Polaronic states in II–VI quantum dot

M. Triki,*, S. Jaziri

Abstract

In self-assembled quantum dots, the strong electron–phonon interaction should lead to some polaron effects in optical spectra (absorption and Raman scattering). We study the influence of the longitudinal optical phonons on polaron formation in CdS/ZnS self-assembled quantum dots.

Keywords: Polaronic states; Self-assembled quantum dots; Electron–phonon interaction

Investigation of exciton in quantum dots have been attracted much attention in the last decade as it has been possible to produce well characterised quasi-zero-dimensional structures. The optical properties are influenced by electron and hole interaction with longitudinal optical LO phonons [1]. In low dimensional structures, the electron and the phonon become more correlated and give rise to polarons. So the knowledge of the polaron energy spectrum is important for understanding the optical spectra of quantum dots.

In this work, we propose an analytic study to determine the lowest polaronic states in a self-assembled II–VI quantum dot. These semiconductor quantum structures can be considered as a new class of materials of basic interest [2,3]. The shape of the dot (Fig. 1) is modelled by a cone lying on a wetting layer with a radius \( r \), height \( h \) and a fixed ratio \( h/r = 0.21 \). The approach is based on the strong coupling between the electron and the LO phonon.

To be specified, we focus our analysis to the study of the anti-crossings between the electronic and the excitonic states which are separated by the LO phonon energy. So, this work is divided on two parts: firstly, we study the electron-phonon interaction and then we concentrate to the exciton-phonon one.

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

\[
H_i = \frac{p_{z_i}^2}{2m_{i//}} + \frac{p_{\rho_i}^2}{2m_{i\perp}} + V_{\text{dot}}(z_i, \rho_i)
\]

where \( i = e, h \) for electron and hole and || and \( \perp \) stands for parallel and perpendicular to the growth axis \( (z) \), \( m_i \) the effective mass of the electron or the hole and \( V_{\text{dot}}(z_i, \rho_i) \) is the band offset potential quantum dot. It is zero in the dot and \( V_i \) outside. It is assumed to have a cylindrical symmetry along the growth direction. The wave function is simplified to the form \( \Psi_{n}(\rho_i) = e^{i\rho_i\phi_{n}(\rho_i, z_i)} \) due to the commutation \( [L_z, H_i] = 0 \) between the Hamiltonian and the angular momentum \( L_z \) induced by the symmetry. The electron and hole wave functions are calculated by
numerical diagonalization on a Fourier–Bessel function basis:

\[
\chi_{n,l,m}(\vec{r}) = \alpha_n^l e^{i n \theta} J_n \left( \frac{\rho_i}{R} \right) \sin \left( \frac{\pi m z_i}{Z} \right)
\]  

(2)

where \(Z\) and \(R\) are the high and the radius of a large cylinder. \(\lambda_n^l\) is the \(l\)th root of the \(n\)-order Bessel function \(J_n\), \(\alpha_n^l\) is the normalization constant.

Fig. 2 shows the lowest energies of the electron in a CdS cone versus its radius. It is found that this semiconductor quantum dot displays discrete levels \(E_e < 810\ \text{meV}\). Same results are obtained by most quantum dots [4], reason for what they are usually called artificial atoms. The two first states are with a symmetry \(n = 0\) and \(n = \pm 1\). They will be denoted \(|S_e\rangle\) and \(|P_{e}^{\pm}\rangle\) in the rest of our discussion. The two first states of the hole will be denoted \(|S_h\rangle\) and \(|P_{h}^{\pm}\rangle\), respectively. These calculations have, also, pointed out that the energy gap between \(|S_e\rangle\) and \(|P_{e}^{\pm}\rangle\) states varies between 30 and 120 meV.
But, what can happen after considering phonons contribution?

After considering the phonon contribution, the polaronic Hamiltonian can be expressed:

\[ H_e^p = H_e + H_{ph} + H_{e-ph} \]  

\[ H_{ph} = \hbar \omega_{LO} \sum \tilde{q} \tilde{a}_\tilde{q} \tilde{a}^*_\tilde{q} \]  

\[ H_{e-ph} = -\frac{iA}{q} \sum \tilde{q} \left( e^{i\tilde{q}e} \tilde{a}_\tilde{q} - e^{-i\tilde{q}e} \tilde{a}^*_\tilde{q} \right) \]  

with

\[ A^2 = \frac{4\pi(\hbar \omega_{LO})^{3/2}(<h^2/2m_e>)^{1/2}}{V} \]  

\( H_{ph} \) is the longitudinal optical (LO) phonons Hamiltonian. \( H_{e-ph} \) is the Fröhlich Hamiltonian. \( \alpha_F \) and \( V \) are the Fröhlich constant and the dot volume, respectively. \( \tilde{a}_\tilde{q} \) (\( \tilde{a}^*_\tilde{q} \)) is the creation (annihilation) operator of LO phonon considered as dispersionless with frequency \( \omega_{LO} \). In the following, we restrict our consideration to the lower lying polaron states in which the number of phonon per mode is at most one and only the \( |S_e, 1q_n> \) and \( |P_e, 0q> \) electronic states included. So, we have to diagonalize the polaron Hamiltonian on the subspace \( \{ |S_e, 1q_n>_{n=1,2,...}, |P_e, 0q> \} \). The matrix elements can be written:

\[ \langle S_e, 1q_n|H_e^p|S_e, 1q_n'\rangle = (E_S^e + \hbar \omega_{LO})\delta_{n'n} \]  

\[ \langle P_e, 0q|H_e^p|P_e, 0q\rangle = E_P^e \]  

\[ \langle S_e, 1q_n|H_{e-ph}|P_e, 0q\rangle = \langle S_e, 1q_n|H_{e-ph}|P_e, 0q\rangle = V_{qn} \]  

Such problem admits exact solutions:

\[ E_\mp^e = \frac{1}{2}(E_S^e + E_P^e + \hbar \omega_{LO}) \pm \sqrt{\left(\frac{1}{2}(E_S^e - E_P^e + \hbar \omega_{LO}) \right)^2 + \int dq^2|V_q|^2} \]  

These polaronic states will be estimated by a series over the basis set of the unperturbed Hamiltonian \( H = H_e + H_{ph} \) given by the tensorial product between the two first carrier and the phonon eigenstates \( \{ |S_e, 1q_n>, |P_e, 0q> \} \). The polaron energies, measured from the ground electron state, are plotted versus the cone radius in Fig. 3. The material parameters [5] used are \( m_e = 0.21m_o \), \( m_o \) is the free electron mass, \( \alpha_F = 0.526 \), \( \hbar \omega_{LO} = 38.26 \text{ meV} \), \( V_e = 897 \text{ meV} \). For comparison, we have also plotted, in this same figure, the energies of the non interacting states \( |S_e, 1q> \) and \( |P_e, 0q> \) and

![Fig. 3. The polaron energies, measured from the ground state of the electron, plotted vs. the dot size. The dashed lines represent the unperturbed states \( |S_e, 1q> \) and \( |P_e, 0q> \).](image-url)
$|P_e^\pm, 0q\rangle$ (dashed lines). These non interacting levels cross near $r \approx 145$ Å. This cross means that the electronic levels separation is equal to $\hbar\omega_{\text{LO}}$. It is replaced by large anticrossing energy levels (25 meV). This is the rabi splitting of the electron levels caused by the electron phonon coupling. In such anticrossing, many transitions: $E^e_s \to E^e_\pm$, $E^e_s \to E^e_0 + \hbar\omega_{\text{LO}}$, $E^e_s \to E^e_p$, may take place because the wave functions of these levels are mixed in this region. In this case, electron–LO phonon interaction can never be shown as a weak coupling. In other hand, one can easily note that the rabi splitting obtained in CdS QDs is more significant than that obtained for GaAs ones [6] which seems as promising result.

Considerable efforts are being devoted to the investigation of the effects due to the exciton–phonon interaction on the optical properties of quantum dots, reason for what we should outline the importance of the research of the excitonic polaron spectrum.

The polaronic excitonic Hamiltonian can be expressed:

$H_p^\text{ex} = H_{\text{ex}} + H_{\text{ph}} + H_{\text{ex–ph}}$  \hspace{1cm} (6a)

$H_{\text{ex}} = H_{e} + H_{h} + H_{e-h}$  \hspace{1cm} (6b)

$H_{e-h} = -\frac{\varepsilon^2}{4\pi\varepsilon_0|\vec{r}_e - \vec{r}_h|}$  \hspace{1cm} (6c)

$H_{e-h}$ is the Coulomb Hamiltonian which couples the two particles. We should note that, the coupling between heavy hole states and light hole states in the valence band has been neglected on account of the strain effects and the large energy separation between the zone center states (sub-levels) in small dots. So the mixing of states from these two sub-bands is considerably reduced. Thus, the states of a hole in a dot can be described, in a way, similar to that of the electron states, only with different effective mass (which for a hole is no longer isotropic) and potential discontinuity at the interface. In the other hand, we consider small quantum dots, i.e. the strong confinement regime, which leads to well-separated electron and hole levels within the dot. This allows us to safely treat the Coulomb interaction as a perturbation [7–11]. In CdS/ZnS II–VI semiconductor quantum dots, this energy spacing is about 100–350 meV, which is large compared to other III–V semiconductor quantum dots (for example it is about 50–150 meV for InAs/GaAs QDs). For CdS/ZnS II–VI semiconductor quantum dot with radii little than 150 Å, the single-particle level spacing for electrons and holes is large compared to the temperatures $T < 200$ K explored experimentally. This allows us to restrict our attention to the lowest orbital levels in the conduction and valence band of the QD’s.

After this discussion the excitonic Hamiltonian can be projected on the tensorial product of the two bases of these particles. It is noted that the Coulomb Hamiltonian do not couple two states with different $L_e$. The matrix element is given by:

$\langle \psi_{ne}\psi_{nh}|H_{\text{ex}}|\psi_{me}\psi_{mh}\rangle$

\begin{align*}
&= E_{ne}\delta_{ne,me} + E_{nh}\delta_{nh,me} - \frac{\varepsilon^2}{4\pi\varepsilon_0|\vec{r}_e - \vec{r}_h|} \\
&\times \int \int d^3\vec{r}_e d^3\vec{r}_h \frac{\psi_{ne}^\ast(\vec{r}_e)\psi_{me}(\vec{r}_e)\psi_{nh}^\ast(\vec{r}_h)\psi_{mh}(\vec{r}_h)}{|\vec{r}_e - \vec{r}_h|}
\end{align*}

(7a)

Using Fourier transformation this matrix element is rewritten:

$\langle \psi_{ne}\psi_{nh}|H_{\text{ex}}|\psi_{me}\psi_{mh}\rangle$

\begin{align*}
&= E_{ne}\delta_{ne,me} + E_{nh}\delta_{nh,me} \\
&- \frac{\varepsilon^2}{\varepsilon_0\varepsilon_r} \int \frac{d^3\vec{q}}{q^2} \int d^3\vec{r}_e \psi_{ne}^\ast(\vec{r}_e)\psi_{me}(\vec{r}_e)\xi e^{i\vec{q}\cdot\vec{r}_e} \\
&\times \int d^3\vec{r}_h \psi_{nh}^\ast(\vec{r}_h)\psi_{mh}(\vec{r}_h)e^{-i\vec{q}\cdot\vec{r}_h}
\end{align*}

(7b)

This expression can be easily deduced from the previous calculation of the Fröhlich Hamiltonian. After diagonalizing such Hamiltonian, we obtain the excitonic states, which are slowly mixed with the Coulomb interaction. For example the excitonic state $|S_e\tilde{P}_h\rangle$ is mainly formed of $|S_eP_h\rangle$ and slowly mixed with $|P_eS_h\rangle$.

Next, we consider the pair electron-hole as one particle interacting with phonons. Using the excitonic polaron Fröhlich Hamiltonian given by:

$H_{\text{ex–ph}} = H_{e-ph} + H_{h-ph} = -\frac{IA}{q} \\
\times \left\{ \sum_q \left( e^{i\vec{q}\cdot\vec{r}_e}a_q - e^{-i\vec{q}\cdot\vec{r}_e}a_q^\dagger \right) \right\}
\left\{ \sum_q \left( e^{i\vec{q}\cdot\vec{r}_h}a_q - e^{-i\vec{q}\cdot\vec{r}_h}a_q^\dagger \right) \right\}$

(8)

we are able to deduce, by the same technique, the excitonic polaron spectrum.
Similar results are obtained for excitonic polaron levels. In fact, two large anticrossings (11 and 13 meV) are obtained. In fact, Fig. 4 shows, for a self assembled CdSe/ZnSe quantum dot, the \( r \) dependence of the polaron energies measured from the ground exciton state (solid lines). We have also plotted, in this figure, the excitonic energy states (long dashed lines) and the excitonic energy states plus one phonon (short dashed states). We find two crossing. The first is for \( r = 95 \) Å and it is between the second excited state plus one phonon \( |P_e S_h, 1q\rangle \) and the third excited state \( |P_e P_h, 0q\rangle \). The second is for \( r = 155 \) Å. It results from the ground state plus one phonon \( |S_e S_h, 1q\rangle \) and the first excited state. After diagonalization the polaron Hamiltonian in the two subspaces \{\( |S_e S_h, 1q\rangle \), \( |S_e P_h, 0q\rangle \)\} and \{\( |P_e S_h, 1q\rangle \), \( |P_e P_h, 0q\rangle \)\}, these two crossings are replaced by two large anti-crossings: 11 meV and 13 meV, respectively.

In conclusion, we have plotted the polaron energy spectrum in a self assembled II–VI quantum dot. We find that the magnitude of the splitting between the coupled modes in these semiconductor quantum dots are enhanced in comparison with the III–V ones.

References