# Theory of optical spectra of polar quantum wells: Temperature effects

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Theoretical and numerical calculations of the optical absorption spectra of excitons interacting with longitudinal-optical phonons in quasi-two-dimensional polar semiconductors are presented. In II-VI semiconductor quantum wells, exciton binding energy can be tuned on and off resonance with the longitudinal-optical phonon energy by varying the quantum well width. A comprehensive picture of this tuning effect on the temperature-dependent exciton absorption spectrum is derived, using the exciton Green's function formalism at finite temperature. The effective exciton-phonon interaction is included in the Bethe-Salpeter equation. Numerical results are illustrated for ZnSe-based quantum wells. At low temperatures, both a single-exciton peak and a continuum resonance state are found in the optical absorption spectra. By constrast, at high enough temperatures, a splitting of the exciton line due to real phonon absorption processes is predicted. Possible previous experimental observations of this splitting are discussed.

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## I. INTRODUCTION

Low-dimensional semiconductor structures provide many surprising properties that have never been observed in bulk materials. One of the most interesting properties of II-VI semiconductor-based nanostructures is the observation of well-resolved heavy- and light-hole exciton peaks in the absorption spectra, even at room temperature.[1] It has been proposed that the lasing mechanism in highly excited II-VI quantum wells (QW's) corresponds to a coherent recombination of excitons.[1–4] It is therefore expected that excitons remain stable in the presence of high carrier densities, thus playing an important role in the operation of blue-green diode lasers. However, the potentialities of II-VI compound heterostructures to obtain reliable excitonic devices depend strongly upon the strength, the width of the resonances, and the nature of the exciton scattering processes at room temperature. Indeed one of the main scattering mechanisms to be considered is the interaction of excitons with longitudinal-optical (LO) phonons,[5] a problem of an enormous interest from both the experimental and theoretical point of views.

A major difference between III-V and II-VI semiconductors is the highly polar character of the latter. As a consequence, the coupling of charge carriers (electrons and holes) with LO phonons is stronger in II-VI than in III-V compounds. A convenient measure of the coupling strength is the dimensionless Fröhlich constant $\alpha$. The electron-phonon complex represents a quasiparticle, called a polaron, which in the weak-coupling limit, $\alpha \ll 1$ as appropriate for GaAs ($\alpha = 0.06$), slightly renormalizes the electron properties. II-VI compounds like ZnSe should be described by an intermediate-coupling theory since for this last compound $\alpha = 0.43$, about an order of magnitude larger than in GaAs. Besides that, the exciton binding energy $E_X$ in II-VI QW's can be made comparable to or even greater than the LO-phonon energy $\omega_{LO}$ (here and in the following $\hbar = 1$) by varying the well width. In particular, for ZnSe, the binding energy of the bulk exciton, $E_X^{3D} \approx 20$ meV, while in two dimensions, $E_X^{2D} = 4E_X^{3D}$; the LO-phonon energy is $\omega_{LO} \approx 30$ meV in the bulk. Therefore, three regimes can be expected in II-VI low-dimensional structures: (1) $E_X > \omega_{LO}$, (2) $E_X < \omega_{LO}$, and (3) $E_X \approx \omega_{LO}$, to which we will refer from now on as *the resonant regime*. Cases (1) and (2) have been extensively considered: for the first case, a single LO-phonon absorption cannot dissociate the exciton into the electron-hole continuum. Furthermore, the exciton Bohr radius is smaller than the polaron radius, and consequently the electron-hole pair is weakly influenced by phonons; i.e., they interact through a Coulomb interaction screened by the static dielectric constant.[6] Hence, the coupling of excitons with LO phonons via the Fröhlich interaction can be substantially reduced, yielding to strong exciton absorption, even at room temperature.[1–4,7–9] For the second case, the electron-hole Coulomb interaction will be screened by the lattice vibrations and other excitations.[6,10] Therefore, the exciton should be easily ionized, affecting the optoelectronic properties of the semiconductor system.

The third case at finite temperature, to the best of our knowledge, has been ignored in theoretical studies. In the limit of vanishing temperature, previous works on II-VI heterostructures show that the exciton–LO-phonon interaction weakens with decreasing well width and predict a small feature in the exciton continuum spectrum, the so-called exciton–LO-phonon quasibound state.[7,11] It is explained based on the large Fröhlich coupling between excitons and LO phonons in those compounds. Similar but weaker effects have also been reported for II-VI bulk systems.[12–14] Clearly, there is a lack of theoretical works on exciton–LO-phonon complexes in the resonant regime at high enough temperatures ($77\ \text{K} \leqslant T \leqslant 330\ \text{K}$) for such materials.

The main goal of this work is to study the exciton absorption line shape in the resonant regime as a function of temperature. *At high temperatures* a peak splitting is predicted, corresponding to exciton–LO-phonon absorption processes. In the resonant regime both of these split peaks have roughly the same oscillator strength. Therefore, this new feature should be considered for understanding the structure and dynamics of the optical response of II-VI QW's.[15] Broadening and splitting of the exciton peak at the lower band edge in

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III-V bulk systems have been reported,[16] and they have been explained as a consequence of the increasing of the phonon density of states. However, the exciton splitting in this last system is vaguely visible for two reasons: (i) the Fröhlich coupling is roughly one order of magnitude lower than in II-VI heteroestructures, and (ii) the resonance between the exciton binding energy and LO-phonon energy cannot be achieved. By contrast, in our systems these last two points are met, yielding to an enhancement of the oscillator strength. Therefore, the exciton splitting should become clearly visible in II-VI heterostructures.

In the present work a theory of exciton–LO-phonon complexes using a Green's function (GF) formalism at finite temperature is developed. Using this formalism the linear optical absorption for II-VI-based QW's is obtained.[17,18] Most of previous theoretical works employ the variational formalism to obtain exciton properties,[19–22] with severe limitations to fit the whole absorption spectrum. A crucial difference between the present work and previous studies is that the GF method employed here allows us to include all the information about both bound and continuum exciton states, going clearly beyond the usual variational treatments. As a consequence, the whole absorption spectrum, instead of just ground-state properties, can be determined. Although there are a few theoretical calculations of the linear optical absorption using the GF formalism,[10,11,17] they do not explore the joint effects: temperature and QW width variations. The GF formalism used here allows a comprehensive picture of light absorption, treating quasiparticles and their interactions on the same footing.

The article is organized as follows: Section II gives a brief survey of GF formalism as applied to the exciton–LO-phonon problem; in particular, self-energy and vertex contributions as well as the effective nonlocal dynamical electron-hole potential are described. In Sec. III the numerically calculated absorption spectra for ZnSe/ZnSeS QW's are discussed. In Sec. IV vertex and self-energy contributions to the optical absorption are separately considered . Finally, Sec. V summarizes the main conclusions of this work.

## II. THEORETICAL MODEL

Using a Fröhlich Hamiltonian[23] an electron-hole pair confined in an infinite barrier potential QW of width $a$ ($z$ direction) is considered. In this work only the lowest electron and heavy-hole subbands are taken into account. Extension to include multisubband effects is straightforward. Each particle interacts with bulk LO phonons assumed dispersionless. The total Hamiltonian describing the exciton–LO-phonon complexes is written as

$$H=\sum_{p,\vec{k}} E^p(\vec{k})c_{\vec{k}}^{p\dagger}c_{\vec{k}}^{p}+\omega_{LO}\sum_{\vec{Q}} b_{\vec{Q}}^{\dagger}b_{\vec{Q}} + \sum_{p,\vec{k},\vec{Q}} M_{\vec{Q}}^{p}\frac{1}{|Q|}c_{\vec{k}}^{p\dagger}c_{\vec{k}-\vec{q}}^{p}(b_{\vec{Q}}+b_{-\vec{Q}}^{\dagger}) + \sum_{\vec{k},\vec{k}',\vec{q}} V_0^{e-h}(q)c_{\vec{k}'+\vec{q}}^{e\dagger}c_{\vec{k}'}^{e},c_{\vec{k}-\vec{q}}^{h\dagger}c_{\vec{k}}^{h}, \quad (1)$$

where $E^p(\vec{k})$ represents the parabolic dispersion relation for $p$-type particles ($p$ = electron or hole), $c_{\vec{k}}^{p,\dagger}$ ($c_{\vec{k}}^{p}$) is the corresponding creation (annihilation) operator with two-dimensional wave number $\vec{k}$, $b_{\vec{Q}}^{\dagger}$ ($b_{\vec{Q}}$) is the creation (annihilation) operator for LO phonons with momentum $|\vec{Q}|=(q^2+q_z^2)^{1/2}$ ($\vec{q}$ is the phonon wave vector component parallel to the $xy$ plane), $M_{\vec{Q}}^{p}$ is the particle-phonon interaction matrix element,[24] and $V_0^{e-h}$ is the bare electron-hole Coulomb matrix element, with the dielectric constant $\epsilon_0$ replaced by $\epsilon_\infty$.[17,18] Herein, $\epsilon_0$ and $\epsilon_\infty$ are the low- and high-frequency limits of the dielectric function, respectively.

### A. First-order self-energy corrections

Due to the large electron- and hole-LO phonon couplings, each carrier interacts with its self-induced polarization in the polar semiconductor, the so-called polaron. Therefore, the carrier energy must be modified by self-energy corrections given by[18,24]

$$\Sigma^p(\vec{k},\Omega)=-\frac{1}{\beta}\sum_{\vec{q},i\nu} V(\vec{q},i\nu)\mathcal{G}_p^0(\vec{k}-\vec{q},\Omega-i\nu) =\frac{\alpha_p\omega_{LO}^{3/2}}{2\pi(2m_p^*)^{1/2}}\int\frac{d^2q}{q}F(q)\left[\frac{N_0}{\Omega+\omega_{LO}-E^p(\vec{k}-\vec{q})} +\frac{N_0+1}{\Omega-\omega_{LO}-E^p(\vec{k}-\vec{q})}\right], \quad (2)$$

where $V(\vec{q},i\nu)$ represents the LO-phonon-mediated effective electron-electron interaction, $\mathcal{G}_p^0$ is the free $p$-particle propagator, $N_0=1/(e^{\beta\omega_{LO}}-1)$ is the phonon population, and $\beta=1/k_BT$. The Fermi factors in Eq. (2) are set to zero, because many electron effects are ignored here. $F(x)$ denotes the structure factor of the infinite QW,

$$F(q)=\int_0^a dz\int_0^a dz'\,\phi(z)\phi^*(z)e^{-q|z-z'|}\phi(z')\phi^*(z'), \quad (3)$$

with $\phi(z)$ the single-particle wave function in the QW growth direction and $\alpha_p$ is the Fröhlich coupling constant for each kind of particle. The first term in the square brackets in Eq. (2) represents the absorption of phonons, while the second one is associated with the emission of phonons. Notice that absorption processes can occur only at different from zero temperatures.

### B. Exciton–LO-phonon vertex corrections

One of the most interesting aspects of the problem is that polarons do not interact instantaneously. Therefore, the real electron-hole interaction, in general, is nonlocal in space and time. This nonlocality effect is very important in polar semiconductors, modifying dramatically the bare interaction. In order to account for the effective dressed electron-hole Cou-

lomb interaction, vertex and self-energy corrections must be taken into account on an equal footing. The vertex corrections are expressed as[17,18]

$$I_{eff}^{e\text{-}h}(\vec{q},i\nu_m)=\sum_{q_z}\frac{2\pi\gamma}{q^2+q_z^2}F(q_z)D_{LO}(\vec{Q},i\nu_m), \tag{4}$$

where $\gamma=e^2\omega_{LO}[1/\epsilon_\infty-1/\epsilon_0]$ and $D_{LO}(\vec{Q},i\nu_m)$ represents the LO-phonon propagator.

The effective electron-hole nonlocal interaction within Shindo's approximation[25] is

$$V_{eff}^{e\text{-}h}(\vec{k},\vec{k}',\Omega)=\frac{1}{\beta^2}\sum_{i\nu_n,i\nu_n'}[\mathcal{G}_e^0(\vec{k},\Omega-i\nu_n)+\mathcal{G}_h^0(-\vec{k},i\nu_n)]\times I_{eff}^{e\text{-}h}(\vec{k}-\vec{k}',i\nu_n-i\nu_n')[\mathcal{G}_e^0(\vec{k}',\Omega-i\nu_n')+\mathcal{G}_h^0(-\vec{k}',i\nu_n')]. \tag{5}$$

By summing over the Matsubara frequencies an explicit expression for the effective electron-hole nonlocal interaction results as

$$V_{eff}^{e\text{-}h}(\vec{k},\vec{k}',\Omega)=V_0^{e\text{-}h}(\vec{k}-\vec{k}')\left[1+\frac{N_0\epsilon_\infty\omega_{LO}}{2\epsilon_0}\left(\frac{1}{\Omega-E^e(\vec{k})-E^h(\vec{k}')+\omega_{LO}}+(\vec{k}\leftrightarrow\vec{k}')\right)+\frac{(N_0+1)\epsilon_\infty\omega_{LO}}{2\epsilon_0}\left(\frac{1}{\Omega-E^e(\vec{k})-E^h(\vec{k}')-\omega_{LO}}+(\vec{k}\leftrightarrow\vec{k}')\right)\right]. \tag{6}$$

From this last expression it becomes obvious that at different from zero temperatures the effective potential shows singularities at $\Omega=E^e(\vec{k})+E^h(\vec{k}')-\omega_{LO}$. These singularities increase the exciton–LO-phonon scattering close to $E_X$ for small $k$ values, due to the enhancement of the phonon density of states in the lower and upper band edges. Equation (6) is similar to that found for the three-dimensional case, where first-order corrections to the single-particle self-energies have been included in the effective electron-hole Coulomb interaction screened by an electron-hole plasma.[17] The second and third terms in the square brackets, Eq. (6), represent the modification of the bare Coulomb potential by phonon effects. These terms describe the dynamical screening of the electron-hole interaction and take into account the interband scattering of electron-hole pairs by absorption or emission of phonons. Some previous theoretical works[6,10,25] assumed the static single-pole exciton approximation by replacing $\Omega\rightarrow\Omega-E_X$ both in the carrier self-energy and effective potential. Therefore, peaks at $E_X\pm\omega_{LO}$ in the absorption spectrum are expected. Within the static single-pole exciton approximation and Fourier transforming Eq. (6) to real space a modified Coulomb electron-hole interaction is found, the so-called Haken potential.[26] Therefore, the full expression for the effective potential in Eq. (6) goes beyond the usual static and zero-temperature effective potential.

### C. Exciton–LO-phonon GF

Since the creation of electron-hole pairs by the absorption of photons is more efficient in semiconductors of direct gap, only electron-hole pair states with zero center-of-mass momentum are considered. A systematic way of deriving the exciton-phonon complex properties starts by considering the two-particle correlation function.[6,10,17,25] After a long but straightforward algebra a Bethe-Salpeter equation for the interacting electron–hole–LO-phonon GF is obtained:

$$\mathcal{G}(\vec{k},\vec{k}',i\nu_n,\Omega)=\mathcal{G}^0(\vec{k},\vec{k}',i\nu_n,\Omega)+\frac{1}{\beta}\sum_{\vec{k}'',\vec{k}''',i\nu_n'}\mathcal{G}^0(\vec{k},\vec{k}'',i\nu_n,\Omega)I_{eff}^{e\text{-}h}(\vec{k}''-\vec{k}''',i\nu_n-i\nu_n')\mathcal{G}(\vec{k}''',\vec{k}',i\nu_n',\Omega), \tag{7}$$

with

$$\mathcal{G}^0(\vec{k},\vec{k}',i\nu_n,\Omega)=\frac{\delta_{\vec{k},\vec{k}'}}{[i\nu_n-E^e(\vec{k})-\Sigma^e(\vec{k},\Omega-i\nu_n)][i\nu_n-E^h(\vec{k})-\Sigma^h(-\vec{k},i\nu_n)]}. \tag{8}$$

The terms in the first set of parenthesis term in the denominator represent the inverse of the dressed by phonons electron propagator and the terms in the second set the analogous one for a hole. After summing over $\vec{k}'$, the following closed dressed two-particle GF is obtained:

$$G(\vec{k},i\nu_n,\Omega)=G^0(\vec{k},i\nu_n,\Omega)+\frac{1}{\beta}G^0(\vec{k},i\nu_n,\Omega)\sum_{\vec{k}',i\nu_n'}I_{eff}^{e\text{-}h}(\vec{k}-\vec{k}',i\nu_n-i\nu_n')G(\vec{k}',i\nu_n',\Omega). \tag{9}$$

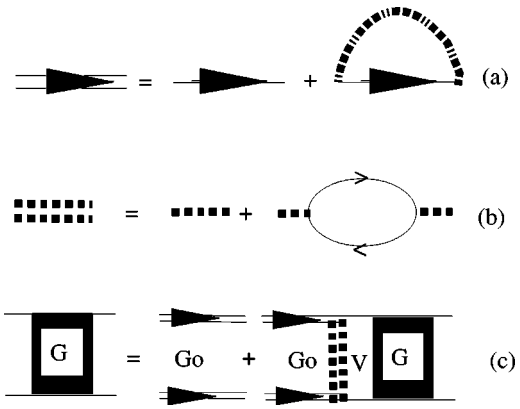


FIG. 1. (a) Dressed by phonons carrier propagator, Eq. (2). (b) Diagrammatic contribution to the effective electron-hole interactions dressed by LO phonons, Eq. (4). (c) Green's function equation for the exciton and LO phonon, Eq. (9).

with

$$G(\vec{k},i\nu_n,\Omega)=\sum_{\vec{k}'}\mathcal{G}(\vec{k},\vec{k}',i\nu_n,\Omega). \tag{10}$$

Using the vertex corrections, Eq. (4), in the Bethe-Salpeter equation (9) and performing the frequency summation, the exciton–LO-phonon GF is

$$G(\vec{k},\Omega)=G^0(\vec{k},\Omega)-G^0(\vec{k},\Omega)\times\sum_{\vec{k}'}V_{eff}^{e\text{-}h}(\vec{k},\vec{k}',\Omega)G(\vec{k}',\Omega), \tag{11}$$

with

$$G^0(\vec{k},\Omega)=\sum_{\vec{k}',i\nu_n}\mathcal{G}^0(\vec{k},\vec{k}',i\nu_n,\Omega)=\frac{1}{\Omega-E^e(\vec{k})-E^h(-\vec{k})-\Delta_{e-h}(\vec{k},\Omega)},$$

$$G(\vec{k},\Omega)=\sum_{i\nu_n}G(\vec{k},i\nu_n,\Omega), \tag{12}$$

where

$$\Delta_{e\text{-}h}(\vec{k},\Omega)=-\frac{1}{\beta}\sum_{i\nu_n}[\mathcal{G}_e^0(\vec{k},\Omega-i\nu_n)+\mathcal{G}_h^0(-\vec{k},i\nu_n)]\times[\Sigma^e(\vec{k},\Omega-i\nu_n)+\Sigma^h(-\vec{k},i\nu_n)]. \tag{13}$$

The diagrammatic representations of Eqs. (2), (4), and (9) are shown in Fig. 1. In order to treat vertex and self-energy corrections on an equal footing, at any temperature, the following relation (Ward identity) must be held:

$$\Delta_{e\text{-}h}(\vec{k},\Omega)=\sum_{\vec{k}'}[V_{eff}^{e\text{-}h}(\vec{k},\vec{k}',\Omega)-V_0^{e\text{-}h}(\vec{k}-\vec{k}')]. \tag{14}$$

This last relation is easily probed by using Eqs. (2), (6), and (13).

Broadening effects, coming from other sources different from LO-phonon scattering, are included phenomenologically by taking $\Omega=\omega+i\delta$. The coupled equations (2), (6), and (11) describe the *whole exciton–LO-phonon complex spectrum with both discrete and continuum exciton states taken into account*. Temperature effects are considered, both in the self-energy and vertex corrections. By solving numerically these equations, the linear absorption spectrum, given by the imaginary part of the exciton GF equation (11), as a function of QW width and temperature can be obtained.

## III. ABSORPTION SPECTRUM

In order to illustrate the behavior of the exciton–LO-phonon complexes in both the resonant and nonresonant regimes in II-VI semiconductor QW's, the absorption spectrum for ZnSe/ZnSeS heterostructures is calculated. The following parameters are used in the numerical calculations: $m_e=0.16m_0$, $m_h=0.6m_0$, $\epsilon_0=8.8$, $\epsilon_\infty=5.6$, and $\omega_{LO}=31.8$ meV.[2] The results should be reliable for well widths $a\leqslant 100$ Å, given that only the lowest electron and highest hole subbands are considered. Typically the broadening of the exciton peak ($\delta$) due to impurities, interface roughness, acoustical phonons, strain, etc., is roughly the bulk effective Rydberg energy ($Ry=22.4$ meV for ZnSe).[8] In order to stress the LO-phonon effects the broadening is reduced to $\delta=Ry/2$, which was kept fixed for the entire range of temperatures and QW widths. Bulk LO phonons, i.e., unaffected by the well width, are assumed.

### A. Continuum resonant state

First, the exciton absorption in the continuum part of the spectrum is considered. Results for different temperatures $0\ \text{K}\leqslant T\leqslant 330$ K are discussed. In Fig. 2 the absorption spectra, as a function of photon energy for two different well widths $a=30$ Å [Fig. 2(a)] and $a=80$ Å [Fig. 2(b)] are plotted. Results in Fig. 2(a) correspond to a quasi-two-dimensional (quasi-2D) case while results appropriate to a quasi-3D case are shown in Fig. 2(b). The low-temperature results provide us with an important test of the present formalism: the exciton effect is quite significant as should be expected. Besides that, and more important, an additional peak at $\omega_{LO}$ is present. This feature can be explained by the fact that the first-order carrier self-energy corrections show a logarithmic divergence due to phonon emission. If vertex corrections were not included, the height of this peak would be reduced. Additionally, multiphonon contributions, being very weak (they scale like $\approx\alpha^n$),[18] should smooth the resonant state line shape but do not destroy it. It is worth noting that the resonant state is still present as a weak shoulder at high enough temperatures. However, this peak does not correspond exactly to the so-called quasibound state at $\Omega=E_X+\omega_{LO}$.[12–14] In order to recover this last feature, the present formalism could be modified by making the standard static pole approximation for both the self-energy [Eq. (2)] and the

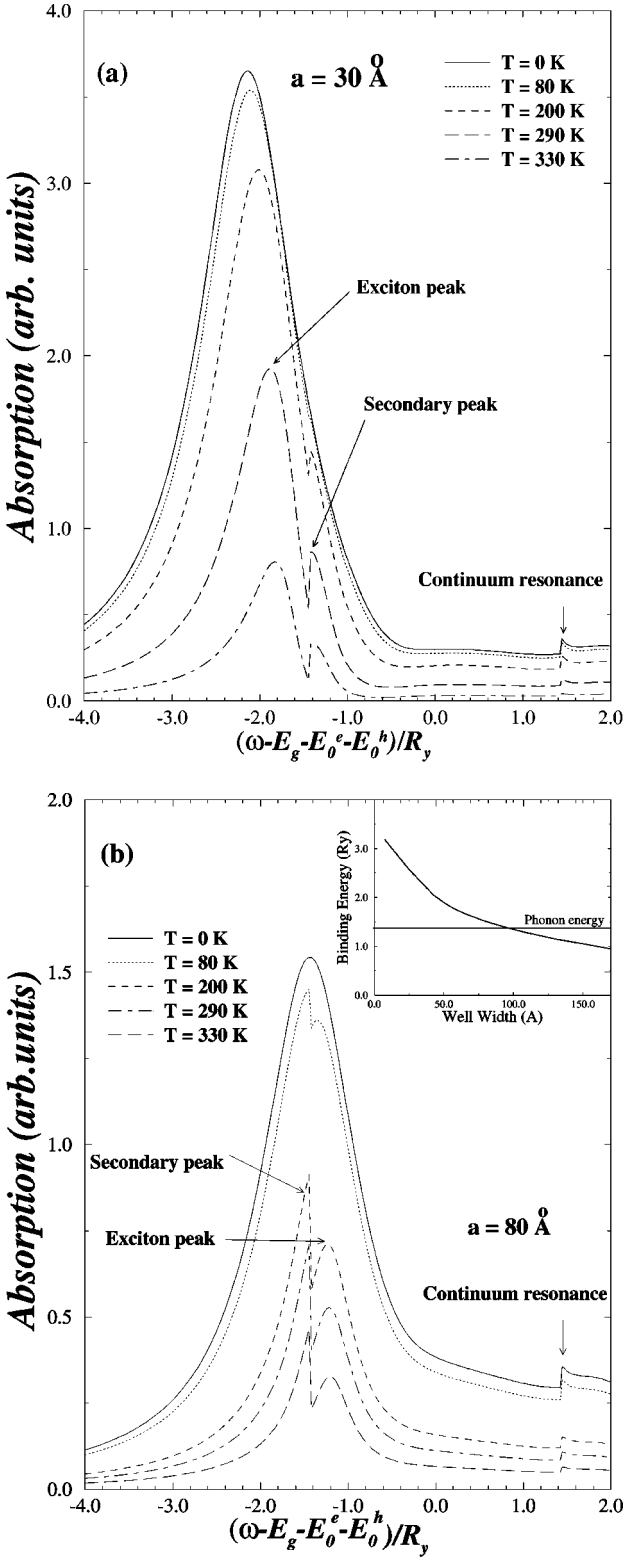


FIG. 2. Absorption spectrum for ZnSe QW's of $a=30$ Å (a) and $a=80$ Å (b) for different temperatures. The inset shows the bare exciton binding energy (solid line) and the bulk LO-phonon energy (dotted line) as a function of the well width. The arrow in the continuum part shows the exciton-phonon resonance of the spectrum. $E_g$, $E_0^e$, and $E_0^h$ are the band gap and the zero-point energy for electrons and holes, respectively.

exciton-phonon interaction [Eq. (6)], i.e., by replacing $\Omega \rightarrow \Omega - E_X$. As a consequence of this modification, the exciton-phonon interaction develops a strong peak at the exciton binding energy, in agreement with previous theoretical works.[6,10,25] However, although the present formalism is capable of reproducing well-known results by using such a phenomenological approach, the main interest in the present work is related to a systematic perturbative calculation without such kind of procedures. A full self-consistent treatment must be done in order to place the quasibound-state peak position at the correct energy, i.e., $E_X+\omega_{LO}$. As is well known, such a treatment implies that the self-energy should be calculated in terms of the full Green's function which in turn depends on the self-energy. This kind of calculation has been reported for the three-dimensional case in Ref. 14 where a real-space static Haken potential has been used. Nevertheless, dynamic effects in the effective Coulomb interaction have not been taken into account. By contrast, the present formalism is as a first-order approximation where the Ward identities are fulfilled and a dynamical effective interaction, for the exciton-phonon problem, is included. However, a full dynamical self-consistent calculation is out of the scope of the present work.

### B. Exciton peak split

At high enough temperatures, a new result is evident: *the exciton peak is split*. In order to clarify this fact, the inset in Fig. 2(b) shows the theoretical bare exciton binding energy (solid line), i.e., without LO-phonon effects, and the LO-phonon energy (dotted line) as a function of the QW width. For a narrow well width, Fig. 2(a), the exciton binding energy is larger than the LO-phonon energy. In this case, the number of states into which the exciton can scatter is vanishingly small and consequently the effective exciton-LO phonon coupling is reduced.

Both peaks can be easily identified: one of them corresponds to the main exciton peak which is redshifted as the temperature is increased; the other one, with a very asymmetrical shape, has an energy position centered at $-\omega_{LO}$ with respect to the onset of the continuum part of the spectrum. Similarly to the continuum resonant state, the asymmetrical line shape of this new peak should be smoothed by including higher-order LO-phonon processes.

Now, in the resonance regime, where a crossing of exciton-binding LO-phonon energies occurs, is to be considered. In Fig. 2(b), as the temperature rises from 0 to 330 K, the main exciton peak is quasi-3D-like and shifts to higher energies. By contrast, the secondary peak preserves a constant energy position which is fixed only by the LO-phonon energy. Its intensity becomes smaller and its linewidth broadens for high temperatures, due to the fact that the density of phonons increases. Clearly, these features suggest that the contribution from the phonon absorption terms in the self-energy and vertex corrections should be observable in the optical absorption spectra. Similar but weaker peaks have been reported by Donlagic and Ostreich[16] for bulk III-V systems using a tight binding model. However, in this last case

a resonant regime cannot be achieved because the binding exciton energy is approximately one-half the LO-phonon energy.

As the main conclusion of this section, it can be stated that when the temperature has risen, the exciton peak splitting should be clearly seen, remaining visible up to $T=330$ K.[8] In order to see this splitting the quasi-2D exciton binding energy must be in resonance with the LO-phonon energy which can be achieved by varying the QW width in II-VI polar heterostructures.

When the crossing of energies occurs ($E_X \approx \omega_{LO}$), the dynamical effective electron-hole pair interaction becomes very large, and multiple-scattering events are dominant [see Eq. (11)]. From the experimental point of view unexplained shoulders in the exciton main peak absorption have been reported by Pelekanos *et al.*[7] and Miyajima *et al.*[27] In the light of the present theoretical results, those unexplained facts might be associated with nonresolved exciton peak splitting. Consequently, to observe experimentally this peak splitting, the samples should be grown in such a way that the resonance condition is met and the absorption spectrum recorded above the liquid nitrogen temperatures.

## IV. EXCITON–LO-PHONON COUPLING

The main points discussed in the previous section are (i) an exciton peak splitting and (ii) the presence of a continuum resonant state. Up to this point, the present model describes successfully these main facts. Now the two above-mentioned points are to be discussed based on the characteristics of the effective electron-hole potential and self-energy effects. The fact that the self-energy is included in the free carrier GF implies that the effective electron-hole pair interaction dressed by phonons must be treated properly in order to satisfy the Ward identity [Eq. (14)] with clear consequences in the absorption spectra. In order to give an ample discussion of the excitonic peak splitting, the effects coming from both self-energy and vertex corrections are to be discussed separately.

In order to assess the validity of the present results, different contributions from self-energy and vertex corrections are plotted in Fig. 3. Particularly, the thick solid line shows the main result of this work, that is, the inclusion of both self-energy and vertex corrections for a 90 Å well width and $T=200$ K. With these parameters, the excitonic peak splitting is clearly seen. In order to come to an understanding of this splitting, the contribution from diagrams that violate Eq. (14) are also considered.

In the next section, the absorption spectra for free electron-hole pair recombination, dressed electron-hole pair recombination, dressed electron-hole bare Coulomb interaction, electron-hole bare Coulomb interaction, electron-hole screened Coulomb interaction, and dressed electron-hole screened Coulomb interaction are separately displayed in Fig. 3. Each one of these cases corresponds to a different diagram plotted in the right side of Fig. 3. Notice that some of them do not satisfy the Ward identity, Eq. (14). In spite of that, their study can contribute to a deeper understanding on the origin of exciton–LO-phonon complexes.

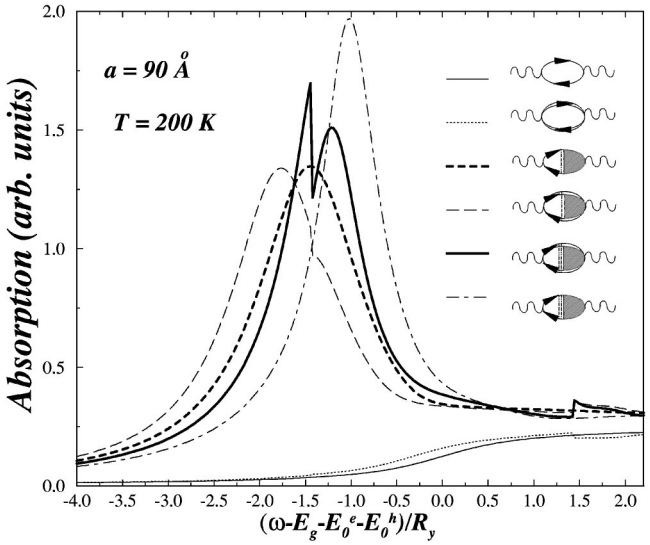


FIG. 3. Absorption spectrum at $T=200$ K for a ZnSe QW of $a=90$ Å. The thin solid line represents the free electron-hole pair absorption. The dotted line is the result of dressing only the free carrier propagators by LO bulk phonons. The thick dashed line represents the exciton absorption without including the vertex and self-energy corrections. The dashed line displays the excitonic absorption including only the self-energy corrections for free carriers. The dot-dashed line represents the excitonic absorption without self-energy carrier effects but including the LO-phonon vertex correction. The thick solid line depicts the absorption spectrum including both self-energy and vertex corrections.

### A. Self-energy contributions

In order to understand the exciton splitting, the self-energy effects are first considered. Clearly two peaks at $-\omega_{LO}$ and $\omega_{LO}$ are seen in the absorption spectra, Fig. 3. These peaks have a strong asymmetric shape due to the singularity of the self-energy. The self-energy at $E=E_p(k) \pm \omega_{LO}$ [Eq. (2)] has a discontinuity in its real part as well as a logarithmic divergence in its imaginary part. It means that the spectral function shows a strong singular character. The line shape of the spectral function might be slightly modified by the inclusion of second-order contributions. It is important to highlight that both the resonant carrier-phonon continuum state and the excitonic peak splitting come essentially from the dressed single-particle properties enhanced by Coulomb interactions.

For comparison, results with and without self-energy effects are also shown in Fig. 3. The thin solid line denotes the case corresponding to the free electron-hole pair recombination; i.e., the exciton effects, self-energies, and vertex corrections are not included. At high energies the absorption spectrum is fully similar to a step joint density of states, as it should be. The dotted line denotes the case where only self-energy effects are included without Coulomb interaction effects. For $T=200$ K both absorption and emission of phonons are allowed. Emission effects of the dressed electron-hole pairs on the absorption spectrum is clearly visible at $\omega_{LO}$ as a shoulder, which will increase when Coulomb effects are added. However, phonon absorption effects are

hardly visible at $-\omega_{LO}$ due to the vanishing optical density of the electron-hole pair in the gap region.

Next, the bare Coulomb interaction as well as carrier-phonon dressed effects on the exciton absorption (thin dashed line) are taken into account. The optical spectrum shows that the exciton peak is redshifted due to the real part of the self-energy correction, $\approx(\alpha_e+\alpha_h)\omega_{LO}/2$, and a new shoulder close to the exciton peak is now visible. It is important to note that both the continuum resonance and this new shoulder are enhanced by the Coulomb electron-hole interaction.

### B. Vertex corrections

In this section the contributions from both the bare Coulomb interaction and vertex corrections to the absorption spectrum are discussed. In Fig. 3 the thick dashed line represents the typical exciton peak with a 3D character ($E_X=-1.43$ Ry). For this case the binding exciton energy is close to $-\omega_{LO}$. Now, if the self-energy is not included but the vertex corrections are (dot-dashed line), the electron-hole interaction is weakened by the phonon screening and consequently the exciton peak moves to the continuum part of the spectrum. Shoulders at $-\omega_{LO}$ and $\omega_{LO}$ disappear, confirming that these features come essentially from self-energy contributions. Therefore, both self-energy and vertex corrections must be taken into account. These corrections are shown as a thick solid line in Fig. 3. The exciton peak is redshifted, and the resonances at $E=\pm\omega_{LO}$ are enhanced by the multiple electron-hole scattering.

The temperature-dependent effective electron-hole potential $V_{eff}^{e\text{-}h}(k,k',\Omega)$, averaged over the polar angle between $\vec{k}$ and $\vec{k}'$, is plotted in Fig. 4 as a function of the magnitude of one wave vector $k'$. Due to the long wavelength of the optical phonons, the effective interaction will be more efficient at small $k$. In order to illustrate this effect $k=0.05a_B$ and a 40-Å well width is considered. Figures 4(a), 4(b), and 4(c), show the effective potential (Ry units) for $\Omega=\omega_{LO}$, $\Omega=0$, and $\Omega=-\omega_{LO}$, respectively. In these figures, the bare effective Coulomb interaction is also plotted for the sake of comparison (thick solid line). The bare Coulomb potential is peaked at $(k=k')$ weighted by the structure factor and a similar singularity is found for arbitrary $\Omega$. In Fig. 4(a) the presence of two singularities below $k=k'$ can be seen. These singularities, coming from the terms in the first square brackets in Eq. (6), reflect the fact that at different from zero temperatures the absorption of real phonons by electron-hole pairs is allowed and must be considered in order to satisfy the Ward identity, Eq. (14). Decreasing the temperature, these singularities disappear but the third term in Eq. (6) still remain, enhancing in this way the continuum resonance state in the spectra. For a static case, Fig. 4(b), only one extra singularity is found. In Fig. 4(c) it can be seen that the effective electron-hole potential is similar to the bare Coulomb interaction with $\epsilon_\infty$ replacing $\epsilon_0$. Clearly, these results reflect the nonlocal character of the effective Coulomb interaction and the importance of the vertex corrections at small $k$ values. Therefore, it is expected that by Fourier transforming $V_{eff}^{e\text{-}h}(k,k',\Omega)$ to real space the local Haken potential should

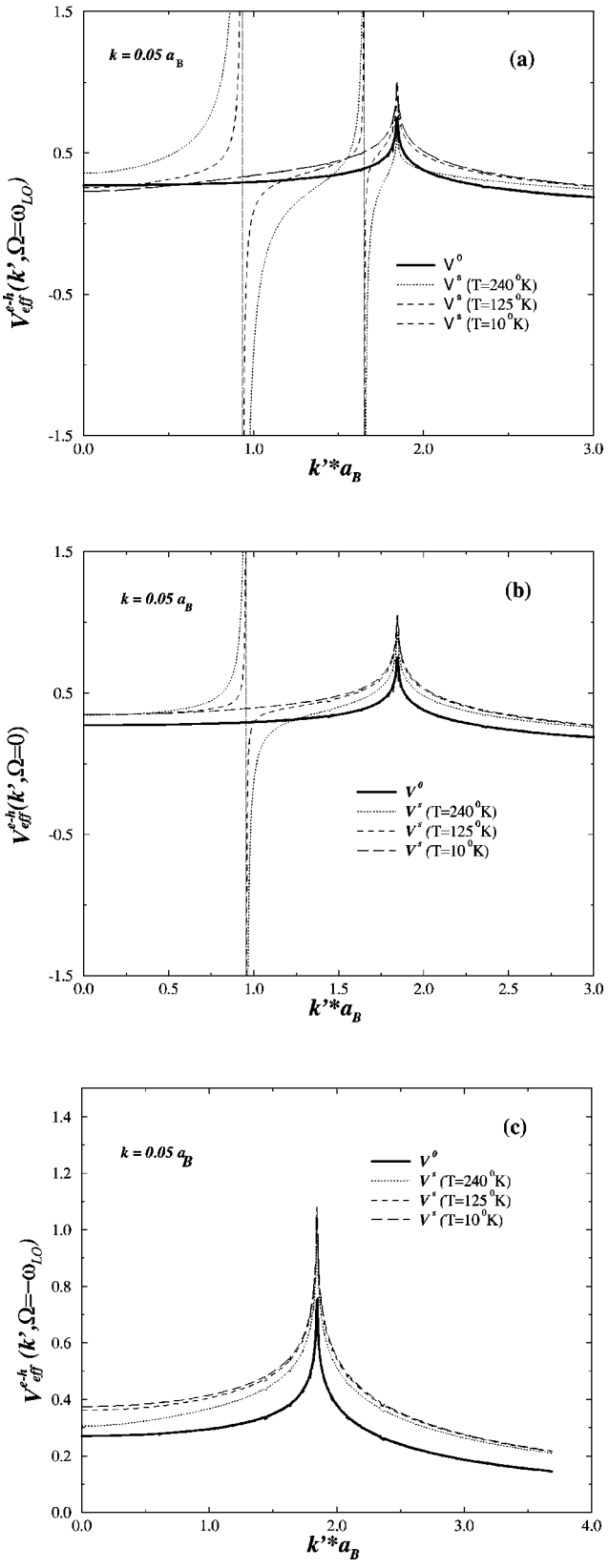


FIG. 4. Effective dynamical nonlocal electron-hole Coulomb potential as a function of $k'$ for different temperatures at (a) $\Omega=\omega_{LO}$, (b) $\Omega=0$, and (c) $\Omega=-\omega_{LO}$ for $k=0.05a_B$ and well width of $a=40$ Å.

be modified.[28] The degree of this nonlocality depends on the energy separation of $\mu^*(E \pm \omega_{LO})^{-1}$, with $\mu$ the exciton reduced mass.

Experimental results in a related QW system (ZnCdSe/ZnSe) present an anomalous plateau in the full width at half maximum[2,3] as a function of the well width. It is tempting to associate this anomalous behavior with the peak splitting predicted in the resonance region. However, this last system is in some sense different from the ZnSe-based QW calculated here, because in that case the QW compound is an alloy and disorder effects must also be taken into account. This same GF formalism was applied to GaAs QW's, but due to the weak polar character of this last material, the main results mentioned above could not be seen, confirming the necessity of a highly polar material to observe them.

### C. Well width and temperature effects

Now the optical spectra for different well widths and temperatures are discussed. By varying the well width the binding exciton energy can be tuned from above the phonon energy to the resonance region. Figure 5 shows the absorption spectrum at $T=80$ K [Fig. 5(a)] and $T=200$ K (Fig. 5(b). By increasing the well width, the intensity of the excitonic peak decreases, due to the weakness of the effective electron-hole Coulomb interaction. However, the splitting of the excitonic peak is still evident. For $a=80$ Å well width the intensities of both peaks are roughly the same. This is a consequence of the fact that vertex corrections and self-energy are treated on an equal footing, even at finite temperature. The self-energy and vertex corrections cause a small redshift respect to the bare exciton peak of the order $\omega_{LO}(\alpha_e+\alpha_h)\pi/2$. For $E_X > \omega_{LO}$ it is expected that self-energy corrections are not very important. This is clear from Fig. 5 for $a=40$ Å where the main contribution comes from the symmetrical exciton peak, while the secondary peak is weaker and it is located on the high-energy side of the main peak. By contrast, for a QW width of $a=80$ Å, a resonant exciton-binding LO-phonon energy crossing occurs [see inset in Fig. 2(b)], the splitting is evident with the two peak positions exchanged (the secondary peak on the low-energy side of the main peak) but their intensities are still similar. This splitting is possible because at this temperature there is an important population of phonons which can be absorbed by the electron-hole pair, which explains why this effect has not been observed at low temperatures. It is worth noting that in both cases and for any well width the continuum resonance is always seen as a consequence that LO-phonon emission is allowed as it has been previously reported.[7]

It is important to stress that this new resonance is different from the well-known phonon replica which corresponds to a peak at $-\omega_{LO}$ below the main exciton peak and it should be only observable at very low temperature. By contrast, the peak splitting predicted here corresponds to a main exciton (symmetric) peak and a secondary peak shifted by $-\omega_{LO}$ with respect to the onset of the continuum part of the spectrum and it should be visible only at high enough temperature. This peak splitting could be observed experimentally in the absorption spectrum of a similar II-VI QW (CdTe) as

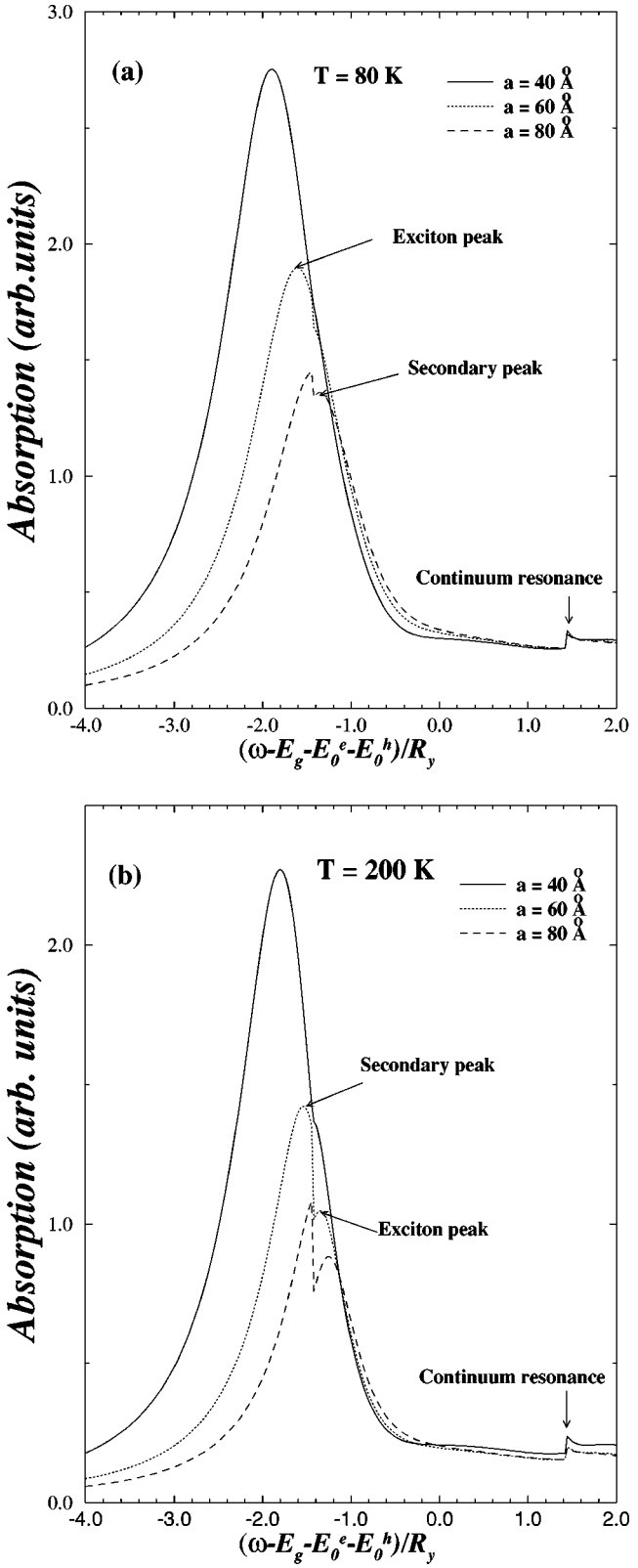


FIG. 5. Absorption spectrum of ZnSe QW's at $T=80$ K (a) and $T=200$ K (b) for different well widths. The arrow in the continuum part shows the exciton-phonon resonance of the spectrum. $E_g$, $E_0^e$, and $E_0^h$ are the band gap and the zero-point energy for electrons and holes, respectively.

ashoulder at room temperature in the resonance region, but no comment was given about it (see Fig. 3 in Ref. 7 and Fig. 1 in Ref. 27. The present results suggest that a splitting of the excitonic peak can be observed if a systematic control of the inhomogeneous broadening is performed. This new peak should be important to understand the relaxation and thermodynamic properties of excitons.[15]

On the other hand, a similar peak splitting has been theoretically predicted by Castella and Wilkens[19] invoking disorder effects in the low-temperature regime. The effective electron-hole interaction for that case corresponds to a static potential yielding to elastic exciton scattering events. By contrast, in the present work, a fully nonlocal and dynamical interaction is responsible for the exciton splitting. Moreover, inelastic exciton scattering effects have been taken into account.

The formalism used in this work can be extended to study the contribution arising from acoustic phonons, both confined and interface LO phonons and finite potential QW effects. Confined phonon effects in II-VI materials should not be very important since the dielectric constants of them are very close to each other and therefore bulk LO-phonon energies are very similar. Hence, the assumption of the bulk LO-phonon energy unaffected by QW width adopted here should be a reasonable approximation.

## V. SUMMARY

In summary, the linear optical exciton absorption of quasi-two-dimensional II-VI systems in the presence of LO phonons has been studied. A Green's function formalism has been developed which takes into account the contribution of both discrete and continuum exciton states, at difference from other works based on the variational formalism. For such systems, it should be emphasized that self-energy effects and vertex corrections must be consistently included on the same footing.

The main result of this work is the prediction of the splitting of the excitonic peak when the following conditions are met: (i) the exciton binding energy is comparable to the LO-phonon energy and (ii) the temperature is different from zero. The observation of a secondary peak, arising from phonon absorption processes, indicates a strong exciton–LO-phonon interaction in II-VI QW's. This splitting is vaguely visible in III-V systems, because the exciton binding energy in QW's is always smaller than the LO-phonon energy and the particle-phonon interaction is weaker than in II-VI systems.[16]

Besides that striking feature, a shoulder in the continuum part of the optical spectrum is obtained within the present theoretical approach. The calculated absorption spectra are in good agreement with both experimental and previous theoretical results. Nevertheless, the secondary peak in the present work is sharper and more asymmetrical as compared with the experimental data. The asymmetrical shape of the secondary peak suggests that LO-phonon processes, beyond first-order contributions, and exciton impurity scattering would partially modify the line shape of this new peak. Unexplained experimental shoulders in previous works on the exciton main peak absorption could be associated with poorly resolved exciton features. Although the present procedure has been developed to treat exciton–LO-phonon complexes, it can also be used to study other effects in low-dimensional semiconductors. In particular, disorder-induced effects on the exciton absorption spectrum could be systematically studied. These studies could lead to a deeper understanding of the linear optical properties of low-dimensional polar systems.

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