Nonperturbative theory of exciton-phonon resonances in semiconductor absorption

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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.

The interaction between electronic and vibrational degrees of freedom is of fundamental importance for the optical and transport properties of many physical systems. A classical example is given by the absorption spectra $\alpha(\omega)$ of an atom (or molecule) coupled to a phonon mode with frequency $\omega_{ph}$. 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 $e_{ex}$ and electron-phonon couplings $g$. Then, $\alpha(\omega)$ can be obtained exactly and yields (at zero temperature) the textbook formula:

$$\alpha(\omega) \propto e^{-\frac{G_{cl}(m)}{m!}} \delta(E_{ex} - E_{g} + m\hbar\omega_{ph} - \hbar\omega).$$

There are two phonon-induced modifications: (i) a small level shift to lower energies $(E_{0} = \epsilon_{ex} - \hbar\omega_{ph}g_{1}^{2})$ and, more importantly, (ii) the emergence of phonon replicas at multiple frequencies $\hbar\omega_{ph}$ above $E_{ex} - \epsilon_{ex}$, with a Poisson distribution of their respective weights that is governed by the effective coupling $G_{cl} = (g_{1} - g_{2})^{2}$.

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 description of the near-band-gap absorption in semiconductors, despite the fact that exciton-phonon sidebands are commonly observed in semiconductor spectroscopy. 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. 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 $E_{exc}/\hbar\omega_{ph}$, and the exciton-phonon coupling strength) and is, hence, in practice 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 but exclusively for the description of the first phonon replica. Here, we go beyond such perturbational approximations and develop a nonperturbative theory using the method of canonical transformation, thus extending previous work on the polaron problem towards the description of near-band-gap absorption of semiconductors.

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

$$H_{el} = \sum_{\alpha k} \left( e_{\alpha k} + \sum_{q} \hbar V_{q}^{\alpha k} b_{q k} \right) a_{\alpha k}^{\dagger} a_{\alpha k},$$

$$H_{el-ph} = \sum_{\alpha q k} \frac{1}{2} \hbar V_{q}^{\alpha k} (b_{q k}^{\dagger} a_{\alpha k} + a_{\alpha k}^{\dagger} b_{q k}),$$

$$H_{ph} = \sum_{q} \hbar \omega_{q} (b_{q k}^{\dagger} b_{q k} + \frac{1}{2}).$$

describe the electrons, the electron-electron interaction, the electron-phonon coupling, and the phonons, respectively. The operators $a_{\alpha k}^{\dagger}$ annihilate (create) electrons with Bloch wave vector $k$ and energy $\epsilon_{\alpha k}$ in band $\alpha$, whereas the operators $b_{q k}^{\dagger}$ and $b_{q k}$ phonons with wave vector $q$ and frequency $\omega_{q}$. 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., $\epsilon_{\alpha k} = \pm E_{g} / 2 \pm \hbar^{2} k^{2} / 2m_{e,\alpha}$. 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 carrier-carryer densities $n_{\alpha q} = (g_{\alpha q}^{2})$. In the ground state at $T = 0$, K, it holds that $n_{\alpha q} = 1$ and $n_{\alpha q} = 0$. The Coulomb potential in Eqs. (2) and (3) is denoted as $V_{q}$ and the electron-phonon coupling in Eq. (4) is described by the dimensionless quantities $g_{\alpha q}$.

In order to treat effects due to the electron-phonon coupling in a nonperturbative manner, we introduce transformed operators $A_{\alpha k}^{(i)} = e^{iU b_{q k}^{(i)} a_{\alpha k}^{(i)} e^{-U}}$, $B_{q k}^{(i)} = e^{iU b_{q k}^{(i)} e^{-U}}$ representing annihilation (creation) operators of polarons and phonons of a distorted lattice, as described below. The anti-Hermitian operator $U$ is defined as $U = \sum_{\alpha k q} g^{\alpha q k} a_{\alpha k}^{(i)} b_{q k}^{(i)} (b_{q k}^{(i)} - b_{q k})$ and the transformation rules are obtained by application of the
Baker-Campbell-Hausdorff theorem $e^{U_f}e^{-U_f} = e^{[U_f]} + (1/2)[U, U_f] + \cdots$. As a result, we obtain the relations
\[
a_{\alpha k} = \sum_k (e^{\epsilon_\alpha})_{kk'}A_{\alpha k'}, \quad b_q = B_q - \sum_{\alpha k} g_{\alpha q} a_{\alpha k}^\dagger a_{\alpha k}, \quad (6)
\]
where we have introduced a compact matrix notation for the exponential operators by means of the short-hand definition
\[
(C_{\alpha k})_{kk'} = g_{\alpha k-k'}(B_{k-k'}-\delta_{k'_k}).
\]

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
\[
H_{\text{pol}} = \sum_{\alpha q} \left( E_{\alpha k} + \sum_q g_{\alpha q} V^{\text{eff}}_{\alpha k} A_{\alpha k}^\dagger A_{\alpha k} \right),
\]
\[
H_{\text{pol-pol}} = \sum_{\alpha_1 \alpha_2 q_1 q_2} \frac{1}{2} g_{\alpha_1 q_1} g_{\alpha_2 q_2} A_{\alpha_1 k_1}^\dagger A_{\alpha_2 k_2}^\dagger A_{\alpha_2 k_2} A_{\alpha_1 k_1} + q_1 A_{\alpha_2 k_2} - q_2 A_{\alpha_1 k_1} - q_2 A_{\alpha_1 k_1} + q_1 A_{\alpha_2 k_2},
\]
\[
H_{\text{ph}} = \sum_q \hbar \omega_q (B_q^* B_q + \frac{1}{2})
\]
describe the polaron, 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 $E_{\alpha k}$ which, in general, contain also phonon operators. For the purpose of our work, we follow the spirit of earlier work on the polaron problem and replace the phonon operators in $E_{\alpha k}$ by their thermal averages. The neglected effects such as line broadening and recoil effects are of minor importance for the present paper that focuses on the description of exciton-phonon sidebands. As a result, the polaron dispersions (at $T = 0$ K) are approximately given by the expressions $E_{\epsilon k_c} = \bar{\epsilon}_{\epsilon k_c} - \Delta_c$ and $E_{\epsilon k} = \bar{\epsilon}_{\epsilon k} + \Delta_c$, the derivation of which is straightforward but lengthy and will be given elsewhere. Here, we used the shorthand notations $\Delta_c = 2\hbar \omega q_{\alpha q} q_{\alpha q}$, $\bar{\epsilon}_{\epsilon k_c} = e^{-\bar{g}_{\alpha q} \sum_k e_{\epsilon k_c}} g_{\alpha q} \sum_k$, and $(G_{\alpha q})_{kk'} = g_{\alpha q}^2 \delta_{kk'}$. Compared to the original electron dispersions $e_{\epsilon k_c}$, we find a shrinkage of the band gap ("polaron shift") because $\Delta_c > 0$ and a narrowing of the bandwidth due to the exponential renormalizations in $\bar{\epsilon}_{\epsilon k_c}$. The latter effect is especially important in materials with strong electron-phonon coupling such as organic crystals, but within our effective mass approximation it corresponds simply to a mass enhancement for 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
\[
P_{\text{ref}}(t) = \Theta(t) \frac{1}{i\hbar} \sum_{kk'} \sum_{\alpha} \sum_{\epsilon k} (a^\dagger_{\alpha k}(t)a_{\alpha k}(t) + a^\dagger_{\alpha k}(0)a_{\alpha k}(0)).
\]
Here, the time dependence of the electron operators is governed by the Hamiltonian $H$ according to $a_{\alpha k}(t) = e^{i(h \bar{g}_{\alpha q} q_{\alpha q} t)} e^{-i(h \bar{g}_{\alpha q} q_{\alpha q} t)}$ and $\Theta$ denotes a normalization volume. In the following, we will evaluate $P_{\text{ref}}$ 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
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\]
\[ e^{i\hbar H_{\text{eff}} t} A_{k_1}^\dagger A_{k_2} e^{-i\hbar H_{\text{eff}} t} = \sum_{k_1'k_2'} \left[ e^{-i\hbar S_{\text{eff}} t_{k_1k_2k_1'k_2'}} \right]_{k_1k_2k_1'k_2'} A_{k_1'}^\dagger A_{k_2'}. \]  

(13)

If we insert the relation (13) into Eq. (11) and perform the thermal average over the polaron operators assuming the ground state \( \langle A_{k_1}^\dagger A_{k_2}^\dagger A_{k_1} A_{k_2} \rangle = \delta_{k_1k_2} \delta_{k_1'k_2'} \), the retarded polarization function adopts the form

\[ P_{\text{ret}}(t) = \frac{\Theta(t)}{i\hbar} \sum_{k_1k_2} \left[ e^{-i\hbar S_{\text{eff}} t} \right]_{k_1k_2k_1k_2} X_{k_1k_2}(t), \]  

(14)

\[ X_{k_1k_2}(t) = \left( \langle e^{iC_{\text{eff}}(0)} \rangle_{k_1k_2} \langle e^{C_{\text{eff}}(0) - C(0)} \rangle_{k_1k_2} \right). \]  

(15)

For the remaining evaluation of the thermal averages over the phonon operators in Eq. (15), we expand \( X_{k_1k_2}(t) \) in a power series of \( g_{\text{eq}} - g_{\text{eq}} \). The zeroth-order term is simply given by \( X_{k_1k_2}(0) = \delta_{k_1k_2} \), and, apart from the renormalization \( e_{\text{eq}} \rightarrow E_{\text{eq}} \), 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 \( H_{k\text{eff}}(0) = (E_{\text{eq}} - E_{\text{eq}}) \delta_{k\text{eff}} - V_{\text{eff}} \), and express the zeroth-order polarization as \( P_{\text{ret}}(0) = \langle \Theta(t)/i\hbar \rangle \times (1/\Omega) \sum_{k\text{eff}} \left[ e^{-i\hbar H_{\text{eff}}(0)t} \right]_{k\text{eff}} \). Then, the absorption signal becomes

\[ \alpha(\omega) \propto -e^{-\omega\delta_{k\text{eff}}} \text{Im} \frac{1}{\Omega} \sum_{k\text{eff}} \frac{1}{m!} P_{kk}(\omega)^m, \]  

(19)

where the quantities \( P_{kk}(\omega) \) have to be determined self-consistently from the equations

\[ [E_{\text{eq}} - E_{\text{eq}} + m\hbar \omega_{\text{ph}} - \hbar(\omega + i0)]P_{kk}(\omega) = -\sum_q V_{q,q}^m P_{q,k-k,q}^m(\omega) = -[\langle G_{\text{eff}}(m) \rangle_{kk}]^2. \]  

(21)

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

\[ \langle G_{\text{eff}}(m) \rangle_{kk} = \sum_{k_1k_2} \langle G_{\text{eff}}(m) \rangle_{k_1k_2} \cdots \langle G_{\text{eff}}(m) \rangle_{k_{m-1}k_m} \]  

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 \( I_{kk}(\omega) \) can be obtained algebraically and the absorption (19) reduces to

\[ \alpha(\omega) \propto e^{-\omega\delta_{k\text{eff}}} \sum_{k\text{eff}} \frac{1}{\Omega} \sum_{m=0}^{\infty} \frac{[\langle G_{\text{eff}}(m) \rangle_{kk}]^m}{m!} \delta(E_{\text{eq}} - E_{\text{eq}} + m\hbar \omega_{\text{ph}} - \hbar \omega) \].  

(22)

This formula is strikingly reminiscent of the textbook for-
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 \(V = 0.50\hbar\omega_{ph}\), \(G_{\text{eff}} = 0.45\), and a small Lorentzian line broadening of \(0.17\hbar\omega_{ph}\). The phonon energy is fixed at \(\hbar \omega_{ph} = 3\) in units of \(\frac{3}{2}m^e(e^2/4\pi e_0\epsilon_{ph}^2\hbar)^2\) and the \(k\) space is discretized on an equidistant mesh of 800 points with an energy-cutoff of \(E_{\text{cutoff}} = E_0 + 25\hbar\omega_{ph}\).

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 \(H_{\text{ph}}^{(0)}\) 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 excitation peak just below \(E_0\), 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 \(m\hbar\omega_{ph}\) 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 \(E_0 + m\hbar\omega_{ph}\), i.e., at the thresholds for emission of \(m\) photons. While the resulting increase on the high-energy side of the spectra may be less pronounced for more realistic models [e.g., a 3D crystal with \((G_{\text{eff}}/k^2) \propto 1/|k-k'|^2\)], 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.

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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1 See, e.g., G. D. Mahan, Many-Particle Physics (Plenum Press, London, 1990), and references therein.
15 K. Hannewald et al. (unpublished).