Electron–phonon interaction in CdS/ZnS quantum dot

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Abstract

Electron–phonon effects on the two first electronic states in both CdS and GaAs quantum dots are investigated. Both confined longitudinal optical (LO) and surface optical (SO) phonons are considered. We use the intermediate-type variational approach. We find that, shifts caused by phonon contribution on electronic energies are more significant for CdS quantum dot. We find, also, that, contrary to GaAs based quantum dots, we shouldn’t neglect the SO phonon contribution for CdS based ones, especially for small dots.

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During the last few years II–VI semiconductor heterostructures have been developed by novel growth and fabrication technologies. These semiconductor heterostructures are considered as promising candidates for device applications due to e.g. the significant polar contribution to the crystal bonds. Due to e.g. its influences on optical properties, electron–phonon interaction presents one of the particularly interesting researches in nanostructures, in general, and, in particular, in II–VI based nanostructures. A number of authors [1–6] have studied this problem. Most of them deal with III–V semiconductor...
based quantum dots such as GaAs. In such semiconductors they found that SO phonons
don’t affect the carrier levels.

In this work, we propose, an analytic study of the electronic energy shifts caused by
electron–phonon interaction in II–VI quantum dots. CdS is the chosen semiconductor
based quantum dot. Both LO and SO phonons are considered. The shape of the dot is
modelled by a cylinder lying on a wetting layer with a thickness of \( d \). \( 2h \) and \( R \) are
the height and the radius of the cylinder respectively (Fig. 1). The approach is based
on the intermediate-type variational method [7,8]. We will show that electron–phonon
interaction is more significant for II–VI than for III–V quantum dots and, contrary to
III–V semiconductor quantum dots, we shouldn’t neglect the structural imperfections
of the interface between the dot and the bulk which it surrounds, i.e. the phonons of the
surface, specially for small dots.

Within the effective-mass approximation, the polaron Hamiltonian can be written:

\[
H = H_e + H_{ph} + H_{e-ph}.
\]

The first two terms describe the electron and the phonon parts seen as independent
elements.

\[
H_e = \frac{p^2}{2m} + V_{\text{conf}}
\]  

(2-a)

where \( V_{\text{conf}} \) is the confinement potential for the electron. It is zero inside the dot and
\( V_e = 897 \) meV outside. \( m = 0.21m_o \) [9] is the effective mass and \( m_o \) is the free electron
mass.

Following previous work of Li and Chen [10], we specify, in addition to longitudinal
optical phonons (LO phonons), two types of surface optical phonons: the top surface
optical phonons (TSO) and the side surface optical ones (SSO).

\[
H_{ph} = H_{LO} + H_{SSO} + H_{TSO}
\]

(2-b)

with:

\[
H_{LO} = \sum_{m,l} \hbar \omega_{LO} a_m^+ a_m
\]

(2-b-1)
For phonons of the cylinder. The wetting layer is considered as a cylinder with infinite radius $R_L$ ($R_L \rightarrow +\infty$). In this case, we have:

\[ H_{e-LO}^L = - \sum_{m=1,2,\ldots} J_0 \left( \frac{\chi_m}{R_L} \right) \left[ \sum_{l=1,3,\ldots} V_{ml}^L \cos \left( \frac{l\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) \right] (a_{ml} + a_{ml}^+) \]

\[ + \sum_{l=2,4,\ldots} V_{ml}^L \sin \left( \frac{l\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) (a_{ml} + a_{ml}^+) \]  

\[ H_{e-SSO}^L = - \sum_{m=2,4,\ldots} \Gamma_m I_0 \left( \frac{m\pi}{2\hbar} \rho \right) \cos \left( \frac{m\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) (b_m + b_m^+) \]

\[ - \sum_{m=2,4,\ldots} \Gamma_m I_0 \left( \frac{m\pi}{2\hbar} \rho \right) \sin \left( \frac{m\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) (b_m + b_m^+) \]  

\[ H_{e-TSO}^L = - \sum_{m^+} V_{ml}^{cyl} J_0(q_{+m}\rho)ch(q_{+m}\zeta)(B_{m^+} + B_{m^+}) \]

\[ - \sum_{m^-} V_{ml}^{cyl} J_0(q_{-m}\rho)sh(q_{-m}\zeta)(B_{m^-} + B_{m^-}) \]  

for phonons of the cylinder. The wetting layer is considered as a cylinder with infinite radius $R_L$ ($R_L \rightarrow +\infty$). In this case, we have:

\[ H_{SSO} = \sum_m \hbar \omega_{SS} b_m^+ b_m \]

\[ H_{TSO} = \sum_m \hbar \omega_{TSO} B_m^+ B_m^\dagger \]  

$a_{ml}^+(a_{ml}), b_m^+(b_m), B_m^+ (B_m^\dagger)$ denote the creation and annihilation operator of LO, SSO and TSO phonons with frequency $\omega_{LO}, \omega_{SS}, \omega_{TS}$ of the $(m, l)$th, $m$th and $(m^\dagger)$th mode respectively. The last term in Eq. (1) describes the coupling between electron and phonons. In quantum dots, not only carriers but also phonons receive the confinement effect and the carrier–phonon interaction has its own character, being different from the bulk. These electron–phonon couplings can be expressed as:

\[ H_{e-LO}^{\text{cyl}} = - \sum_{m=1,2,\ldots} J_0 \left( \frac{\chi_m}{R} \right) \left[ \sum_{l=1,3,\ldots} V_{ml}^{\text{cyl}} \cos \left( \frac{l\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) \right] (a_{ml} + a_{ml}^+) \]

\[ + \sum_{l=2,4,\ldots} V_{ml}^{\text{cyl}} \sin \left( \frac{l\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) (a_{ml} + a_{ml}^+) \]  

\[ H_{e-SSO}^{\text{cyl}} = - \sum_{m=2,4,\ldots} \Gamma_m I_0 \left( \frac{m\pi}{2\hbar} \rho \right) \cos \left( \frac{m\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) (b_m + b_m^+) \]

\[ - \sum_{m=2,4,\ldots} \Gamma_m I_0 \left( \frac{m\pi}{2\hbar} \rho \right) \sin \left( \frac{m\pi}{2\hbar} (\zeta + h + \frac{d}{2}) \right) (b_m + b_m^+) \]  

\[ H_{e-TSO}^{\text{cyl}} = - \sum_{m^+} V_{ml}^{\text{cyl}} J_0(q_{+m}\rho)ch(q_{+m}\zeta)(B_{m^+} + B_{m^+}) \]

\[ - \sum_{m^-} V_{ml}^{\text{cyl}} J_0(q_{-m}\rho)sh(q_{-m}\zeta)(B_{m^-} + B_{m^-}) \]  

with:

\[ [V_{ml}^{\text{cyl}} L]_2 = \frac{1}{V_i} \left[ \left( \frac{2\hbar}{\hbar} \right)^2 J_2^2 (\chi_m) + \left( \frac{2\hbar}{\hbar} \right)^2 J_1^2 (\chi_m) \right] \times \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) \]  

(2-c-6)
The wave function of the system is described by the coherent state:

\[ |\psi\rangle = \sum_{n} a_{n}^{+} a_{n} |n\rangle \]

where \( a_{n}^{+} \) and \( a_{n} \) are the creation and annihilation operators, respectively. The number of wave vectors \( q_{i} \) is the mth solution of

\[ (1 + e^{-2q_{i}^{2}}) J_{1}(q R_{i}) + \frac{1 - e^{-2q_{i}^{2}}}{J_{1}(q R_{i}) + N_{1}(q R_{i})} = 0 \] (2-c-10)

and \( q'_{i} \) is the nth solution of:

\[ (1 + e^{-2q'_{i}^{2}}) J_{1}(q R_{i}) + \frac{1 + e^{-2q'_{i}^{2}}}{J_{1}(q R_{i}) + N_{1}(q R_{i})} = 0. \] (2-c-11)

The number of wave vectors \( q_{i} \) is limited by the Brillouin zone, i.e. \( q_{i} \leq \pi / 2a \), where \( a \) is the lattice constant of the crystal. \( V_{i}, \Omega_{i}, J_{1} \) and \( R_{i} \) are the volume, the thickness, the cross-sectional (perpendicular to z) area and the radius of the cylinder and the layer respectively. \( \varepsilon_{0} \) and \( \varepsilon_{\infty} \) are the static and optical dielectric constants, respectively. \( \varepsilon_{\omega_{+}} = -\text{cht}(q_{+}, m) \) and \( \varepsilon_{\omega_{-}} = -\text{th}(q_{-}, m) \). \( J_{m}, I_{m} \) and \( N_{m} \) are the mth-order Bessel and modified Bessel functions of the first and second kind, respectively. \( \chi_{m} \) is the mth-root of \( J_{0}(k m) \) with \( m = 2, 4, \ldots \).

To solve such a Hamiltonian, we use the intermediate-coupling-type method. The trial wave function of the system is described by the coherent state:

\[ |\Theta_{n}\rangle = \Psi_{n}(\rho, z)U_{LO}U_{SS}U_{TS}|0\rangle \] (3)

|0\rangle is the phonon vacuum state. And the unitary operators \( U_{LO}, U_{SS} \) and \( U_{+} \) are given by

\[ U_{LO} = \exp \left( \sum_{m,l} (a_{m,l}^{+} f_{m,l}^{+} + a_{m,l} f_{m,l}) \right) \] (3-a)

\[ U_{SS} = \exp \left( \sum_{m} (b_{m}^{+} g_{m}^{+} + b_{m} g_{m}) \right) \] (3-b)

\[ U_{TS} = \exp \left( \sum_{m} (B_{m}^{+} G_{m}^{+} + B_{m} G_{m}) \right) \] (3-c)

\( f_{m,l}, g_{m} \) and \( G_{m} \) are variational functions which can be obtained by minimizing the \( \langle \psi | H | \psi \rangle \) with respect to \( f_{m,l}^{+}, g_{m}^{+} \) and \( G_{m}^{+} \). Then the expectation value of \( E = \langle \psi | H | \psi \rangle \)
turns out to be:

\[ E_n = \langle \Psi_n(\rho, z)|H_e|\Psi_n(\rho, z)\rangle + \Delta E_{LO} + \Delta E_{SO} = E_n^e + \Delta E_{LO} + \Delta E_{SO} \quad (4) \]

where

\[ \Delta E_{LO} = - \sum_{m=1,2,\ldots, \text{cyl.L}} \frac{|V^1_m|^2}{\hbar \omega_{LO}} \left| \langle \Psi_n(\rho, z)|J_0 \left( \frac{x_m}{R_i} \right) \left( \frac{2l \pi}{\hbar} \right) \gamma_i \right| \right|^2 \]

\[ - \sum_{m=1,2,\ldots, \text{cyl.L}} \frac{|V^1_m|^2}{\hbar \omega_{LO}} \left| \langle \Psi_n(\rho, z)|J_0 \left( \frac{x_m}{R_i} \right) \left( \frac{2l \pi}{\hbar} \right) \gamma_i \right| \right|^2 \quad (4-a) \]

and

\[ \Delta E_{SO} = - \sum_{m=2,4,\ldots} \frac{\Gamma_{SO}^2}{\hbar \omega_{SS}} \left| \langle \Psi_n(\rho, z)|J_0 \left( \frac{m \pi}{2\hbar} \right) \gamma_i \right| \right|^2 \]

\[ - \sum_{m=2,4,\ldots} \frac{\Gamma_{SO}^2}{\hbar \omega_{SS}} \left| \langle \Psi_n(\rho, z)|J_0 \left( \frac{m \pi}{2\hbar} \right) \gamma_i \right| \right|^2 \]

\[ - \sum_{m=2,4,\ldots} \frac{|V^1_{m+1}|^2}{\hbar \omega_{SS}} \left| \langle \Psi_n(\rho, z)|J_0(q_{+m}\gamma_i) \gamma_i \right| \Psi_n(\rho, z) \right| \right|^2 \]

\[ - \sum_{m=2,4,\ldots} \frac{|V^1_{m-1}|^2}{\hbar \omega_{SS}} \left| \langle \Psi_n(\rho, z)|J_0(q_{-m}\gamma_i) \gamma_i \right| \Psi_n(\rho, z) \right| \right|^2 \quad (4-b) \]

\[ \sigma_{\text{cyl}} = z \quad \text{and} \quad \sigma_L = z + h + d/2. \]

To solve the electronic part, we use the variational approach. We restrict the research at the two first electronic states. Two variational parameters are also included \( \lambda_0, \lambda_1 \)

\[ \psi_n(r) = \phi_n(\rho, \lambda_n) \chi(z) \quad (5) \]

with:

\[ \chi(z) = \begin{cases} 
A \cos \left\{ k_1 \left( z + \frac{d}{2} \right) \right\} & -d - h < z < h \\
B \exp \left\{ -k_2 \left( z + \frac{d}{2} \right) \right\} & \text{otherwise} 
\end{cases} \quad (5-a) \]

\[ \phi_0(\rho, \lambda) = N_{\lambda_0} e^{-\left( \frac{\rho}{\lambda_0} \right)^2} \quad (5-b) \]

\[ \phi_1(\rho, \lambda) = N_{\lambda_1} \rho \cos(\theta) e^{-\left( \frac{\rho}{\lambda_1} \right)^2} \quad (5-c) \]

\( \lambda_0 \) and \( \lambda_1 \) are chosen such that the expectation value of the Hamiltonian of the system under the state \( |\Psi_n\rangle \) reaches its minimum. \( N_{\lambda_0} \) and \( N_{\lambda_1} \) are the normalization constants.
Fig. 2. The two first state energies of an electron confined in a CdS cylindrical quantum with a fixed height ($2h = 2$ nm) versus its radius $R$. The wetting layer is with a thickness of $d = 0.3$ nm. The solid and dashed lines are associated to without and with phonon effects, respectively.

In the above section, we have used, for CdS, the following values of parameters [11,12]: $\varepsilon_\infty = 5.32$, $\varepsilon_0 = 9.83$, $\hbar\omega_{LO} = 38.26$ meV and the Frohlich constant $\alpha = 0.527$. For GaAs quantum dot we have taken $\varepsilon_\infty = 10.2$, $\varepsilon_0 = 12.7$, $\hbar\omega_{LO} = 36.7$ meV and the Frohlich constant $\alpha = 0.058$.

Calculated results of the two first energy states of the perturbate electron are plotted, as a function of the radius of the CdS/ZnS quantum dot, in Fig. 2. For comparison, the two first state energies of the electron without phonon interaction are also calculated from $E_n = \text{min}(\langle \Psi_n | H_e | \Psi_n \rangle)$ and results are also plotted in Fig. 2. It is clearly seen that important shifts ($\approx 15–10$ meV) are caused by the electron–phonon interaction if $D = 2R < 50$ Å. These shifts are more important for small dots which means that they become more correlated. In large dots, we show that the electron energies approach to perturbate electron ones which is the bulk limit: in bulk limit, the electron–phonon correlation is very negligible.

To study the electron–phonon interaction in detail, we have plotted in Fig. 3(a) and in Fig. 3(b) the contribution of LO and SO phonons separately. In these figures, we choose a II–VI CdS/ZnS and III–V GaAs/InAs based quantum dots. Many constitution are concluded. Firstly, we should note that electron–phonon interaction presents more interesting values for CdS/ZnS quantum dot. Secondly, as is shown in other works, SO phonons have negligible effects on electron energies in GaAs/InAs quantum dot. This result isn't valuable for CdS/ZnS QD. In fact, if we pay attention to SO phonon contribution, we can note significant values for small dots ($D = 2R < 50$ Å). We can also, note that such contribution decreases rapidly as a function of the dot size. This result can be explained
Fig. 3(a). LO and SO phonon contributions to the electron ground state energy in a CdS/ZnS quantum dot (solid lines) and in GaAs/InAs quantum dot (dashed lines) versus the cylinder radius.

Fig. 3(b). LO and SO phonon contributions to the electron first excited state energy in a CdS/ZnS quantum dot (solid lines) and in GaAs/InAs quantum dot (dashed lines) versus the cylinder radius. The cylinder is chosen with a fixed height \(2h = 2\) nm. The thickness of the wetting layer is \(d = 0.3\) nm.
by the fact that in CdS/ZnS dots, important imperfections at the interface between the two materials forming this nanostructure exist. These imperfections give rise to SO phonon modes which, in small dots, interact with electron wave functions which are concentrated inside the cylinder (Fig. 2). In large dots these SO phonon modes become far from the electron wave functions and their influences have no further importance. Finally, we note that LO phonons play, for two nanostructures, a dominant role.

In conclusion, we have calculated shifts of the two first electron energies caused by electron–phonon interaction in both CdS and GaAs quantum dot. Results show that electron–phonon interaction is more significant for CdS than for GaAs quantum dots and, contrary to GaAs based quantum dots, we shouldn’t neglect, for CdS based ones, the contribution of the phonons of the surface, specially, for small dots.

References