Optical Dynamics in Crystal Slabs: Crossover from Superradiant Excitons to Bulk Polaritons

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The radiative-excited-state dynamics in crystal slabs is studied as a function of the slab thickness L. A general dispersion relation is derived that interpolates between the superradiant-exciton regime at thicknesses small compared to an optical wavelength λ and bulk polaritons in thick crystals. It is shown that previous results predicting superradiance in thick slabs ($L \gg \lambda$) arise from invalid pole approximations.

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Currently, there is a strong interest in the optical properties of systems with restricted geometries. In particular, much attention is focused on exciton superradiance from, e.g., molecular aggregates [1,2], polymers [3], semiconductor microcrystallites [4–6], quantum wells [6,7], and monolayers [8,9]. Exciton superradiance is the phenomenon that an electronic excitation (Frenkel or Wannier) that is coherently delocalized over N unit cells exhibits a spontaneous emission rate that is proportional to N and is thus much larger than typical molecular radiative decay rates. Superradiance originates from the fact that for systems small compared to an optical wavelength, all oscillator strength is collected in one collective superradiant excited state; all other excited states have no transition dipole to the system's ground state and are subradiant or dark. However, it is well known that the enhancement of the emission rate with system size does not continue forever: In infinite bulk crystals, irreversible radiative decay cannot occur, because the translational symmetry dictates that each exciton mode is coupled to precisely one radiation-field mode. Therefore, the proper eigenmodes of bulk crystals are the radiatively *stable* polaritons: mixed modes in which energy oscillates back and forth between the exciton (polarization field) and the radiation field [10]. Probing the dynamics of polaritons by nonlinear optical techniques is another topic that has attracted much attention lately [11]. Obviously, superradiant excitons and bulk polaritons are intimately related and it is an interesting challenge to study the transition from one regime to the other with growing system size. In this paper, we approach this problem by studying the radiative-exciton dynamics in molecular crystal slabs of arbitrary thickness, varying from monolayers to bulk crystals. Crystal slabs have been studied before [12,13], but no systematic investigation of the thickness dependence and the crossover between the superradiant and the polariton regimes has been published so far.

We consider a crystal slab with simple cubic structure which consists of a stack of N identical monolayers. The lattice sites are occupied by harmonic molecules with electronic transition frequency Ω and transition dipoles μ. All dipoles have the same orientation, which for simplicity we assume to be parallel to the molecular planes. We will confine our attention to crystal states that are modulated in the direction perpendicular to the slab (the z direction) only, so that all molecules in a single plane are completely equivalent. Let $B_l^\dagger(t)$ [$B_l(t)$] denote the expectation value of the creation (annihilation) operator for an excitation on an arbitrary molecule in the lth plane at time t ($l=1,\ldots,N$). From these operators, Frenkel exciton operators are constructed by the canonical transformation $B_k=\sum_{l=1}^{N} B_l \exp(-ikla)/\sqrt{N}$ (and the complex conjugate for $B_k^\dagger$). Here, a denotes the lattice constant and k is the exciton wave number that takes the values $k=2\pi m/Na$, with m an integer that is limited to one Brillouin zone ($m=0,\ldots,N-1$). We use the standard minimal coupling ($\mathbf{p}\cdot\mathbf{A}$) Hamiltonian [11]. Then, the radiative dynamics of the electronic eigenmodes of the slab can be derived from the coupled Heisenberg equations of motion for the exciton operators and the vector potential. It is straightforward to eliminate the vector potential from these equations and in the frequency domain [$f(\omega)\equiv\int_0^\infty dt\, f(t)\exp(i\omega t)$] we have

$$(\omega-\Omega)B_k(\omega)-\sum_{k'}[J\delta_{k,k'}+F_{kk'}(N;\omega)] \times[B_{k'}(\omega)+B^\dagger_{-k'}(\omega)]=iB_k \quad (t=0), \qquad (1)$$

and an analogous equation for $B_k^\dagger(\omega)$, which is obtained by complex conjugation of Eq. (1). In deriving this equation, we used vacuum initial conditions for the radiation field, as is appropriate for spontaneous emission problems. The most important ingredients in Eq. (1) are the interactions J and F. $J\delta_{k,k'}$ derives from the static dipole-dipole interactions in the slab, where J is the total interaction between a dipole and all other dipoles lying in the same plane. It is known that the static dipole interactions between planes have a very short range and that the overwhelming part (97%) of the crystal's static Coulomb energy arises from interactions within a single plane [14]. This justifies the use of periodic boundary conditions when accounting for static interactions (k stays a good quantum number) and the neglect of k and N dependence of the static energy. Generalizations that account for end effects and (or) spatial dispersion are possible, but do not affect the main conclusions of this paper. $F_{kk'}(N;\omega)$ is the effective radiative interaction, resulting from the exchange of photons with wave vector $(0,0,q)$ between the

excitons k and k':

$$F_{kk'}(\omega)=\frac{\omega a f^2}{4\pi c^2}\int_{-\infty}^{+\infty}dq\frac{O(k'-q)O(q-k)}{(\omega/c)^2-q^2}, \quad (2a)$$

$$O(p)\equiv\frac{\sin(pNa/2)}{\sqrt{N}\sin(pa/2)}e^{ip(N+1)a/2}. \quad (2b)$$

Here, c is the vacuum velocity of light and $f^2\equiv 8\pi\Omega\mu^2/\hbar a^3$, which is a measure of the density of oscillator strength in the slab. In contrast to k and k', the photon wave number q is a continuous variable, as the radiation field is quantized in an infinite box that is not limited by the finite thickness of the slab. This is crucial for the description of spontaneous decay from the slab. The function $O(p)$ gives the overlap between the exciton and the photon wave functions. We observe that $F_{kk'}(N;\omega)$ vanishes for $\omega/c\rightarrow 0$, illustrating the fact that it is a retarded interaction. Furthermore, we note that if in Eq. (1) we replace $F_{kk'}(N;\omega)$ by $F_{kk'}(N;\Omega)$, we recover the superradiance master equation [15]; this equation is very useful to study cooperative emission effects [2], but cannot describe polaritons in bulk crystals.

Equation (1), together with its analog for $B_k^\dagger(\omega)$, defines a set of $2N$ coupled linear equations that determine the full excited-state dynamics of the slab. In general, solution of this set requires numerical techniques, but the problem simplifies considerably if the off-diagonal elements of $F_{kk'}$ may be neglected. This can, of course, always be done during the initial decay of an exciton k, but a more general justification is found in the following. The function $O(p)$ is peaked around $p=0$ with a width $\Delta p=2\pi/Na$. Using this in Eq. (2a) together with the fact that both k and k' vary discretely with steps $2\pi/Na$, we conclude that $F_{kk'}(N;\omega)$ is strongly peaked around $k=k'$ and is diagonal to a good approximation. Within this approximation, $B_k(\omega)$ and $B^\dagger_{-k}(\omega)$ are easily solved in terms of their initial conditions and these solutions must be transformed back to the time domain in order to obtain the radiative-exciton decay. This transformation involves the poles of $B_k(\omega)$ and $B^\dagger_{-k}(\omega)$, which can be directly determined from the secular equation of Eq. (1) (in approximate form) and its analog for $B^\dagger_{-k}(\omega)$. We obtain

$$\omega^2-\omega_{ex}^2-2\omega F_{kk}(N;\omega)=0, \quad (3)$$

where $\omega_{ex}\equiv(\Omega^2+2\Omega J)^{1/2}$, the frequency of the static excitons. Performing the q integral in Eq. (2a) in the complex plane, we find for the radiative self-energy

$$F_{kk}(N;\omega)=\frac{af^2}{8Nc}\left\{\frac{\sin(N\phi^-)}{\sin^2(\phi^-)}e^{-iN\phi^-}+(\phi^-\leftrightarrow-\phi^+)\right\}+\frac{\omega f^2}{2c^2}\sum_{n=-\infty}^{\infty}\left\{\left(\frac{\omega}{c}\right)^2-\left(k+\frac{2n\pi}{a}\right)^2\right\}^{-1}, \quad (4)$$

with $\phi^\pm\equiv(k\pm\omega/c)a/2$. Equations (3) and (4) define our general dispersion relation of the coupled exciton-photon modes for a slab of arbitrary thickness and constitute the central result of this paper, of which all further results are special applications.

We first discuss the limiting cases $N=1$ (monolayer) and $N=\infty$ (bulk), for which the restriction to $F_{kk'}=\delta_{kk'}F_{kk}$ is no approximation. For $N=1$, we only have one k value ($k=0$) and it can be shown that the real part of Eq. (4) vanishes identically, so that $F_{00}(1;\omega)=-iaf^2/4c$. This yields for the decay rate of the monolayer exciton the value $\gamma_0\equiv af^2/4c$, which is superradiant, as it roughly equals the spontaneous emission rate of a single molecule multipled by $(c/\Omega a)^2$ (typically 10^5–10^6) [8,9]. For $N=\infty$, only the summation over n in Eq. (4) remains and we find a purely real self-energy $F_{kk}(\infty;\omega)$. Keeping only the $n=0$ term in the summation is equivalent to neglecting umklapp contributions. Within this common approximation, Eq. (3) reduces to the standard quartic dispersion relation for bulk polaritons [10,11]:

$$(kc/\omega)^2=1+f^2/(\omega_{ex}^2-\omega^2)\equiv\varepsilon(\omega), \quad (5)$$

with $\varepsilon(\omega)$ the crystal's dielectric function. The solutions to Eq. (5) are real, confirming radiative stability of the bulk polaritons, and they lie on the two polariton branches depicted in Fig. 1.

For general N, it is impossible to solve the dispersion relation Eq. (3) exactly, but several interesting results can be obtained using pole approximations. Considering the term $2\omega F(\omega)$ in Eq. (3) a small perturbation to the static-exciton dispersion relation, it is found that

$$\omega\approx\omega_{ex}+F_{kk}(N;\omega_{ex}). \quad (6)$$

This is the *exciton-pole approximation*, which is equivalent to second-order perturbation theory in the exciton-photon interaction. $\mathrm{Re}[F_{kk}(N;\omega_{ex})]$ is now the radiation-induced energy shift of the exciton and $-\mathrm{Im}[F_{kk}(N;\omega_{ex})]$ the radiative damping rate (identical to the Fermi "golden rule"). Straightforward analysis of $\mathrm{Im}[F_{kk}(N;\omega_{ex})]$ shows that for slabs with a thickness small compared to an optical wavelength ($L\ll\lambda$, with

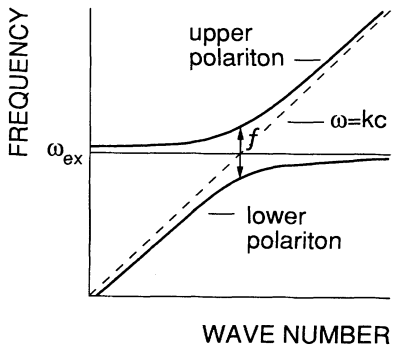

FIG. 1. Polariton dispersion diagram [cf. Eq. (5)].

$L \equiv Na$ and $\lambda \equiv 2\pi c/\omega_{ex}$), the $k=0$ state is superradiant with decay rate N times the monolayer rate γ_0, whereas all other k states are relatively dark, with spontaneous emission rates that are orders of magnitude smaller. The superradiant nature of the $k=0$ state breaks down when the slab thickness gets in the order of λ, as can be seen in Fig. 2. More precisely, the maximum rate is reached at $L=0.37\lambda$ and equals $0.23(\lambda/a)\gamma_0$. The maximum cooperativity volume of the dipoles in the slab is thus of the order λ^3. For $L>\lambda$, the decay rate shows oscillatory dependence on L, as a result of interference between the radiation fields emitted by the various molecules in the slab. The amplitude of these oscillations drops off as $1/L$, so that for $k=0$ we indeed predict a smooth crossover from the superradiant exciton to the stable bulk polariton when varying N from 1 to ∞.

The situation is more complicated for wave numbers $k \approx \omega_{ex}/c$ (the photon-exciton band-crossing region). From Eq. (4), it follows that in this region $\mathrm{Im}[F_{kk}(N;\omega_{ex})]$ scales linearly with N *for all values of* N, which implies that superradiant behavior persists for slabs with $L \gg \lambda$ and leads to a decay rate that diverges linearly for large L. This result, which is obtained in *any* pole approximation that evaluates $F_{kk}(N;\omega)$ at the point $k \approx \omega/c$ [16], contradicts the polariton concept and suggests that the radiative stability of the bulk polariton is merely a peculiarity of the truly infinite system that cannot be found by extrapolation from finite crystals. However, the noted divergence is an artifact caused by the breakdown of the exciton-pole approximation at $k \approx \omega_{ex}/c$, because $F_{kk}(N;\omega_{ex})$ is not a smooth function in that region (in contrast to the situation at $k=0$). The relevant singularity in the self-energy is the photon Green function given by the $n=0$ term in Eq. (4), and the divergence problem can be solved by extracting this term from $F_{kk}(N;\omega)$ and treating it nonperturbatively. The dispersion relation [Eq. (3)] then obtains the representation

$$(\omega^2-\omega_{k1}^2)(\omega^2-\omega_{k2}^2)+(\omega f)^2 - 2\omega[\omega^2-(kc)^2]F_{kk}(N;\omega)=0. \quad (7)$$

Here, ω_{kj} $(j=1,2)$ denotes the frequency of the bulk polariton with wave number k in branch j. We now introduce the *polariton-pole approximation* by considering the last two terms in Eq. (7), which are *well behaved* everywhere in the Brillouin zone, small perturbations to the bulk polariton dispersion relation given by the first term. From this, we obtain the damping rate of the polariton with wave number k in branch 1 in a finite crystal:

$$\gamma_{k1}(N) = -\frac{\omega_{k1}^2-(kc)^2}{\omega_{k1}^2-\omega_{k2}^2}\,\mathrm{Im}F_{kk}(N;\omega_{k1}). \quad (8)$$

$\gamma_{k2}(N)$ is obtained by interchanging the branch labels in this expression. The exciton decay can now be expressed in terms of $\gamma_{k1}(N)$ and $\gamma_{k2}(N)$ and will in general not be monoexponential. Without going into a detailed analysis,

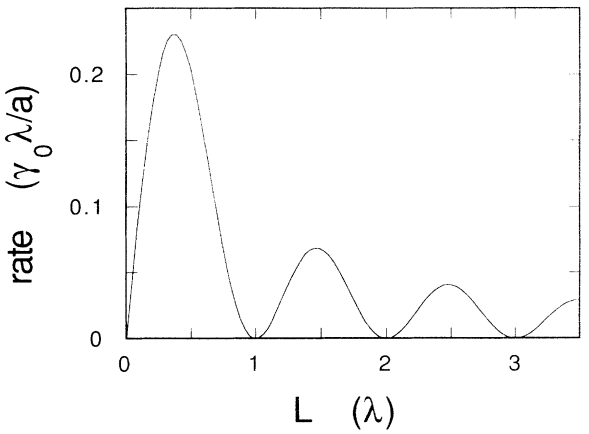

FIG. 2. Radiative decay rate of the $k=0$ exciton as a function of crystal thickness in the exciton-pole approximation. Note that λ/a typically equals 10^3.

several important remarks can be made. (1) At wave numbers far from ω_{ex}/c, Eq. (8) reduces to the exciton-pole approximation, which is thus indeed found to be a good approximation away from the crossing region. (2) As $kc \neq \omega_{kj}$ for every k, the linear divergence observed in the exciton-pole approximation at $kc \approx \omega_{ex}$ cannot occur in the polariton-pole approximation. In fact, Eq. (8) always predicts a decay rate proportional to $1/L$ for large L, showing proper crossover to the stable bulk polariton at every wave number. (3) From macroscopic electrodynamics, one expects that a polariton wave packet decays by transmission through the slab surfaces into the external space. In combination with the time of flight needed to reach the surface, this yields a decay rate [8,9]

$$\tilde{\gamma}_{kj}(N) = (1-R_{kj})v_{kj}/L, \quad (9)$$

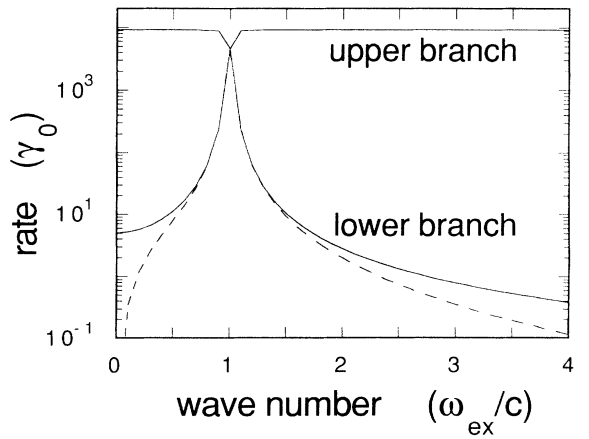

FIG. 3. Radiative decay rate of polaritons as a function of wave number in the optical region for a crystal of $N=10^4$ layers, with $\lambda/a=10^3$ and $f/\omega_{ex}=1/30$. Solid curves are obtained from the microscopic result [Eq. (8)] and dashed curves represent the macroscopic rate [Eq. (9)].

where R_{kj} is the internal reflection coefficient of the polariton and v_{kj} its group velocity. In Fig. 3, Eq. (9) is compared with a wave-packet decay rate obtained from our microscopic result [Eq. (8)] by replacing the factor $\sin^2(\omega_{kj}L/2c)$ in $\mathrm{Im}[F_{kk}(N;\omega_{kj})]$ by its average $\frac{1}{2}$ (large L). Excellent agreement between the two predictions is observed near the crossing region and for photonlike polaritons; this agreement can also be shown analytically. No agreement is found for the excitonlike polaritons, however. In our system of harmonic molecules, there is no obvious reason why these polaritons should behave in a less classical way than the photonlike polaritons, but the observation that the $k=0$ excitonlike polariton has no group velocity (not even when spatial dispersion is added) already indicates the limited validity of Eq. (9). Also note that in the macroscopic wave-packet picture, the polariton decay rate in the crossing region ($v_{kj}\approx c$) may exceed an optical frequency for $L\lesssim\lambda$, which poses a natural boundary on this model; the full result [Eq. (8)] does not suffer from this limitation.

In conclusion, we have derived a general exciton dispersion relation for crystal slabs of arbitrary thickness that accounts for (multiple) interactions with the radiation field. Our theory smoothly interpolates between superradiant-exciton behavior at small thickness and stable bulk polaritons at large thickness. We have demonstrated that predictions about superradiance in thick crystal slabs ($L\gg\lambda$) result from invalid pole approximations that equate the frequency and the wave vector in the radiative self-energy, and we have made a comparison with the radiative lifetime of polaritons as obtained from macroscopic transmission and time-of-flight arguments. Finally, we note that in practice both exciton superradiance and the observation of polariton effects are limited by static disorder and phonon scattering (see, e.g., Refs. [2], [11], and [17]). In this paper, we have not addressed these complications, in order not to obscure the main issue: the transition from superradiant excitons to stable polaritons.

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