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Nonperturbative theory of exciton-phonon resonances in semiconductor absorption

K. Hannewald and P. A. Bobbert
Group Polymer Physics, Eindhoven University of Technology, P.O.Box 513, 5600 MB Eindhoven, The Netherlands

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We develop a theory of exciton-phonon sidebands in the absorption spectra of semiconductors. The theory does not rely on an *ad hoc* exciton-phonon picture, but is based on a more fundamental electron-phonon Hamiltonian, thus avoiding *a priori* assumptions about excited-state properties. We derive a nonperturbative compact solution that can be looked upon as the semiconductor version of the textbook absorption formula for a two-level system coupled to phonons. Accompanied by an illustrative numerical example, the importance and usefulness of our approach with respect to practical applications for semiconductors is demonstrated.

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The interaction between electronic and vibrational degrees of freedom is of fundamental importance for the optical and transport properties of many physical systems.[1] A classical example is given by the absorption spectra $\alpha(\omega)$ of an atom (or molecule) coupled to a phonon mode with frequency ω_{ph}. These systems are often modelled excellently within the two-level approximation, i.e., assuming an upper empty level and a lower occupied level with energies $e_{c,v}$ and electron-phonon couplings $g_{c,v}$. Then, $\alpha(\omega)$ can be obtained exactly and yields (at zero temperature) the textbook formula[1]

$$\alpha(\omega) \propto e^{-G_{\text{eff}}} \sum_{m=0}^{\infty} \frac{(G_{\text{eff}})^m}{m!} \delta(E_c - E_v + m\hbar\omega_{\text{ph}} - \hbar\omega). \tag{1}$$

There are two phonon-induced modifications: (i) a small level shift to lower energies ($E_\alpha = e_\alpha - \hbar\omega_{\text{ph}} g_\alpha^2$) and, more importantly, (ii) the emergence of phonon replicas at multiple phonon energies $m\hbar\omega_{\text{ph}}$ above $E_c - E_v$, with a Poisson distribution of their respective weights that is governed by the effective coupling $G_{\text{eff}} = (g_c - g_v)^2$.

While Eq. (1) has been a long-standing paradigm in the analysis of absorption spectra for molecular systems, there is no equivalent formula available for the decription of the near-band-gap absorption in semiconductors, despite the fact that exciton-phonon sidebands are commonly observed in semiconductor spectroscopy.[2] The difficulties arise from the fact that a corresponding theory must simultaneously take into account band dispersion and electron-electron interaction (i.e., excitonic effects) while, at the same time, allowing for the electron-phonon interaction in a nonperturbative manner. So far, the most sophisticated approaches to solve this problem are based on an *ad hoc* exciton-phonon picture.[3–8] However, the use of this picture inevitably requires to make *a priori* assumptions about excited-state properties (such as the exciton binding energies E_{exc}, the ratios $E_{\text{exc}}/\hbar\omega_{\text{ph}}$, and the exciton-phonon coupling strength) and is, hence, *in praxi* often limited to the lowest-lying excitons. Here, we overcome these limitations by developing a theory of exciton-phonon resonances within the more fundamental electron-phonon picture, where both the carrier's band structure and their coupling strengths to the phonons may be inputted directly from *ab initio* calculations, see, e.g., Ref. 9. This picture has been used before by others,[10–12] but exclusively for the description of the first phonon replica. Here, we go beyond such perturbational approaches and develop a nonperturbative theory using the method of canonical transformation, thus extending previous work on the polaron problem[1] towards the description of near-band-gap absorption of semiconductors.

We consider a Hamiltonian of the form $H = H_{\text{el}} + H_{\text{el-el}} + H_{\text{el-ph}} + H_{\text{ph}}$, where

$$H_{\text{el}} = \sum_{\alpha\mathbf{k}} \left(e_{\alpha\mathbf{k}} + \sum_{\mathbf{q}} n_{\alpha\mathbf{q}} V_{\mathbf{q}} \right) a^\dagger_{\alpha\mathbf{k}} a_{\alpha\mathbf{k}}, \tag{2}$$

$$H_{\text{el-el}} = \sum_{\alpha\beta\mathbf{k}\mathbf{k}'\mathbf{q}} \tfrac{1}{2} V_{\mathbf{q}} a^\dagger_{\alpha\mathbf{k}} a^\dagger_{\beta\mathbf{k}'} a_{\beta\mathbf{k}'+\mathbf{q}} a_{\alpha\mathbf{k}-\mathbf{q}}, \tag{3}$$

$$H_{\text{el-ph}} = \sum_{\alpha\mathbf{k}\mathbf{q}} \hbar\omega_{\mathbf{q}} g_{\alpha\mathbf{q}} a^\dagger_{\alpha\mathbf{k}-\mathbf{q}} a_{\alpha\mathbf{k}} (b_{-\mathbf{q}} + b^\dagger_{\mathbf{q}}), \tag{4}$$

$$H_{\text{ph}} = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} \left(b^\dagger_{\mathbf{q}} b_{\mathbf{q}} + \tfrac{1}{2} \right) \tag{5}$$

describe the electrons, the electron-electron interaction, the electron-phonon coupling, and the phonons, respectively. The operators $a^{(\dagger)}_{\alpha\mathbf{k}}$ annihilate (create) electrons with Bloch wave vector $\mathbf{k}$ and energy $e_{\alpha\mathbf{k}}$ in band α, whereas the operators $b^{(\dagger)}_{\mathbf{q}}$ annihilate (create) phonons with wave vector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$. While our theoretical framework is applicable to arbitrary band structures, we will consider here exclusively the case of a direct two-band semiconductor within the effective mass approximation, i.e., $e_{c,v\mathbf{k}} = \pm E_g/2 \pm \hbar^2 k^2 / 2m_{e,h}$, in order to emphasize the essential physics of our approach. Note that Eq. (2) contains also a Coulomb renormalization term that is nonzero for finite charge-carrier densities $n_{\alpha\mathbf{q}} = \langle a^\dagger_{\alpha\mathbf{q}} a_{\alpha\mathbf{q}} \rangle$. In the ground state at $T = 0$ K, it holds that $n_{v\mathbf{q}} \equiv 1$ and $n_{c\mathbf{q}} \equiv 0$. The Coulomb potential in Eqs. (2) and (3) is denoted as $V_{\mathbf{q}}$ and the electron-phonon coupling in Eq. (4) is described by the dimensionless quantities $g_{\alpha\mathbf{q}}$.

In order to treat effects due to the electron-phonon coupling in a nonperturbative manner, we introduce transformed operators $A^{(\dagger)}_{\alpha\mathbf{k}} = e^U a^{(\dagger)}_{\alpha\mathbf{k}} e^{U^\dagger}$, $B^{(\dagger)}_{\mathbf{q}} = e^U b^{(\dagger)}_{\mathbf{q}} e^{U^\dagger}$ representing annihilation (creation) operators of polarons and phonons of a distorted lattice, as described below. The anti-Hermitian operator U is defined as $U = \sum_{\alpha\mathbf{k}\mathbf{q}} g_{\alpha\mathbf{q}} a^\dagger_{\alpha\mathbf{k}-\mathbf{q}} a_{\alpha\mathbf{k}} (b_{-\mathbf{q}} - b^\dagger_{\mathbf{q}})$ and the transformation rules are obtained by application of the

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Baker-Campbell-Hausdorff theorem $e^{U}fe^{-U}=f+[U,f]+(1/2!)[U,[U,f]]+\cdots$. As a result, we obtain the relations

$$a_{\alpha\mathbf{k}}=\sum_{\mathbf{k}'}(e^{C_\alpha})_{\mathbf{k}\mathbf{k}'}A_{\alpha\mathbf{k}'},\quad b_{\mathbf{q}}=B_{\mathbf{q}}-\sum_{\alpha\mathbf{k}}g_{\alpha\mathbf{q}}A^{\dagger}_{\alpha\mathbf{k}-\mathbf{q}}A_{\alpha\mathbf{k}},\qquad(6)$$

where we have introduced a compact matrix notation for the exponential operators by means of the short-hand definition $(C_\alpha)_{\mathbf{k}\mathbf{k}'}=g_{\alpha\mathbf{k}-\mathbf{k}'}(B_{\mathbf{k}-\mathbf{k}'}-B^{\dagger}_{\mathbf{k}'-\mathbf{k}})$.

By virtue of the transformation rules (6), the original four-part Hamiltonian can be rewritten as a sum of just three terms $H=H_{\text{pol}}+H_{\text{pol-pol}}+H_{\text{ph}'}$, where

$$H_{\text{pol}}=\sum_{\alpha\mathbf{k}}\left(E_{\alpha\mathbf{k}}+\sum_{\mathbf{q}}n_{\alpha\mathbf{q}}V^{\alpha\alpha}_{\mathbf{q}}\right)A^{\dagger}_{\alpha\mathbf{k}}A_{\alpha\mathbf{k}},\qquad(7)$$

$$H_{\text{pol-pol}}=\sum_{\alpha\beta\mathbf{k}\mathbf{k}'\mathbf{q}}\tfrac{1}{2}V^{\alpha\beta}_{\mathbf{q}}A^{\dagger}_{\alpha\mathbf{k}}A^{\dagger}_{\beta\mathbf{k}'}A_{\beta\mathbf{k}'+\mathbf{q}}A_{\alpha\mathbf{k}-\mathbf{q}},\qquad(8)$$

$$H_{\text{ph}'}=\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}\left(B^{\dagger}_{\mathbf{q}}B_{\mathbf{q}}+\tfrac{1}{2}\right)\qquad(9)$$

describe the polarons, the polaron-polaron interaction, and the phonons of the distorted lattice, respectively. Here, the coupling between the electronic and lattice degrees of freedom does not appear explicitly anymore but is incorporated into the polaronic quantities $E_{\alpha\mathbf{k}}$ which, in general, contain also phonon operators. For the purpose of our work, we follow the spirit of earlier work on the polaron problem[1] and replace the phonon operators in $E_{\alpha\mathbf{k}}$ by their thermal averages. The neglected effects such as line broadening and recoil effects are of minor importance for the present paper that focusses on the description of exciton-phonon sidebands. As a result, the polaron dispersions (at $T=0$ K) are approximately given by the expressions $E_{c\mathbf{k}}\approx\tilde{e}_{c\mathbf{k}}-\Delta_c$ and $E_{v\mathbf{k}}\approx\tilde{e}_{v\mathbf{k}}+\Delta_v$, the derivation of which is straightforward but lengthy and will be given elsewhere.[13] Here, we used the shorthand notations $\Delta_\alpha=\Sigma_{\mathbf{q}}\hbar\omega_{\mathbf{q}}g^{2}_{\alpha\mathbf{q}}$, $\tilde{e}_{\alpha\mathbf{k}}=e^{-\bar{G}_\alpha}\Sigma_{\mathbf{k}'}e_{\alpha\mathbf{k}'}(e^{G_\alpha})_{\mathbf{k}'\mathbf{k}}$, $\bar{G}_\alpha=\Sigma_{\mathbf{q}}g^{2}_{\alpha\mathbf{q}}$, and $(G_\alpha)_{\mathbf{k}\mathbf{k}'}=g^{2}_{\alpha\mathbf{k}-\mathbf{k}'}$. Compared to the original electron dispersions $e_{c,v\mathbf{k}}$, we find a shrinkage of the band gap ("polaron shift") because $\Delta_{c,v}\geqslant 0$ and a narrowing of the bandwidth due to the exponential renormalizations in $\tilde{e}_{c,v\mathbf{k}}$. The latter effect is especially important in materials with strong electron-phonon coupling such as organic crystals,[9,14,15] but within our effective mass approximation it corresponds simply to a mass enhancement of the charge carriers. In fact, for the purpose of the present work, the exact knowledge of the polaron bands is not essential and, instead, we will use the approximate expressions $E_{c,v\mathbf{k}}=\pm E^{*}_{g}/2\pm\hbar^2k^2/2m^{*}_{e,h}$, where the phonon-induced changes are accounted for by the introduction of an effective band gap E^{*}_{g} and effective electron/hole masses $m^{*}_{e,h}$. Another effect of the electron-phonon interaction is the modification of the Coulomb potential in Eqs. (7) and (8) which now contains additional contributions, i.e., screening due to the presence of phonons, that lead to the renormalization $V^{\alpha\beta}_{\mathbf{q}}=V_{\mathbf{q}}-2\hbar\omega_{\mathbf{q}}g_{\alpha\mathbf{q}}g_{\beta\mathbf{q}}$.

After the above preparatory considerations, we proceed with the calculation of the ground-state absorption spectrum $\alpha(\omega)\propto-\text{Im}\,P_{\text{ret}}(\omega)$, where the retarded polarization function is defined as

$$P_{\text{ret}}(t)=\frac{\Theta(t)}{i\hbar}\frac{1}{\Omega}\sum_{\mathbf{k}\mathbf{k}'}\langle a^{\dagger}_{v\mathbf{k}}(t)a_{c\mathbf{k}}(t)a^{\dagger}_{c\mathbf{k}'}(0)a_{v\mathbf{k}'}(0)\rangle.\qquad(10)$$

Here, the time dependence of the electron operators is governed by the Hamiltonian H according to $a^{(\dagger)}_{\alpha\mathbf{k}}(t)=e^{(i/\hbar)Ht}a^{(\dagger)}_{\alpha\mathbf{k}}e^{-(i/\hbar)Ht}$ and Ω denotes a normalization volume. In the following, we will evaluate P_{ret} by means of the above polaron concept, i.e., by incorporating the electron-phonon interaction nonperturbatively.

The direct evaluation of Eq. (10) is complicated by the fact that the original Hamiltonian (2)–(5) is not diagonal with respect to the electron and phonon operators. Therefore, it is instead advantageous to use the representation (7)–(9) where the interaction between the charge carriers and the lattice is already incorporated into the polaronic terms. From the physics point of view, this approach can be best rationalized by looking at the underlying physical picture: first, the electron-phonon interaction leads to the formation of polarons and, then, optical transitions take place between the polaron bands. Despite its approximate nature as discussed above, this approach turns out to be very powerful and, in particular, allows us to describe the phonon replicas of the excitonic resonances in all orders without invoking an *ad hoc* exciton-phonon picture. In technical terms, we apply the transformation rules (6) to the right-hand side of Eq. (10), which yields

$$P_{\text{ret}}(t)=\frac{\Theta(t)}{i\hbar}\frac{1}{\Omega}\sum_{\mathbf{k}_1\cdots\mathbf{k}_4}\langle e^{(i/\hbar)H_pt}A^{\dagger}_{v\mathbf{k}_1}A_{c\mathbf{k}_2}e^{-(i/\hbar)H_pt}A^{\dagger}_{c\mathbf{k}_3}A_{v\mathbf{k}_4}\rangle\times\langle[e^{C_c(t)-C_v(t)}]_{\mathbf{k}_1\mathbf{k}_2}[e^{C_v(0)-C_c(0)}]_{\mathbf{k}_3\mathbf{k}_4}\rangle,\qquad(11)$$

where we used the abbreviations $H_p=H_{\text{pol}}+H_{\text{pol-pol}}$ and $[C_\alpha(t)]_{\mathbf{k}\mathbf{k}'}=g_{\alpha\mathbf{k}-\mathbf{k}'}(B_{\mathbf{k}-\mathbf{k}'}e^{-i\omega_{\mathbf{k}-\mathbf{k}'}t}-B^{\dagger}_{\mathbf{k}'-\mathbf{k}}e^{i\omega_{\mathbf{k}'-\mathbf{k}}t})$. The advantage of the new representation (11) can be seen immediately: the polaronic and phononic terms are completely separated and, hence, their thermal averages can be performed independently which significantly simplifies the remaining calculations.

For the evaluation of the thermal average over the polaronic part, we apply the Baker-Campbell-Hausdorff theorem to the quantity $e^{(i/\hbar)H_pt}A^{\dagger}_{v\mathbf{k}_1}A_{c\mathbf{k}_2}e^{-(i/\hbar)H_pt}$. In order to avoid the typical hierarchy problems encounterd in theories including Coulomb interaction, we make use of the mean-field approximation, which yields the commutator $[H_p,A^{\dagger}_{v\mathbf{k}_1}A_{c\mathbf{k}_2}]\approx-\Sigma_{\mathbf{k}_1'\mathbf{k}_2'}S_{\mathbf{k}_1\mathbf{k}_2,\mathbf{k}_1'\mathbf{k}_2'}A^{\dagger}_{v\mathbf{k}_1'}A_{c\mathbf{k}_2'}$, where the S matrices, defined as

$$S_{\mathbf{k}_1\mathbf{k}_2,\mathbf{k}_1'\mathbf{k}_2'}=[(E_{c\mathbf{k}_2}-E_{v\mathbf{k}_1})\delta_{\mathbf{k}_1\mathbf{k}_1'}-V^{vc}_{\mathbf{k}_1-\mathbf{k}_1'}]\delta_{\mathbf{k}_1-\mathbf{k}_2,\mathbf{k}_1'-\mathbf{k}_2'},\qquad(12)$$

contain both the relevant interband transitions and the screened Coulomb interaction. While the neglected correlation effects can be expected to have only a small influence on the linear absorption, the particular strength of the mean-field approach is that it allows us to calculate the thermal averages completely analytically. In fact, extending the above matrix notation to the multiple commutators $[H_p,[H_p,\ldots,[H_p,A^{\dagger}_{v\mathbf{k}_1}A_{c\mathbf{k}_2}]\cdots]]$, the summation over all orders is straightforward and yields the formal identity

$$e^{(i/\hbar)H_p t}A^{\dagger}_{v\mathbf{k}_1}A_{c\mathbf{k}_2}e^{-(i/\hbar)H_p t} = \sum_{\mathbf{k}_1'\mathbf{k}_2'} [e^{-(i/\hbar)St}]_{\mathbf{k}_1\mathbf{k}_2,\mathbf{k}_1'\mathbf{k}_2'}A^{\dagger}_{v\mathbf{k}_1'}A_{c\mathbf{k}_2'}. \tag{13}$$

If we insert the relation (13) into Eq. (11) and perform the thermal average over the polaron operators assuming the ground state $\langle A^{\dagger}_{v\mathbf{k}_1'}A_{c\mathbf{k}_2'}A^{\dagger}_{c\mathbf{k}_3}A_{v\mathbf{k}_4}\rangle = \delta_{\mathbf{k}_1'\mathbf{k}_4}\delta_{\mathbf{k}_2'\mathbf{k}_3}$, the retarded polarization function adopts the form

$$P_{\text{ret}}(t) = \frac{\Theta(t)}{i\hbar}\frac{1}{\Omega}\sum_{\mathbf{k}_1\cdots\mathbf{k}_4}[e^{-(i/\hbar)St}]_{\mathbf{k}_1\mathbf{k}_2,\mathbf{k}_3\mathbf{k}_4}X_{\mathbf{k}_1\mathbf{k}_2}(t), \tag{14}$$

$$X_{\mathbf{k}_1\mathbf{k}_2}(t) = \langle [e^{C_c(t)-C_v(t)}]_{\mathbf{k}_1\mathbf{k}_2}[e^{C_v(0)-C_c(0)}]_{\mathbf{k}_2\mathbf{k}_1}\rangle. \tag{15}$$

For the remaining evaluation of the thermal averages over the phonon operators in Eq. (15), we expand $X_{\mathbf{k}_1\mathbf{k}_2}(t) := \Sigma_{n=0}^{\infty}(1/n!)X^{(n)}_{\mathbf{k}_1\mathbf{k}_2}(t)$ into a power series of $g_{c\mathbf{q}}-g_{v\mathbf{q}}$. The zeroth-order term is simply given by $X^{(0)}_{\mathbf{k}_1\mathbf{k}_2}(t)=\delta_{\mathbf{k}_1\mathbf{k}_2}$ and, apart from the renormalization $e_{\alpha\mathbf{k}}\rightarrow E_{\alpha\mathbf{k}}$, leads to a well-known result for the absorption in the absence of electron-phonon coupling. This is best seen if we define an effective Hamiltonian $H^{(0)}_{\mathbf{k}k'}=(E_{c\mathbf{k}}-E_{v\mathbf{k}})\delta_{\mathbf{k}\mathbf{k}'}-V^{vc}_{\mathbf{k}-\mathbf{k}'}$ and express the zeroth-order polarization as $P^{(0)}_{\text{ret}}(t)=[\Theta(t)/i\hbar]\times(1/\Omega)\Sigma_{\mathbf{k}\mathbf{k}'}[e^{-(i/\hbar)H^{(0)}t}]_{\mathbf{k}k'}$. Then, the absorption signal becomes

$$\alpha^{(0)}(\omega) \propto \text{Im}\,\frac{1}{\Omega}\sum_{\mathbf{k}\mathbf{k}'}[H^{(0)}-\hbar(\omega+i0)]^{-1}_{\mathbf{k}\mathbf{k}'}, \tag{16}$$

which is basically Elliott's famous formula for the absorption of direct semiconductors[16] that includes excitonic effects via the Coulomb term in $H^{(0)}_{\mathbf{k}\mathbf{k}'}$.

While the above zeroth-order result provides an important consistency check of our theory, the phonon sidebands emerge from the higher-order terms $X^{(n)}_{\mathbf{k}_1\mathbf{k}_2}(t)$. For the explicit evaluation of these contributions, we utilize the fact that only the even orders $n=2m$ are nonzero and assume dispersionless phonons ($\omega_{\mathbf{q}}\rightarrow\omega_{\text{ph}}$) at zero temperature. Then, the lowest term is readily obtained and gives $X^{(2)}_{\mathbf{k}_1\mathbf{k}_2}(t)=-2[\bar{G}-G(t)]_{\mathbf{k}_1\mathbf{k}_2}$, where we have abbreviated $(\bar{G})_{\mathbf{k}_1\mathbf{k}_2}=\bar{G}\delta_{\mathbf{k}_1\mathbf{k}_2}$, $\bar{G}=\Sigma_{\mathbf{q}}(G_{\text{eff}})_{\mathbf{q}0}$, and $[G(t)]_{\mathbf{k}_1\mathbf{k}_2}=(G_{\text{eff}})_{\mathbf{k}_1\mathbf{k}_2}e^{-i\omega_{\text{ph}}t}$ with effective interband coupling matrix-elements defined as

$$(G_{\text{eff}})_{\mathbf{k}_1\mathbf{k}_2} = (g_{c\mathbf{k}_1-\mathbf{k}_2}-g_{v\mathbf{k}_1-\mathbf{k}_2})^2. \tag{17}$$

If the coupling to the phonons is exactly the same for conduction and valence electrons, i.e., $(G_{\text{eff}})_{\mathbf{k}_1\mathbf{k}_2}\equiv 0$, then the polarization (14) reduces to $P^{(0)}_{\text{ret}}$ and there are no phononic sidebands at all in the absorption spectrum.

The evaluation of the higher orders $X^{(2m)}_{\mathbf{k}_1\mathbf{k}_2}(t)$ by application of Wick's theorem is much more complicated and we skip the details of the tedious calculation. Yet, after an appropriate regrouping of all terms, the final result can be condensed into $X^{(2m)}_{\mathbf{k}_1\mathbf{k}_2}(t)=[(-1)^m(2m)!/m!][[\bar{G}-G(t)]^m]_{\mathbf{k}_1\mathbf{k}_2}$, which can be looked upon as a generalization of the above second-order contribution. Using this result, the summation of the whole power series is easily done and gives the compact expression

$$X_{\mathbf{k}_1\mathbf{k}_2}(t) = e^{-\bar{G}}[e^{G(t)}]_{\mathbf{k}_1\mathbf{k}_2}. \tag{18}$$

If inserted into Eq. (14), an explicit (though formal) expression for the retarded polarization $P_{\text{ret}}(t)$ is obtained that, compared to the actual complexity of the problem, constitutes a surprisingly compact result.

In order to gain deeper physical insight into our findings, we expand the exponential matrices $[e^{G(t)}]_{\mathbf{k}_1\mathbf{k}_2}$ into a power series of $(G_{\text{eff}})_{\mathbf{k}_1\mathbf{k}_2}$. Then, the polarization (14) can be cast into the form $P_{\text{ret}}(t)=e^{-\bar{G}}(1/\Omega)\Sigma_{\mathbf{k}k'}\Sigma_{m=0}^{\infty}(1/m!)P^{(m)}_{\mathbf{k}\mathbf{k}'}(t)$, where the contributions from optical transitions involving m phonons are given by $P^{(m)}_{\mathbf{k}\mathbf{k}'}(t)=[\Theta(t)/i\hbar]\Sigma_{\mathbf{k}_1\mathbf{k}_2}[(G_{\text{eff}})^m]_{\mathbf{k}_1\mathbf{k}_2}[e^{-(i/\hbar)St}]_{\mathbf{k}_1\mathbf{k}_2,\mathbf{k}\mathbf{k}'}e^{-im\omega_{\text{ph}}t}$. From this, a clear-cut physical picture is obtained after applying the definition (12) of the S matrices and performing the Fourier transformation into frequency domain. Then, the absorption signal becomes simply

$$\alpha(\omega) \propto -e^{-\Sigma_{\mathbf{q}}(G_{\text{eff}})_{\mathbf{q}0}}\,\text{Im}\,\frac{1}{\Omega}\sum_{\mathbf{k}\mathbf{k}'}\sum_{m=0}^{\infty}\frac{1}{m!}P^{(m)}_{\mathbf{k}\mathbf{k}'}(\omega), \tag{19}$$

where the quantities $P^{(m)}_{\mathbf{k}\mathbf{k}'}(\omega)$ have to be determined selfconsistently from the equations

$$[E_{c\mathbf{k}}-E_{v\mathbf{k}'}+m\hbar\omega_{\text{ph}}-\hbar(\omega+i0)]P^{(m)}_{\mathbf{k}\mathbf{k}'}(\omega) - \sum_{\mathbf{q}}V^{vc}_{\mathbf{q}}P^{(m)}_{\mathbf{k}-\mathbf{q},\mathbf{k}'-\mathbf{q}}(\omega) = -[(G_{\text{eff}})^m]_{\mathbf{k}\mathbf{k}'}. \tag{20}$$

The interpretation of Eq. (20) is straightforward and very intuitive. It decribes the excitation of electrons (or, more strictly, polarons) from a valence-band state with energy $E_{v\mathbf{k}'}$ to a conduction-band state with energy $E_{c\mathbf{k}}$ under simultaneous emission of m phonons with energy $\hbar\omega_{\text{ph}}$. The corresponding effective coupling matrix element

$$[(G_{\text{eff}})^m]_{\mathbf{k}\mathbf{k}'} = \sum_{\mathbf{k}_1\cdots\mathbf{k}_{m-1}}(G_{\text{eff}})_{\mathbf{k}\mathbf{k}_1}(G_{\text{eff}})_{\mathbf{k}_1\mathbf{k}_2}\cdots(G_{\text{eff}})_{\mathbf{k}_{m-1}\mathbf{k}'} \tag{21}$$

accounts for the m electron-phonon scattering processes including all possible combinations of intermediate wave vectors involved. Furthermore, the Coulomb term in Eq. (20) has the structure of a vertex correction and allows for interband exciton-phonon interaction. Most importantly, in the absorption signal $\alpha(\omega)$ it gives rise to phonon sidebands at multiple phonon energies $m\hbar\omega_{\text{ph}}$ ($m=1,2,\ldots$) above the excitonic resonances, as demonstrated in the numerical example below.

It is worthwhile to note that if we neglect the Coulomb terms in Eq. (20), the quantities $P^{(m)}_{\mathbf{k}\mathbf{k}'}(\omega)$ can be obtained algebraically and the absorption (19) reduces to

$$\alpha(\omega) \propto e^{-\Sigma_{\mathbf{q}}(G_{\text{eff}})_{\mathbf{q}0}}\frac{1}{\Omega}\sum_{\mathbf{k}\mathbf{k}'}\sum_{m=0}^{\infty}\frac{[(G_{\text{eff}})^m]_{\mathbf{k}\mathbf{k}'}}{m!}\delta(E_{c\mathbf{k}}-E_{v\mathbf{k}'}+m\hbar\omega_{\text{ph}}-\hbar\omega). \tag{22}$$

This formula is strikingly reminescent of the textbook formula (1) for a two-level system coupled to phonons,[1] but now including the dispersions of both the electron energies and the electron-phonon coupling strength.

In order to demonstrate the usefulness of our theory, we apply it to a simple but illustrative example, namely, a one-dimensional model crystal within the contact-potential approximation $[V_{\mathbf{q}} \equiv \text{const} =: V/\Omega,\ (G_{\text{eff}})_{\mathbf{kk}'} \equiv \text{const} =: G_{\text{eff}}/\Omega]$. For this system, the numerical solution of Eqs. (19)–(21) becomes particularly easy and provides an excellent playground to investigate the basic phenomena described by our approach. For the explicit calculations, we employ electron-hole symmetry $(m_e^* = m_h^* =: m^*)$ and use the parameters $V = 0.50\hbar\omega_{\text{ph}}$, $G_{\text{eff}} = 0.45$, and a small Lorentzian line broadening of $0.17\hbar\omega_{\text{ph}}$. The phonon energy is fixed at $\hbar\omega_{\text{ph}} = 3$ in units of $\frac{1}{2}m^*(e^2/4\pi\varepsilon_0\varepsilon_\infty\hbar)^2$ and the $\mathbf{k}$ space is discretized on an equidistant mesh of 800 points with an energy-cutoff of $E_{c\mathbf{k}} - E_{v\mathbf{k}} \approx E_g^* + 25\hbar\omega_{\text{ph}}$.

In Fig. 1(a), we start our analysis by the calculation of the zeroth-order absorption signal $\alpha^{(0)}(\omega)$ from Eq. (16), which basically corresponds to the phonon-free result. Consequently, if the Coulomb term in $H_{\mathbf{kk}'}^{(0)}$ is neglected (dashed line), $\alpha^{(0)}(\omega)$ simply reflects the singularity of the 1D-density-of-states at the band gap, whereas the inclusion of the Coulomb potential (solid line) leads to a single exciton peak just below E_g^*, as expected for the contact-potential model. In Fig. 1(b), we proceed with the calculation of the total absorption signal $\alpha(\omega)$. For the full solution including Coulomb interaction [Eqs. (19)–(21), solid line], the strength of our approach is immediately visible from the emergence of the phonon replicas at energies of $m\hbar\omega_{\text{ph}}$ above the exciton line. Importantly, the spectral weights of these replicas do not follow a Poisson distribution as one might naively expect from the atomic case, Eq. (1). The reason for this behavior is that the interaction between the phonons and all *unbound* electron-hole pairs changes the "background" continuum absorption as well. In fact, if we look at the calculations without Coulomb interaction [Eq. (22), dashed line], we observe "steps" at energies of $E_g + m\hbar\omega_{\text{ph}}$, i.e., at the thresholds for emission of m phonons. While the resulting increase on the high-energy side of the spectra may be less pronounced for more realistic models [e.g., a 3D cystal with $(G_{\text{eff}})_{\mathbf{kk}'} \propto 1/|\mathbf{k} - \mathbf{k}'|^2$], our findings clearly show that, in general, valid absorption spectra can only be obtained if the bound and unbound states are described on equal footing, as it is the case in our approach.

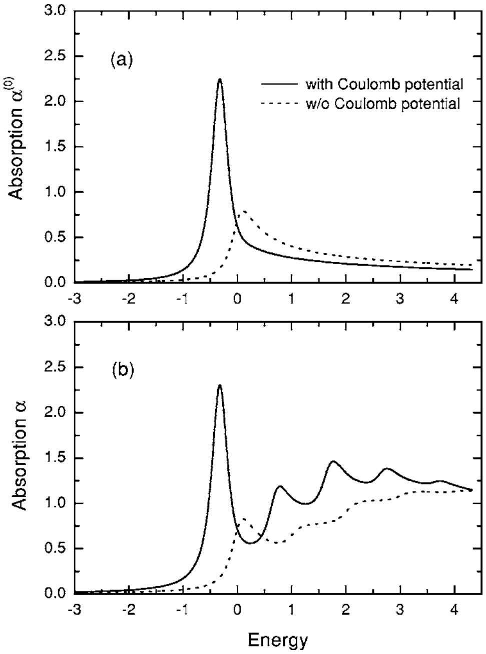

FIG. 1. Absorption signals $\alpha^{(0)}$ and α (in arbitray units) vs energy $\hbar\omega - E_g^*$ (in units of $\hbar\omega_{\text{ph}}$), as calculated from Eqs. (16) and (19)–(21), respectively. Solid (dashed) lines: Coulomb interaction included (excluded). For parameters: see text.

In summary, we have presented a theory of exciton-phonon resonances in semiconductor absorption spectra. Our primary result, Eqs. (19)–(21), generalize the textbook absorption formula (1) for molecules to the case of semiconductors. The particular strength of our approach is the simultaneous inclusion of the dispersive single-particle band structures and the charge-carrier Coulomb interactions (thus avoiding an *ad hoc* exciton-phonon picture) while, at the same time, treating the electron-phonon interaction nonperturbatively. Numerical studies for a simplified model crystal have provided a proof-of-principle for the practical usefulness of our theory, with extensions to more realistic systems being straightforward.

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