Absorption Spectra of Defect-Free Semiconductor Quantum Dots

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Abstract. The presence of accompanying resonances to the longitudinal optical phonon satellites in the optical spectra of semiconductor quantum dots is confirmed theoretically by a non-adiabatic approach of the optical absorption. The theory is applied to simulate features of the optical spectra of spherical quantum dots.

1. Introduction
The optical spectra of polar semiconductor quantum dots (QDs) present several particularities whose understanding is of crucial importance for the technical applications of such nanostructures. Thus, in both emission and absorption spectra longitudinal optical (LO) phonon replicas and accompanying resonances have been observed [1-3]. Also, a red shift with temperature of the 0LO phonon line in the photoluminescence spectra of QDs is reported in experiment [4]. The presence of the strong phonon replicas in the photoluminescence (PL) spectra of QDs of weakly polar III-V compounds is a striking result since no such strong phonon replicas are usually observed in the luminescence of bulk III-V compounds, and not always in the PL spectra of QDs. On the other hand, some theoretical analyses within an adiabatic approach for defect-free QDs fail in calculation of the Huang-Rhys (HR) factors (a measure for the coupling strength of a particular electronic (excitonic) state); the HR factors predicted are smaller from one to four orders of magnitude than by those obtained from experiment [3, 5].

To offer an explanation to the mentioned experimental and theoretical observations, in this paper we consider a non-adiabatic approach of the optical absorption. Non-adiabatic treatments, necessary when the inter-level energy of the electron-hole pair (EHP) induced by irradiation is comparable to the LO phonon energy, have already been proposed [6, 7]. The present work, comparatively to [6, 7] predicts appearance of accompanying resonances in the optical spectra of QDs in addition to the usual LO phonon satellites by an intrinsic mechanism (defect-free QDs in absence of Auger processes and surface optical transitions). Technically, instead of evaluating the lines intensity from the oscillator strength using the eigenstates of the EHP-phonon Hamiltonian with a Fröhlich coupling at temperature $T = 0K$, as in [7], the temperature effect in the absorption spectra is obtained by averaging over the equilibrium phonon states. Completing the work from [8], where only two electronic levels involved in transition are considered, the present treatment is able to take into account several electronic (excitonic) levels.

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The paper is organized as follows. In section 2, a general expression of the linear absorption coefficient is derived by applying a semi-classical theory of the radiation-matter interaction to the EHP-LO phonons system. In section 3, within the effective mass approximation, we describe the energy structure of spherical QDs. The EHP-LO phonon interaction is modelled by Fröhlich interaction and the electron-hole charge separation appears as result of the confinement potentials of the QD heterostructure. The theory is applied to CdSe/ZnS and GaAs/AlAs QDs. In section 4, the EHP-LO phonon coupling matrix elements (CMEs) are calculated, and the absorption coefficient is simulated for spherical CdSe/ZnS and GaAs/AlAs QDs.

2. The Optical Absorption Coefficient

In the non-adiabatic approach the different electronic states are coupled by phonons. For QDs this happens in the medium to weak confinement regime for electronic inter-level energies close to the LO optical phonon energy. The Hamiltonian of the EHP-LO phonon system is described by an extension of the Huang-Rhys model of F centers,

\[ H = \sum_f E_f \mathbf{B}_f \mathbf{B}_f + \sum_q \hbar \omega_q b_q^\dagger b_q + \sum_{q,j,j'} M^{\beta \gamma}_{q,j} b_j^\dagger b_{j'}^\dagger, \]

where the first term is the EHP Hamiltonian, the second term is the LO phonon Hamiltonian, and the third is the EHP-LO phonon interaction Hamiltonian. \( b_j \) (\( b_j^\dagger \)) are creation (annihilation) operators of the EHP, and phonons, respectively, \( E_f \) (\( \{f\} \)) are the EHP eigenvalues (eigenstates), \( M^{\beta \gamma}_{q,j} = \langle f | M_q | \gamma \rangle \) is the CME between the EHP states \( \{f\} \) and \( \{\gamma\} \), \( \omega_q \) is the frequency of the dispersionless LO phonon modes, and \( \mathbf{q} \) is the LO phonon wave vector. The EHPs are considered as bosons (the EHP spin is an integer). This statement, generally valid in the dilute limit of exciton complexes is exact for the case we discuss here, where only one exciton in the QD is considered. On the other hand, in [2] one finds that though the exciton-LO phonon is usually enhanced in QDs, the Fermi Golden Rule is applicable at least for QDs with low relaxation rates. In what follow the optical transition probabilities are computed with the Fermi Golden Rule.

The absorption coefficient for a single QD is given by

\[ \alpha(\omega) = \frac{2n\omega}{nE_0^2v_0} R_{abs} \]

where \( \omega \) is the frequency, \( E_0 \) amplitude of the monochromatic radiation field, \( n \) is the refractive index of the environment, \( V_0 \) is the absorptive volume, and \( R_{abs} \) is the radiation absorption rate. \( R_{abs} \) is given by

\[ R_{abs} = \frac{2\pi}{\hbar} A v \sum_{\zeta,\sigma} |W_{\zeta,\sigma}|^2 \delta(h\omega + E_{\zeta} - E_{\sigma}) \]

The average Av involved by equation (3) means a quantum average over the finite number of the exciton states in the QD and a statistical average over the phonon modes at thermal equilibrium; \( E_{\zeta} \) is the total energy of the system in the ground state \( |\zeta\rangle = |0\rangle |\gamma\rangle \) (\( |\gamma\rangle \) is the phonon state), \( E_{\sigma} \) is the total energy of the system in an exciton+phonons state \( |\sigma\rangle = |f\rangle |\phi\rangle \), and \( W_{\zeta,\sigma} = \langle \zeta | W | \sigma \rangle \) is the transition probability between the initial state \( |\zeta\rangle \) and the final state \( |\sigma\rangle \), with \( W \) the radiation-QD Hamiltonian. Greek characters are used for phonon states, Latin characters for exciton states, and capital handwriting characters for exciton+phonon system. Equation (3) can explicitly be written as follows

\[ R_{abs} = \frac{2\pi}{\hbar} Tr \left\{ \rho \sum_{\zeta,\sigma} |W_{\zeta,\sigma}|^2 \delta(h\omega + E_{\zeta} - E_{\sigma}) \right\} = \frac{2\pi}{\hbar} Tr \left\{ \rho \sum_{\zeta,\sigma} |W_{\zeta,\sigma}|^2 \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} e^{(E_{\zeta} - E_{\sigma})/\hbar} \right\} \]
where $\rho = \sum |v\rangle \rho_v \langle v|$ is the density matrix of the phonons, with $\rho_v = e^{-\beta \omega_v / \sqrt{T}}$ the probability of the phonon state $|v\rangle$ in the equilibrium statistical ensemble of the phonons, $Tr[A] = \sum_v \langle v | A | v \rangle = \sum_v A_v$, and $\langle A \rangle_0 = Tr[\rho A] = \sum_v \rho_v \langle v | A | v \rangle = \sum_v \rho_v A_v$. The closure relation

$$\sum_\mathcal{F} <\mathcal{F}|+\mathcal{G}|\mathcal{G}> = 1 \quad (5)$$

was used in the third equality of equation (4), where $\sum_\mathcal{F} <\mathcal{F}|+\mathcal{G}|\mathcal{G}> = \sum_\mathcal{F} |\mathcal{F}\rangle <\mathcal{F}|0|0\rangle$ that has no effect on the matrix element was inserted. Using the adiabatic picture the state $|\mathcal{F}\rangle$ is written as a product of states, $|\mathcal{F}\rangle = \sum_\mathcal{F} |\mathcal{F}\rangle$, and the significance of the closure relation is more transparent:

$$\sum_\mathcal{F} <\mathcal{F}|+\mathcal{G}|\mathcal{G}> = \sum_\mathcal{F} |\mathcal{F}\rangle <\mathcal{F}|0|0\rangle <\mathcal{F}|\mathcal{F}\rangle = 1 .$$

In equation (4), $\tilde{W}(t) = e^{iH_{\text{ph}} |t\rangle W |0\rangle}$. With equations (2-5) one obtains

$$\alpha(\omega) = \frac{2 \pi e^2}{ncm^2 \omega V_0} \int_{-\infty}^{\infty} dt \text{e}^{it\omega} \sum_{f,j=0}^{\infty} \left| \langle 0 | \tilde{U}(t) | 0 \rangle \right|^2$$

By using the bosonic commutation rules for creation and annihilation of EHP and phonons, and the operator relation $e^{A+B} = e^{A} e^{B / 2} / 2$, one obtains

$$\left<0 | \tilde{U}(t) | 0 \right> = \sum_{f,j=0}^{\infty} \left<0 | B_f e^{iH_{\text{ph}}/h} B^*_j | 0 \right> = \sum_{f,j=0}^{\infty} \left<0 | B_f e^{iH_{\text{ph}}/h} \text{Tr} \left[ e^{iH_{\text{ph}} + H_{\text{EHP}}} / h e^{-iH_{\text{ph}}/h} \right] B^*_j | 0 \right>$$

$$= \sum_{f,j=0}^{\infty} \sum_{f,j=0}^{\infty} e^{-it\omega_j} \left<0 | B_f \langle U(t) \rangle_0 B^*_j | 0 \right>$$

where $\langle U(t) \rangle_0 = Tr[\rho \left[ e^{iH_{\text{ph}}/h} e^{-iH_{\text{ph}}/h} \right] U(t) \rangle_0$ is the statistical average over the phonon system at thermal equilibrium of the time evolution operator, and $H_0 = H_{\text{ph}} + H_{\text{EHP}}$. By expanding the time evolution operator, equation (6) is transformed to the form

$$\alpha(\omega) = \frac{2 \pi e^2}{ncm^2 \omega V_0} \sum_{f,j=0}^{\infty} \int_{-\infty}^{\infty} dt \text{e}^{it\omega} \left[ P_0 P_0 \text{e}^{iH_{\text{ph}}/h} \right] \left<0 | B_f \text{Tr} \left[ \left[ \omega - \omega_j \right] U(t) \right] B^*_j | 0 \right>$$

$$= \frac{2 \pi e^2}{ncm^2 \omega V_0} \sum_{f,j=0}^{\infty} \int_{-\infty}^{\infty} dt \text{e}^{it\omega} \left[ P_0 P_0 \text{e}^{iH_{\text{ph}}/h} \right] \left<0 | B_f \text{Tr} \left[ \left[i \omega_j \right] U(t) \right] B^*_j | 0 \right>$$

(7)

where $\tilde{T}$ is the time-ordered operator, $\tilde{V}(t) = \exp(iH_{\text{ph}}/h) H_{\text{EHP}} - \text{ph} \exp(-iH_{\text{ph}}/h)$, $P_{0f} = \left<0 | e - \omega \cdot \mathbf{P} \right| f \rangle$, and $\mathbf{P} = \sum \mathbf{p}_i$ is the total electronic momentum (with $\mathbf{p}_i$ the electron momentum).
For the linear phononic coupling from equation (7), the cumulant expansion method gives the result that all cumulants higher than the second order vanish. Thus, by using the bosonic commutation rules one obtains

\[
\langle U(t) \rangle_0 = \exp \left[ -\frac{1}{\hbar^2} \sum_{h_i, k_i, s_i, t_i} M^{h_i}_{q} M^{k_i}_{q} \delta B^*_{h_i} B^*_{k_i} B_{t_i} B_{s_i} \right] \\
\times \left[ dt_1 \int dt_2 \exp(it_1 \omega_{h_i}) \exp(it_2 \omega_{k_i}) D^0(t_1 - t_2) \right] = \exp(S)
\]

(8)

where

\[
D^0(t_1 - t_2) = \frac{\overline{N}}{\exp(i\omega_0 |t_1 - t_2|) + (\overline{N} + 1) \exp(-i\omega_0 |t_1 - t_2|)}, \quad \omega_0 = (E_i - E_f)/\hbar, \quad \text{and} \quad \overline{N} = 1/(e^{\beta \omega_0} - 1) \text{ is the phonon occupation number. Using the series expansion of the exponentials in equation (8), we find}
\]

\[
\langle 0|B_f S^n B^{*}_s|0 \rangle = \sum_{i_{k_i}, k_{i_s}, t_{i_2}, t_{i_1}} \left( \sum_{i_k, i_s, t_2, t_1} \sum_{i_k, i_s, t_2, t_1} ... \sum_{i_{k_2}, i_{s_2}, t_{2_2}, t_{1_2}} \right) \text{(cutting)} \left[ \sum_i \left( \alpha_i^{f s} \right) \right]^n
\]

(9)

where

\[
\sum_q \delta^{(i_k, i_s, t_2, t_1)} = \sum_q \left[ M^{k_k}_{q} M^{k_2}_{q} \int_0^t dt \int_0^{\hbar} \exp(it \omega_{k_k}) \exp(it \omega_{k_2}) D^0(t_1 - t_2) \right] = \sum_q \left[ M^{k_k}_{q} M^{k_2}_{q} I(t, k, k', k', p') \right].
\]

A partial resummation (PR) of \( \langle 0|B_f S^n B^{*}_s|0 \rangle \) is obtained by the “cutting” procedure suggested in equation (9). We use the notations \( g_{pppp} = g_p \) is the HR factor and \( G_{pis} = g_{pis} \alpha_p^2 I(t, s, i, s, i) \). The PR yields

\[
\alpha(\omega) = \frac{2 \pi e^2}{n cm^2 \hbar \omega} \sum_{q, s_0, p_0, s_0} P_{0, s_0}^{q, p_0} \delta(\omega - \omega_{p_0}) \exp(-\sum_{i=0} G_{pis})
\]

(10)

Comparatively to the presented in [6], the CMEs do not have to respect the restriction, \( \max\left|M_{q, p}^{pp} \right| \ll 1 \), which may be difficult to fulfill for large \( g_{pppp} \), as long as few LO phononic modes are strongly coupled with the EHPs (see, e.g., [8]). If the off-diagonal coupling terms in equation (1) are disregarded then equation (8) is exact and it recovers the adiabatic limit (the Franck-Condon progression):

\[
\alpha^{ad}(\omega) = \frac{4 \pi e^2}{n cm^2 \hbar \omega} \sum_{q, f_0} \left[ P_{0, f_0}^{q} \right]^2 \exp[-g_f(2\overline{N} + 1)]
\]

\[
\times \sum_{n=0}^{\infty} \int_{n=0}^{\infty} I_n(2g_f \sqrt{N(\overline{N} + 1)}) \exp(n\hbar \omega_{f_0}/2) \delta(\omega - \omega_f + \Delta^{ad}_f - n\omega_0)
\]

(11)

where \( I_n \) are the modified Bessel functions, and \( \Delta^{ad}_f = \omega_0 \sum_q \left( M^{q}_{q} \right)^2 \hbar^2 \omega_0^2 \) is the self-energy. The relative intensity of the absorption lines is given by the coefficients of the Dirac delta functions.

3. Spherical Quantum Dot Model

We consider a spherical QD in the case of size-quantized energies of QD (or equivalently, QD with dimensions smaller than its corresponding exciton Bohr radius so that the exciton effect, Coulombic interaction is neglected) [10]. For spherical QDs the one-band model by which conduction and valence states are computed from single-particle Schrödinger equations in the effective mass approximation is a good approximation for type I heterostructures [11], and we situate our analysis within such an approach.
In order to describe the energy structure, we consider the confinement potential energy \( V_c(r_c) = 0 \) for \( r_c \in [0, R_c] \), and \( V_c(r_c) = V_{oc} \) for \( r_c > R_c \) (similar equation is written for holes by replacing \( r_c \) by \( r_h \)); \( R_0 \) is the QD radius. The single-particle wave function is written as the product \( \psi_{nlm}(r) = R_{nl}(r)Y_{lm}(\theta, \phi) \), where \( R_{nl}(r) \) is the radial function and \( Y_{lm}(\theta, \phi) \) is the spherical harmonics function. By using the second quantization language, and disregarding the spin dependence, the EHP state may be written as \( |f\rangle \rightarrow |\psi_{nlm}\rangle = \int dr_r dr_r \phi_{rlm}(r_c, r_h) a^+_r a^+_h |0\rangle \), where \( a^+_r (a^+_h) \) are the creation (annihilation) fermionic operator of an electron in the conduction band at \( r_c \) (valence band at \( r_h \)) and \( a (b) \) holds for the set of quantum numbers \( n, l, m, n_h, l_h, m_h \) of electrons (holes). The model takes into account the difference in the effective masses between the nano-sphere and its surrounding and considers finite confinement potentials for both electrons and holes. These factors cause a non-vanishing EHP-LO phonon interaction. Following \([12, 13]\), the expression of orthonormalized \( R_{nl}(r) \) and the secular equation of energy are as follows

\[
R_{nl}(r) = \frac{2}{R_0} \left[ j_l^2(x) k_{l+1}(y) - k_l^2(y) j_{l+1}(x) \right] \begin{cases} k_l(y) j_l(x/r_0), & r < R_0 \\ j_l(y) k_l(x/r_0), & r > R_0 \end{cases}
\]

(12)

\[
\mu_2 x_d k_l(y) = \mu_2 x_d y_l(x) k_l(y)
\]

(13)

where \( x = R_0 \sqrt{2(\mu_c E_{nl})/\hbar^2} \), \( y = R_0 \sqrt{2(\mu_v V_{oc} - E_{nl})/\hbar^2} \), \( k_l \) the modified spherical Bessel functions, \( \mu_c, \mu_v \) the effective mass in the dot (surrounding medium), \( V_{oc} \) the band offset of the carriers (c becomes e for electron or h for hole), and \( n, l \rightarrow n_c, l_c \) or \( n_h, l_h \) for electron and hole, respectively.

The optically active EHPs are obtained with the optical selection rules which dictate the allowed transitions. In the linear response theory and long wave approximation the particle-radiation interaction Hamiltonian for a carrier of charge \( Q \) and mass \( M \) reads

\[
H_{Q,R} = -Q(Mc)^{-1} A \cdot P,
\]

(14)

where \( c \) is the speed of light, \( A \) is the vector potential, and \( P \) is the carrier momentum. With Maxwell’s equation \( E = -c^{-1} \partial A/\partial t \), within Coulomb gauge, and with the space-independent electric field \( E = eE_0 \cos \omega t \) (monochromatic field of frequency \( \omega \), amplitude \( E_0 \), and direction of oscillation along the unit polarization vector \( \epsilon \)), the corresponding vector potential reads \( A = -eA_0 \sin \omega t = -eE_0 \epsilon \cos^2 \omega t \). Translated to the EHP problem the momentum operator reads

\[
P = \sum_f \sum_{j0} \langle 0|f|f\rangle P_j f_j + \langle f|f|0\rangle B_j + \langle f|P|0\rangle B_j^\dagger
\]

(15)

where \( |0\rangle \) stands for the EHP vacuum state, and \( P = \sum P_j \) the total electronic momentum (with \( P_j \) the electron momentum). With equations (14, 15) the semi-classical EHP-radiation interaction reads

\[
H_{EHP,R} = -eE_0 (m_0 \omega)^2 \epsilon \cdot \sum_{f, \epsilon} \left( \langle 0|P|f\rangle B_{f j} + h.c.\right) \sin \omega t = W \sin \omega t
\]

(16)

With the EHP eigenstates and the appropriate definition of the momentum [14], \( P = p_{v0}^0 \int dR \epsilon_r a^+_r a^+_h + h.c. \), where \( p_{v0}^0 \) is the momentum matrix element between the valence-band and the conduction-band at the \( \Gamma \) point and \( R \) integrates over unit cells, one obtains the optical matrix element

\[
\langle \psi_{nlm}|P|0\rangle = p_{v0}^0 \delta_{l_d} \delta_{m_r} \int d^2r_r R_{nl}(r) R_{nh}(r) \equiv p_{v0}^0 \delta_{m_r} A_{n, r l_c},
\]

(17)

with \( l_c = l_h = l \). Thus, according to the optical selection rules \( l_c = l_h \) for an optically active state.
Next, we apply the model to concrete heterostructures. First, we consider CdSe microcrystallites embedded in a ZnS matrix (II-VI heterostructures) and simulate the energy structure within an adiabatic approach. The necessary material parameters found in the literature are as follows: bulk CdSe energy gap $E_g = 1.8$ eV, CdSe (ZnS) electron effective mass $\mu_e/m_0 = 0.13$ ( $\mu_e/m_0 = 0.34$), hole effective mass $\mu_h/m_0 = 0.45$ ( $\mu_h/m_0 = 0.23$), conduction band offset $V_{0c} = 1.2$ eV, and the valence band offset $V_{0v} = 0.5$ eV; $m_0$ is the electron mass. The energy spectrum is obtained from equations (12, 13), and the EHP energy $E_{n,l_s,l_m} = E_g + E_{n,l_s} + E_{s,l_m}$ is computed as a function of the QD radius. To obtain values of the absorption lines as reported by experiment [15] (see next section), we increased the bulk CdSe energy gap by 0.43eV. This is in accordance with the mismatch strain effect which increases the energy gap in QD, comparatively to bulk. In figure 1 are shown the first several energy levels that are interesting for the analysis. Some particular levels are labelled by the set of quantum numbers, $(n_e,l_s,m_h;l_m,h_m)$ as follows: A$_0$ $\rightarrow$ (1,0,0;1,0,0) - dark level, B $\rightarrow$ (1,0,0;1,1,0) - dark level, C $\rightarrow$ (1,0,12,0) - dark level, D$_0$ $\rightarrow$ (1,0,2,0,0). According to the energy levels distribution from figure 1, at $R_0 = 20$ Å the phonon coupling is highly improbable at least at low temperatures: $\left|E_B - E_{A_0}\right|/\hbar\omega_0 \approx 5.9$ (CdSe bulk LO phonon energy is $\hbar\omega_0 = 27.3$meV), and the optical spectra are properly discussed in an adiabatic framework.

For GaAs microcrystallites embedded in AlAs matrix (III-V heterostructures), we use the material parameters from [16]: GaAs energy gap $E_g = 1.5177$ eV, GaAs (AlAs) electron effective mass $\mu_e/m_0 = 0.0665$ ( $\mu_e/m_0 = 0.124$), hole effective mass $\mu_h/m_0 = 0.45$ ( $\mu_h/m_0 = 0.5$), conduction band offset $V_{0c} = 0.968$ eV, and the valence band offset $V_{0v} = 0.6543$ eV. GaAs/AlAs is a nearly lattice-matched heterostructure, and the weak strain effect makes the bulk GaAs energy gap to be used in calculation. The energy spectrum obtained from equations (12, 13) is shown in figure 2. Some particular levels are labelled by the set of quantum numbers, $(n_e,l_s,m_h;l_m,h_m)$ as follows: A$_0$ $\rightarrow$ (1,0,0;1,0,0), B $\rightarrow$ (1,0,0;1,1,0) - dark level, C $\rightarrow$ (1,0,0;1,1,0) - dark level, D$_0$ $\rightarrow$ (1,0,2,0,0), E $\rightarrow$ (1,0,1,0,0) - dark level, F $\rightarrow$ (1,0,2,1,0) - dark level, G$_0$ $\rightarrow$ (1,1,0;1,1,0). For B, for...
example, one considers \( m_a = 0 \), the only value for which CME does not vanish. Based on the distribution of energy levels and taking into account the exciton Bohr radius (larger than 100Å), we consider \( R_0 = 50 \) Å as a reasonable upper-limit for neglecting the Coulombic interaction. On the other hand, possible phonon mixing effect could manifest starting with \( R_0 \approx 23 \) Å (see the ellipse mark at figure 2), between the optically active level \( G_0 \) and the dark level \( F \). But, the phonon-assisted transition between \( G_0 \) and \( D_0 \) is improbable (at least in the low temperature limit) since \((E_E - E_{D_0})/\hbar \omega_0 = 3.37 \) \( \text{GaAs LO phonon energy is } \hbar \omega_0 = 36.2 \text{meV} \). For the first two optically active levels, the adiabatic treatment is safe for \( R_0 < 22 \) Å and may be accepted as satisfactory for \( R_0 < 32 \) Å, beyond which the optically active level \( C \) appears.

The quantity \( P_{0f}P_{f0} = \left| \sum_{m_{b}, m_{a}} \hat{A}_{m_{b}m_{a}}(\omega) \delta_{m_{b}m_{a}} \right|^2 \) in equation (7) is obtained by averaging over all space polarization directions. The Fröhlich coupling is written for dispersionless bulk LO phonons (for a spherical QD the interface modes are weak and do not couple with the exciton states, see [17]).

Within the pure-EHP approximation the EHP-phonon interaction reads [18, 19]

\[
M''_{q} \rightarrow M''_{q}^{ab\alpha\beta} = V_{0}^{-1/2} f_{0} q^{-1} \int d\mathbf{r}_{a} d\mathbf{r}_{b} \varphi_{a}^{*}(\mathbf{r}_{a}) \varphi_{\beta}(\mathbf{r}_{b}) \varphi_{\alpha}(\mathbf{r}_{a}) \varphi_{b}(\mathbf{r}_{b}) \left[ \exp(i\mathbf{q}\mathbf{r}_{a}) - \exp(i\mathbf{q}\mathbf{r}_{b}) \right]
\]

for which spherical QDs becomes

\[
M''_{q} \rightarrow M''_{q}^{ab\alpha\beta} = V_{0}^{-1/2} f_{0} q^{-1} \times \left[ \left| \mathbf{R}_{n_{a}/l_{a}}(r) \right| \mathbf{R}_{n_{b}/l_{b}}(r) Q_{l_{a}l_{b}}^{m_{b}}(q,r) - \left| \mathbf{R}_{n_{b}/l_{b}}(r) \right| \mathbf{R}_{n_{a}/l_{a}}(r) Q_{l_{b}l_{a}}^{m_{a}}(q,r) \right]
\]

where

\[
Q_{l_{a}l_{b}}^{m_{a}}(q,r) = \int d\Omega Y_{l_{a}}^{*}(\Omega) Y_{l_{b}}(\Omega) \exp(iqr)
\]

\[
= \sqrt{\frac{2l_{a}+1}{2l_{a}+1}} \delta_{m_{a}m_{b}} \sum_{l_{f}+l_{f}+l_{f}+l_{f}+l_{f}} \int_{\frac{l_{f}}{2}}^{\frac{l_{f}}{2}} \int_{\frac{l_{f}}{2}}^{\frac{l_{f}}{2}} \int_{\frac{l_{f}}{2}}^{\frac{l_{f}}{2}} \int_{\frac{l_{f}}{2}}^{\frac{l_{f}}{2}} \int_{\frac{l_{f}}{2}}^{\frac{l_{f}}{2}} \left| j_{l_{f}}(q\mathbf{r}) \right|^2 \left( \mathbf{r}_{a}, \mathbf{r}_{b} \right)
\]

with \( j_{l}(x) \) the spherical Bessel functions, \( \left| l_{f}l_{f}l_{f}l_{f}l_{f}l_{f} \right| \) the Clebsh-Gordan coefficients, and \( f_{0} = \sqrt{2\pi \hbar \omega_{0}^{2}(\epsilon_{\omega} - \epsilon_{0})} \) the Fröhlich coupling constant. Equation (20) is obtained by using the expansion of plane waves, \( \exp(i\mathbf{q}\mathbf{r}) = \sum_{l=0}^{\infty} l! 4\pi(2l+1) j_{l}(q\mathbf{r}) Y_{0l}(\Omega) \), and the integration of three spherical harmonics over the solid angle. Inspection of equation (19) shows the states \( \varphi_{a\beta}, \varphi_{a\beta} \) are not coupled by phonons if both \( a \neq a' \) and \( b \neq b' \).

3. Application

With the theory developed in section 2, we simulate the absorption coefficient for the semiconductor heterostructures introduced in section 3. First, we consider CdSe/ZnS QD, and evaluate the absorption coefficient for a QD radius \( R = 20 \) Å, case which is appropriate for an adiabatic approach. For the ground EHP state we obtain \( g = 0.094 \), a value close of the value reported in [19], namely 0.07 for a radius of 2nm. In figure 3, we show the absorption coefficient with the typical LO resonances obtained in the optical spectra. The spectrum which is generated by the ground EHP state is obtained with equation (11). The OLO phonon line is in accordance with [15]; for \( R_0 = 23 \) Å the model generates a value of 2.69eV approximately equal to the value of ZnS overcoated CdSe QD of the same radius. One can see the effect of
temperature is of increasing intensity of LO resonances and decreasing intensity of the 0LO line. The right phonon satellites in figure 2 are more intense for higher temperature, where LO phonon population is higher, and consequently probability of LO phonon absorption is increased.

Second, we consider GaAs/AlAs QD, and evaluate the absorption coefficient in more detail. The large values of \[
\sum \int dt \exp[i(\omega - \omega_0)t]
\]
for such nanostructures less polar than CdSe, e.g., are the result of charge separation induced by the finite confinement potential.

For the only two optical levels which appear at \[\omega_0 = R_0\] (see figure 2), with an inter-level energy of approximately \[h\omega_0 \approx 36.2 \text{meV}\], the absorption coefficient from equation (7) reads

\[
\alpha(\omega) = \frac{2\pi e^2}{3ncm^2h \omega_0} \sum \int dt \exp[i(\omega - \omega_0)t]
\times \left[ A_{\omega_0}^{2}\sum \int \left( i \left(U(t)\right)_{0}\right) + A_{\omega_1}^{1}\sum \int \left(U(t)\right)_{0}\right] f
\]

The first term in the integrand of equation (21) can be approximated by using the PR procedure, and the contribution to the absorption coefficient is evaluated by equation (10). The second term of the integrand, responsible for the phonon mixing of different optically active states can be neglected [20]. Thus, equation (21) written for the lines centered on the line \(A_0\) reads

\[
\alpha(\omega) = \frac{2\pi e^2}{3ncm^2h \omega_0} A_{\omega_0}^{2}\sum \int \left( \exp\left(-\Lambda_0\right) \sum \int \left(2g_{21}\sqrt{N(N+1)}\right) \times \frac{N_{g_{2121}}\beta^2}{k!} \left((N+1)g_{1212}\gamma^2\right) \exp\left(-p\hbar\omega_0\right) \frac{2k_BT}{2k_BT} \right) \]

where \[\Lambda_0 = g_1(2(N+1) + g_{1212}(N\beta^2 + (N+1)\gamma^2))\] is the self-energy, \[\beta = \omega_0/(\omega_{21} - \omega_0)\] and \[\gamma = \omega_0/(\omega_{21} + \omega_0)\]. Within the QD model we work with one obtains \[g_1 = 0.117, \quad g_{1212} = 0.314\]. The non-adiabatic corrections are, as expected from the large inter-level
energy, not significant and the non-adiabatic spectrum plotted with equation (22) is practically identical with the adiabatic spectrum obtained with equation (11). The spectra, not plotted here show the ordinary phonon satellites.

Situation is different for $R_0 = 32$ Å, where the the dark level $B$ is located between two optical levels $A_0$ and $D_0$ (see figure 2). The effect of the dark level $B$ is roughly estimated by considering the PR procedure shown in equation (9). Thus, the contribution of the optical and dark levels to the absorption centered on line $A_0$ is described by an equation similar to equation (22), but written to account for the dark level too (see details in [20]). The non-adiabaticity effect is shown in figure 4, where the absorption spectrum at different temperatures is plotted (we dressed the lines by Lorentzians with a finite width of 15 meV to simulate the EHP-acoustic phonons interaction). The adiabatic spectrum obtained with equation (11) has no temperature-induced shift and its maxima are not significantly changed with temperature. The following quantities obtained within the adopted QD model have been used: $E_1 = 1.8822$ eV, $E_2 = 2.0738$ eV, $E_3 = 1.9496$ eV, $g_1 = 0.039$, $g_{1221} = 0.234$, and $g_{1331} = 0.904$. The stronger accompanying resonances are marked by arrows. The energy of some resonances are indicated by factors which multiply the LO phonon energy; they are placed to the left of the lines or arrows. The temperature dependence of the spectra, weak in the case of adiabatic treatment, becomes important now. Thus, decrease of intensity (by 37%) and red shift (from 1.87 eV to 1.85 eV) of the 0PL lines are obtained when temperature increases from 10K to 300K. This agrees with the behavior observed experimentally for CdTe QDs [21]. On the other hand, the simulated HR factors reach values larger by two orders of magnitude than those of the bulk phase (0.0079 in [19]). A similar behavior is reported for small self-assembled InAs/GaAs QDs in [22]. Thus, by the non-adiabatic activated channel at +0.86 LO, the predicted HR factor obtained as the ratio of the line intensities for this accompanying resonance increases from 0.084 at $T = 10K$ to 0.23 at $T = 200K$. On the other hand, the non-adiabatic effect manifests by strong resonances at 2.9 LO (see figure 4), close to the third LO phonon replica as reported by some experiments (see, e.g., [2]). The usual Franck-Condon progression is obtained by the adiabatic treatment (see the gray line in figure 4).

Concluding, the non-adiabatic treatment presented, in accordance with the experimental observation, predicts: (i) accompanying resonances to the LO phonon satellites in the optical spectra of QDs; (ii) a red shift of the 0LO phonon lines and increased intensities of the accompanying resonances with temperature in the absorption spectra of QDs.

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References
[1] See, e.g., Sarkar D, van der Meulen H P, Calleja J M, Becker J M, Haug R J, and Pierz K 2005 Phys. Rev. B 71 081302(R)

[2] Heitz R, Veit M, Ledentsov N N, Hoffmann A, Bimberg D, Ustinov V M, Kop’ev P S, and Alferov Zh I 1997 Phys. Rev. B 56 435

[3] Bissiri M, Baldassarri Höger von Högersthal G, Bhatti A S, Capizzi M, Frova A, Frigeri P, and Franchi S 2000 Phys. Rev. B 62 4642

[4] Besombes L, Kheng K, Marsal L, and Mariette H 2001 Phys. Rev B 63 155307

[5] Krauss T D and Wise F W 1997 Phys. Rev. B 55 9860

[6] Fomin V M, V. N. Gladilin V N, Devreeese J T, Pokatilov E P, Balaban S N, and Klimin S N 1998 Phys. Rev. B 57 2415

[7] Verzelen O, Ferreira R, and Bastard G 2002 Phys. Rev. Lett. 88 146803

[8] Vasilevskiy M I, Anda E V, and Makle S S 2004 Phys. Rev. B 70 035318
[9] Mittin V V, Kochelap V A, Stroscio M A 1999 Quantum Heterostructures. Microelectronics and Optoelectronics (Cambridge: University Press)

[10] Hanamura E 1988 Phys. Rev. B 37 1273

[11] Sercel P C and Vahala K J 1990 Phys. Rev. B 42 3690

[12] Vahala K J 1988 IEEE J. Quantum Electron. 24 523

[13] Chamberlain M P, Trallero-Giner C and Cardona M 1995 Phys. Rev. B 51 1680

[14] Takagahara T 1993 Phys. Rev. B 47 4569

[15] Dabbousi B O, Rodriguez-Viejo J, Mikulec F V, Heine J R, Mattoussi H, Obe r R, Jensen K F, and Bawendi M G 1997 J. Phys. Chem. B 101 9463

[16] Menéndez E, Trallero-Giner C and Cardona M 1997 Phys. Status Solidi (b) 199 81

[17] Melnikov D V and Fowler W B 2002 Phys. Rev. B 64 245320

[18] Voigt J, Spielgelberg F, and Senoner M 1979 Phys. Status Solidi (b) 91 189

[19] Nomura S and Kobayashi T 1992 Phys. Rev. B 45 1305

[20] Cheche T O and Chang M C 2005 Chem. Phys Lett. 406 479

[21] Besombes L, Kheng K, Marsal L, and Mariette H 2001 Phys. Rev B 63 155307

[22] García-Cristóbal A, Minnaert W E, Fomin V M, Devreese J T, Silov A Yu, Haverkort J E M, and Wolter J H 1999 Phys. Status Solidi (b) 215 331