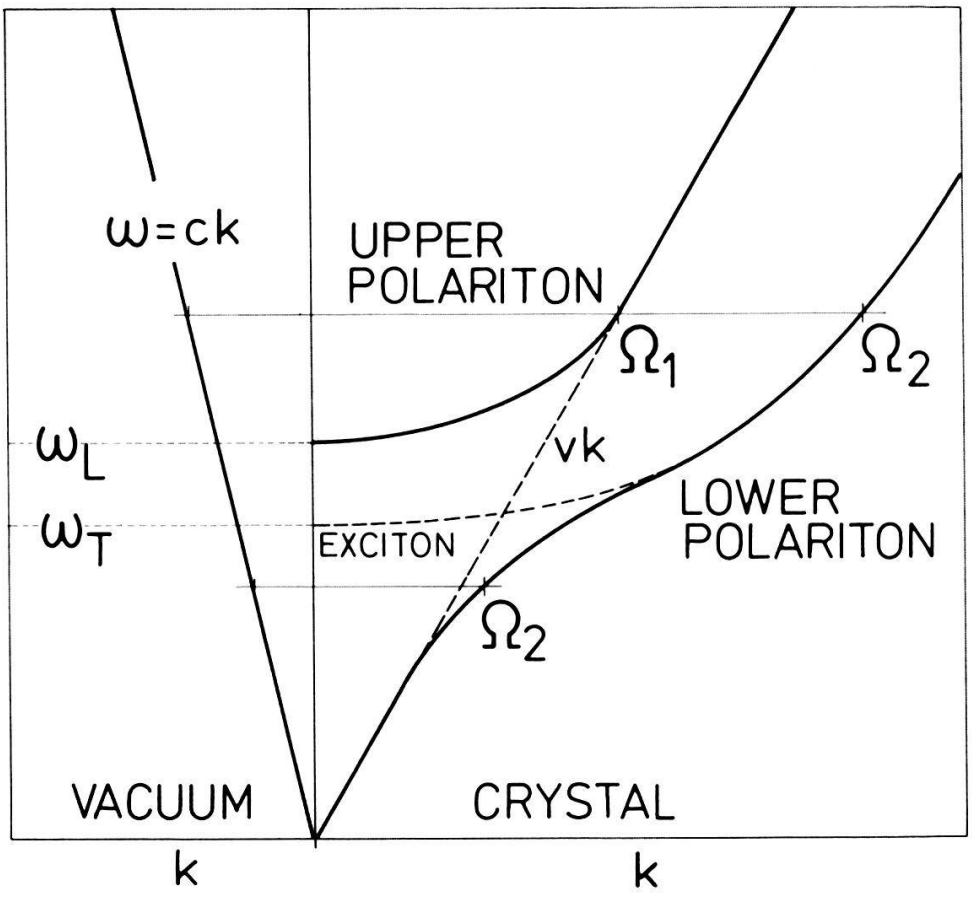

Figure 1
Sketch of the polariton, exciton and phonon dispersion law in crystal and in vacuum.

absorption will be related to the exciton component of the polariton state as given by equation 3. We study the optical absorption by choosing the wave vector of the polariton with the same direction as that of the incoming radiation, as is appropriate for normal incidence. Moreover we impose energy conservation i.e. $\Omega_l = ck = \omega$. We present a schematic diagram of all relevant modes considered in the optical process in Fig. 1.

Only one polariton mode exists for $\omega < \omega_L$ and the dissipation probability is given by $|B_E^{(2)}(k_2)|^2$, where $\vec{k}_2$ is the polariton wave vector corresponding to $\Omega_2(\vec{k}_2) = \omega$. The imaginary part of the dielectric function is related to the absorbed power in the usual way [9], to give

$$\varepsilon_2(\omega) = |B_E^{(2)}(\vec{k}_2)|^2 \, \Gamma^{(2)}(k_2)/\omega, \tag{5}$$

where we have considered the lifetime to be smaller than the transit time of the polariton through the crystal. Since the finite lifetime of the polaritons is due to scattering processes with phonons, impurities and surfaces, which do not involve appreciable energy changes, $\Gamma^{(2)}(k_2)$ turns out to be proportional to the density of states of the lower polaritons. The density of states $\rho_2(\Omega)$ can easily be computed from the dispersion law (2), and the resulting frequency dependence of $\Gamma^{(2)}$ must be inserted into equation (5).

The real part of the dielectric function in the absorbing region is given by

$$\varepsilon_1(\vec{k}, \omega) = \varepsilon_\infty + \frac{\pi}{2} \oint_0^\infty d\omega' \, \frac{\varepsilon_2(\vec{k}, \omega')\omega'}{\omega'^2 - \omega^2}, \tag{6}$$

and the other optical constants can be computed from $\varepsilon_1 \vec{k}, \omega)$ and $\varepsilon_2(\vec{k}, \omega)$ [9].

For $\omega > \omega_L$ two polariton states are possible, and additional conditions are needed in order to specify their relative amplitude. A variety of additional boundary conditions have been suggested in the literature [4], the first one being that of Pekar, which requires zero polarization on the crystal boundary, equivalent to a vanishing exciton component of the polariton. Each one of the *abc* defines combinations of the two polaritons

$$|P, \vec{k}_1, \vec{k}_2, \omega\rangle = c^{(1)}(\vec{k}_1)\,|P^1, k_1(\omega)\rangle + c^{(2)}(\vec{k}_2)\,|P^2, k_2(\omega)\rangle, \tag{7a}$$

with

$$|c^{(1)}(\vec{k}_1)|^2 + |c^{(2)}(\vec{k}_2)|^2 = 1. \tag{7b}$$

Since no unique criterion to define the coefficients $c^{(l)}(\vec{k}_l)$ exists, we dare propose a new condition inspired by irreversible thermodynamics, where in a stationary state the energy dissipation takes its minimum value [10]. Strictly speaking this result applies only to small deviations from equilibrium, but it has been successfully used to evaluate plasma transport coefficients under conditions where the collisional transport theory is not applicable [11]. The condition we propose can be stated as follows: The occupancy of degenerate polariton modes, given by the coefficients $c^{(1)}(\vec{k})$ and $c^{(2)}(\vec{k})$, corresponds to a minimum of energy dissipation. Since the dissipation, in our case, is proportional to

$$D(\omega) = |c^{(1)}(\vec{k}_1) B_E^{(1)}(\vec{k}_1)|^2 + |c^{(2)}(\vec{k}_2) B_E^{(2)}(\vec{k}_2)|^2 \tag{8}$$

with $\Omega_1(\vec{k}_1) = \Omega_2(\vec{k}_2) = \omega$, we can determine $c^{(1)}(\vec{k}_1)$ and $c^{(2)}(\vec{k}_2)$.

In Fig. 2 we give a plot of $D(\omega)$ for $\omega > \omega_L$ as computed from the above stated criterion, and as computed from Pekar criterion of vanishing exciton function of the surface (*abc* 1), or from the criterion of vanishing derivaty of the exciton function at the surface (*abc* 2). The material parameters are those appropriate to CuCl and the coupling parameter β is appropriate to the 1s exciton; for higher exciton states ($n > 1$) the coupling parameter decreases as $1/n^3$ according to (2b) [7]. It can be observed that the minimal dissipation criterion gives the same results for $D(\omega)$ as *abc* 2, but considerably different results compared to *abc* 1. Only detailed experiments will allow a definite choice of the most appropriate criterion to be used [12]. In particular, for $\omega \approx \omega_L$, *abc* 1 leads to $|c^{(1)}| = |c^{(2)}| = 1/\sqrt{2}$, while the other criteria give $|c^{(1)}| \approx 1$. The expression for ε_2 takes the form

$$\varepsilon_2(\omega) = \frac{1}{\omega}\{|c^{(1)}(\vec{k}_1) B_E^{(1)}(k_1)|^2\, \Gamma^{(1)}(\vec{k}_1) + |c^{(2)}(\vec{k}_2) B_E^{(2)}(\vec{k}_2)|^2\, \Gamma^{(2)}(k_2)\}, \tag{9}$$

where $\Gamma^{(1)}(\vec{k}_1)$ and $\Gamma^{(2)}(\vec{k}_2)$ are proportional to the density of states of the respective polariton branches. In a more accurate theory one also should take into account the k-dependence of the scattering matrix elements, which could be different for the two polariton branches and might eventually show a singular behaviour [4].

The optical lineshape for the 1s-exciton in CuCl is given in Fig. 3. We remark that the lineshape is highly asymmetric with a maximum corresponding to ω_L, and a very rapid decrease at higher frequencies in the case where the minimal dissipation criterion is used. This is due to the low density of states of the upper

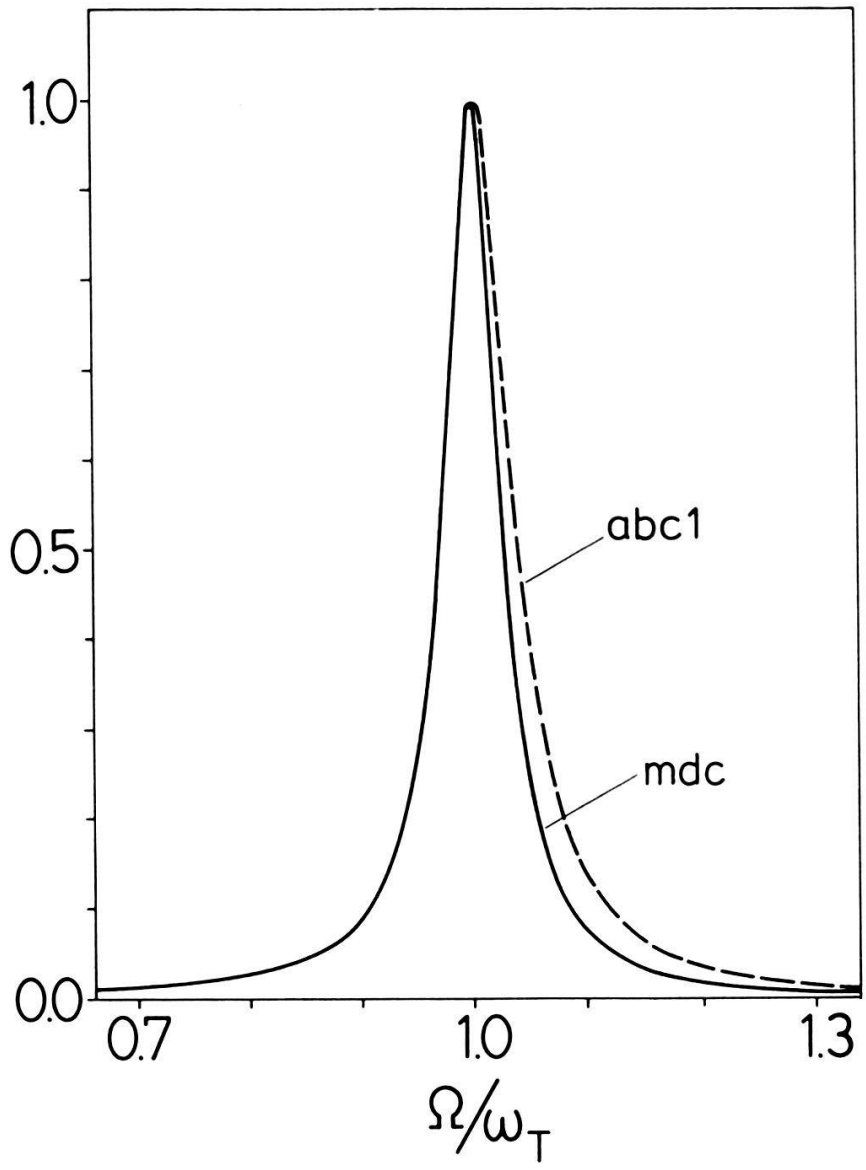

Figure 2
Plot of the dissipation probability $D(\Omega)$ (equation 8) as a function of Ω. For $\Omega > \omega_L$, the curve *mdc* corresponds to the minimum dissipation criterion and *abc* 1 corresponds to Pekar's criterion. The curve obtained from the criterion of vanishing derivaty of the exciton function at the surface (*abc* 2) coincides with *mdc*. Material parameters appropriate to CuCl and measured by Grun et al. [8] are used.

polariton branch, which is the only one to contribute. In the case of Pekar's *abc*, both polariton branches contribute, and the large value of $\Gamma^{(2)}(\vec{k}_2)$ broadens the lineshape by at least one order of magnitude.

It is also instructive to compare our result with the perturbative lineshape [9]

$$\varepsilon_2^P(\omega) = \frac{\beta}{4} \frac{\Gamma_0 \omega_T}{(\omega - \omega_{ex})^2 + (\Gamma_0/2)^2}, \tag{10a}$$

where the frequency ω_{ex} is obtained solving the equation

$$\omega_{ex} = \omega_T + \hbar k^2/2(m_e + m_h) = ck\sqrt{\varepsilon_\infty} \tag{10b}$$

and corresponds to a definite value k_0 of the wave vector. The inverse lifetime Γ_0

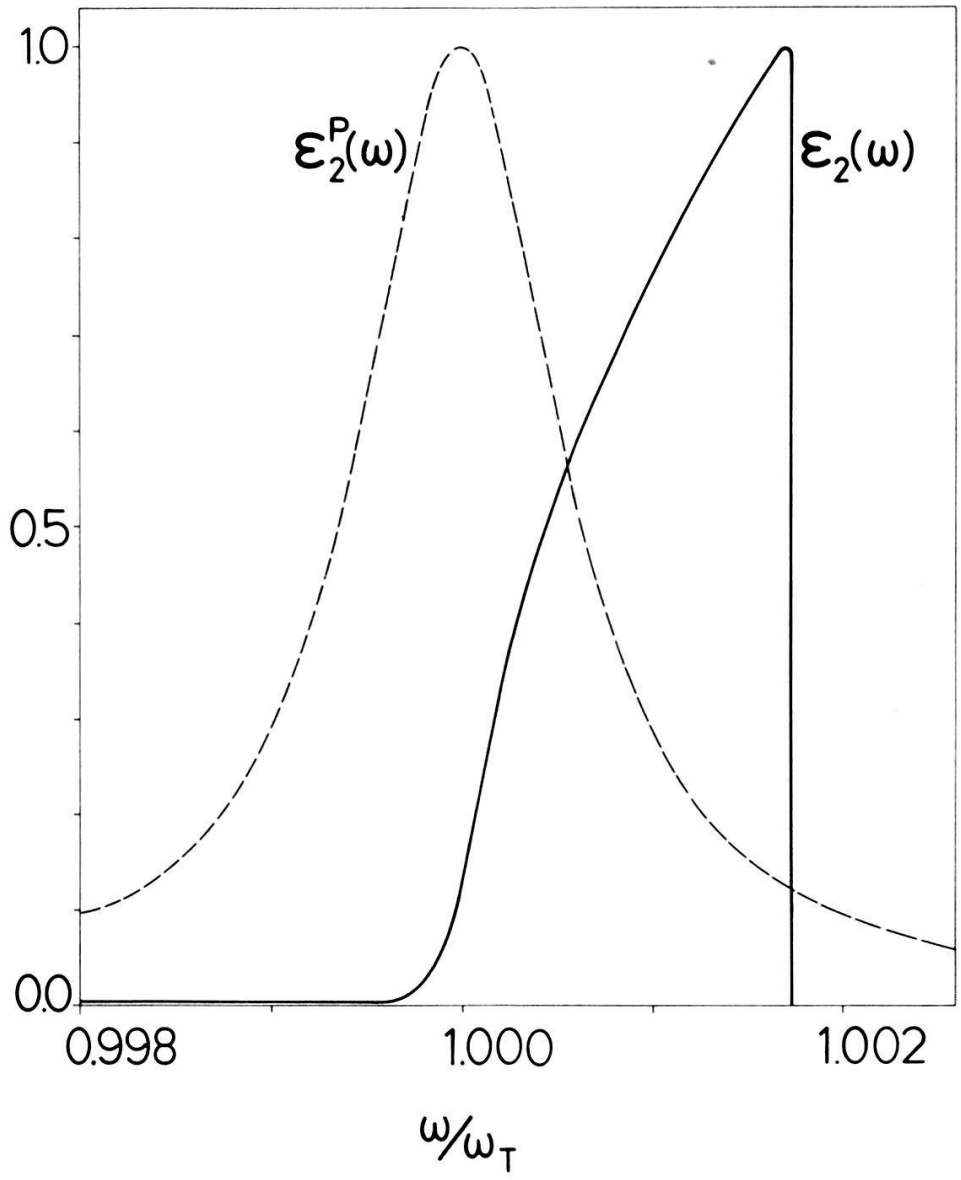

Figure 3
Plot of the optical lineshapes as functions of the frequency of the incoming radiation ω and normalized to their maxima. $\varepsilon_2(\omega)$ refers to Eq. 9 and the minimum dissipation criterion is used for $\omega > \omega_L$. $\varepsilon_2^P(\omega)$ is the Lorentzian lineshape given by equation (10a) with a linewidth $\hbar\Gamma_0 = 4$ meV. Material parameters appropriate to CuCl are used (Grun et al. Ref. 8).

is proportional to the exciton density of states at $\omega_{ex}(k_0)$, and differs therefore from that of the polariton case.

We notice from Fig. 3, that the polariton absorption lineshape is strongly asymmetric and is dominated by the large value of the density of states in the lower polariton branch. The density of states in the upper polariton branch is so small that it does not contribute to ε_2. We also notice the large difference compared to the Lorentzian lineshape. We conclude that the polariton effect on the optical lineshape is indeed important and could be detected. Absorption experiments so far performed in CuCl [13] give a linewidth for the 1s-exciton in basic agreement with our analysis, which leads to a value of about 4 meV, but the lineshape is not sufficiently detailed to discriminate between the different additional conditions.

IV. Discussion of higher order effects

The above analysis is relevant also in the study of higher order effects, like two-photon transitions to polariton states and two-photon transitions to biexciton states. Both effects have been observed in CuCl [13], and the polariton nature of the crystal excitation has been demonstrated with its characteristic dispersion law [14]. In the case of two-photon transitions to polariton states one has to take into account the higher exciton states of the same bands (Mahan model) and the states related to other energy bands (Loudon model). These states are not included in the present treatment of the polariton, but can be brought into the picture by treating perturbatively the interaction with the photons.

However, the polariton character of the states appears also in the perturbative treatment of non linear effects [15]. When the polariton is excited as the result of a two-photon absorption the final state to be considered is that given by equation 3. When the two-photon process leads to the excitation of a higher state, like a biexciton, the polariton nature of the intermediate states is essential to account correctly for the resonance enhancement of the transition rate [14]. In this case also, the state given by equation 3, has to be used.

The use of perturbation theory for two-photon transitions to polariton states is justified only when a complete set of intermediate states is considered, as shown in the exact calculation on the hydrogen atom [16]. However, the approximation is still good when only a few intermediate states are included in a gauge invariant treatment [17].

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