CALCULATIONS OF THE INTERBAND TRANSITION ELECTRON ENERGIES OF THE CDSE/CDS COLLOIDAL CORE-SHELL QUANTUM DOTS

[1]Naira PETROSYAN, [2]Aram MANASELYAN

Center for Modeling and Simulations of Nanostructures, Research Laboratory of Solid State Physics, Institute of Physics, Yerevan State University, Yerevan, Armenia, [1]naira_petrosyan@ysu.am, [2]amanasel@ysu.am

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Abstract

Recently investigated colloidal quantum dots, constructed from chalcogenide materials became very attractive for researchers due to their applications in quantum dot solar cells. In this work the electron and heavy hole states in spherical and ellipsoidal CdSe/CdS colloidal core-shell quantum dot, which is wildly used in solar cells technologies, have been investigated theoretically in the frame of finite element method calculations. Usually CdSe/CdS core-shell quantum dots are type I heterostructures. We have determined the ranges of the sizes of the dot, for which type I - quasi type II transitions of the system can be observed, which means that the electron and the hole can be localizes in different parts of the considered core-shell structure. This effect can change the optical characteristics of the dot. Here we have considered also interband optical transitions between heavy hole ground state to various electron states. The dependencies of optical transition intensities on sizes of quantum dot have been obtained. The effect of external electric filed on electron and hole states and on transition intensities also have been investigated. We have demonstrated that for spherical quantum dots the interband transition energies are changing with the increase of electric field strength, but the intensity of transitions remains almost constant, which shows the stability of considered system from point of view of their usage in solar cell technologies. For the ellipsoidal dots we observed intensity changes in absorption spectrum during the increase of electric field.

Keywords: Quantum dots, electron and hole states, optical transitions

1. INTRODUCTION

Each day, approximately $9 \cdot 10^{22}$ J solar energy reaches the Earth's surface, while humanity consumes approximately $9 \cdot 10^{18}$ J energy per day [1]. Efficient conversion of solar radiation into electrical or chemical energy is one of the most important challenges of the 21st century. This is why there is a huge interest in the creation of high-efficiency and affordable solar cells that directly convert light energy into electricity. Currently, p-n junction based solar cells are widely used [2]. There is a Shockley-Queisser limit of efficiency for power converted by a single p-n junction, which is 30% for an energy gap of 1.1 eV under ideal conditions for 1 solar illumination [3,4]. One of the possible realizations of solar cells with higher efficiency is via implementation of quantum dots in solar cells, constructing so-called quantum dot solar cells. Colloidal quantum dots (CQD) have also been widely studied as potential absorbers that can be applied in various solar technologies. As a result of the introduction of QDs into the depletion region of the p-n junction of the solar cell, an intermediate band consisting of energy levels of QDs is formed in the band gap zone. Theoretical estimates show that the efficiency of solar cells with such an intermediate zone can reach up to 63.1% [5]. One of the growth methods of CQDs is solution-based growth methods [6]. These methods are particularly effective for growing single CQDs, core-shell CQDs, and multilayer CQDs ranging in size from a few nanometers to 20 nanometers, including II-VI semiconductors such as CdS, CdSe, CdTe etc. Core-shell CQDs are usually classified into type

I and II, depending on the arrangement of the conduction and valence band edges of the elements combining in the heterostructure [6].

The purpose of this work is to theoretically study the electron and heavy hole states of the CdSe/CdS core-shell CQDs with spherical and ellipsoidal symmetries, which are widely used in solar cells. We have determined the ranges of the sizes of the dot, for which type I - quasi type II transitions of the system can be observed. Also, the effect of external electric filed on electron and hole states and on optical transition intensities of CQDs have been investigated.

2. THEORY

We study here the electronic states of CdSe/CdS core-shell CQD with core radius R_1 and shell radius R_2, in the presence and absence of external electric field. The electric field is considered to be directed along the x-axis. In the frame of effective mass approximation the Schrödinger equation looks like:

$$\left[-\frac{\hbar^2}{2}\nabla\left(\frac{1}{m(x,y,z)}\nabla\right)+V(x,y,z)+eFx\right]\psi(x,y,z)=E\psi(x,y,z), \tag{1}$$

where e is the electron charge, F is the electric field strength, $V(x,y,z)$ is the confining potential of the system, $m(x,y,z)$ is the effective mass. The confining potential $V(x,y,z)$ and the effective mass $m(x,y,z)$ can be represented as:

$$V(x,y,z)=\begin{cases}0, & \sqrt{\frac{x^2}{\varepsilon_1}+\frac{y^2}{\varepsilon_2}+z^2}<R_1,\\ V_0, & R_1\le\sqrt{\frac{x^2}{\varepsilon_1}+\frac{y^2}{\varepsilon_2}+z^2}\le R_2,\\ \infty, & \sqrt{\frac{x^2}{\varepsilon_1}+\frac{y^2}{\varepsilon_2}+z^2}>R_2,\end{cases}\qquad m(x,y,z)=\begin{cases}m_1, & \sqrt{\frac{x^2}{\varepsilon_1}+\frac{y^2}{\varepsilon_2}+z^2}<R_1,\\ m_2, & R_1\le\sqrt{\frac{x^2}{\varepsilon_1}+\frac{y^2}{\varepsilon_2}+z^2}\le R_2,\end{cases} \tag{2}$$

where m_1 and m_2 are the effective masses of CdSe and CdS respectivaly, V_0 is the height of the potential barier on the interface between CdSe and CdS, ε_1 and ε_2 are the ellipsoidality parameters of the CQD. When $\varepsilon_1=\varepsilon_2=1$ the CQD is spherical, when $\varepsilon_1>\varepsilon_2$ the ellipsoidal CQD is stretched along the x axis, and when $\varepsilon_1<\varepsilon_2$ the ellipsoidal CQD is stretched along the y axis.

Numerical calculations were made using the finite element method (FEM) [7]. In this work, a special package of the Wolfram Mathematica program was used to solve the problem, designed for the calculation of the eigenvalues and eigenfunctions of the Hamiltonian with the FEM. Thus, by solving equation (1) we can obtain the dependences of energy levels and wave functions on the electric field strength. Since the FEM allows to obtain both the energy spectrum of the system and the wave functions, we can also calculate the intensity of the optical transitions from the valence band to the conduction band, that is, study the interband transitions in the CdSe/CdS core-shell colloidal quantum dot. We will consider here the transition from the heavy hole ground state to different states of the conduction band.

Within the dipole approximation, the intensity of the interband optical transition is proportional to the square of the modulus of the following overlap integral:

$$M=\left|\int\psi_e^*(\vec{r})\psi_{h0}(\vec{r})d\vec{r}\right|^2, \tag{3}$$

where $\psi_e^*(\vec{r}))$ is the wave function of the electron in the CQD, and $\psi_{h0}(\vec{r})$ is the wave function of the ground state of the heavy hole. The interband transition energy is defined as $\Delta E=E_e+E_h+E_g$, where E_e and E_h are the electron and hole energies and E_g=1740 meV is the band gap of CdSe [8].

3. RESULTS AND DISCUSSION

Numerical calculations are performed for CdSe/CdS CQD with parameter values $m_{1e} = 0.11m_0$, $m_{2e} = 0.14m_0$ as electron effective masses, $m_{1h} = 0.44m_0$, $m_{2h} = 0.51m_0$ as heavy hole effective masses (m_0 is the free electron mass), and $V_{0e} = 320$ meV, $V_{0h} = 430$ meV are the potential barrier heights for conduction and valence bands respectively [6, 8]. Here we will discuss the obtained results for spherical CQD and for ellipsoidal CQD separately.

3.1 Spherical CQD

Figures 1 (a) and **(c)** show the squares of the modulus of the electron wave functions of the first few states for fixed values of the core and shell radii $R_1 = 1.5$ nm, $R_2 = 5$ nm **(a)** and $R_1 = 5$ nm, $R_2 = 10$ nm **(c)** respectively. The electron and heavy hole ground state probability densities are presented in **Figure 1 (b)** and **(d)** as a function of radial coordinate. As can be seen from the **Figure1 (b)**, in the case of CQD with smaller sizes, the electron is localized in the shell, and the hole in the core, therefore, with the specified values of the radii, the system becomes of the quasi type II. This circumstance can have a significant effect on the interband optical transitions of a spherical quantum dot. From **Figure 1 (d)**, it can be seen that for larger CQD both the electron and the hole are localized in the core region, therefore, with the indicated values of the radii, the system is of the type I.

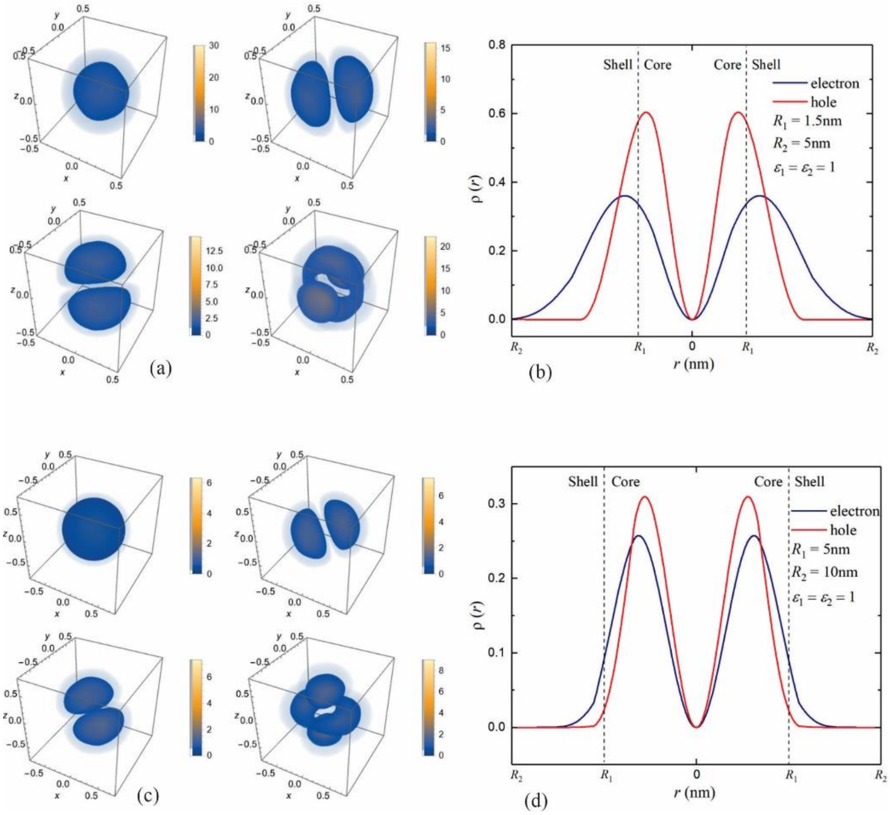

Figure 1 The modulus square of the electron wave functions (a), (c) and the dependence of electron and hole ground state probability density on radial coordinate (b), (d)

In **Figure 2** the dependences of the first few energy levels of the electron (a) and (b) and hole (c) and (d) on the electric field strength are presented for fixed values of R_1 and R_2. As can be seen from the figures, an increase in the electric field leads to a decrease in the energy levels of both the electron and the hole, as well as a partial elimination of degeneracy. It should be noted that due to the small sizes of the CQD, there is a strong size quantization, due to which the effect of the field on the energy levels is quite weak.

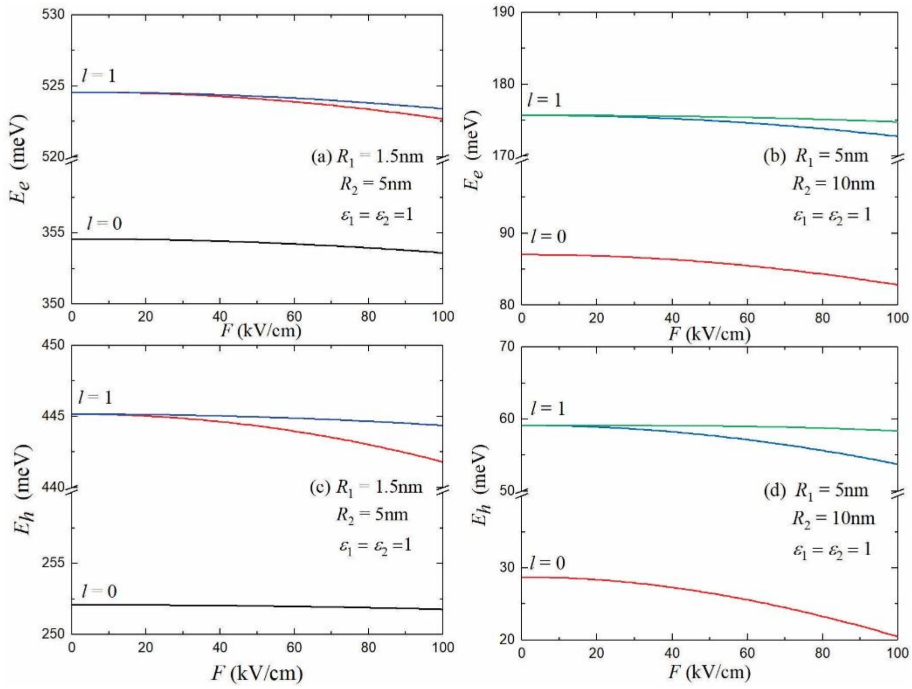

Figure 2 Dependences of the first few energy levels of an electron (a), (b) and a heavy hole (c), (d) on the electric field strength for various sizes of CQD

In **Figure 3** the dependences of the transition energies and intensities of interband transitions on the electric field strength are presented for two sizes of CQD. Here, the size of the points indicates the intensity of the transition, and the color indicates the final state of the transition in conduction band.

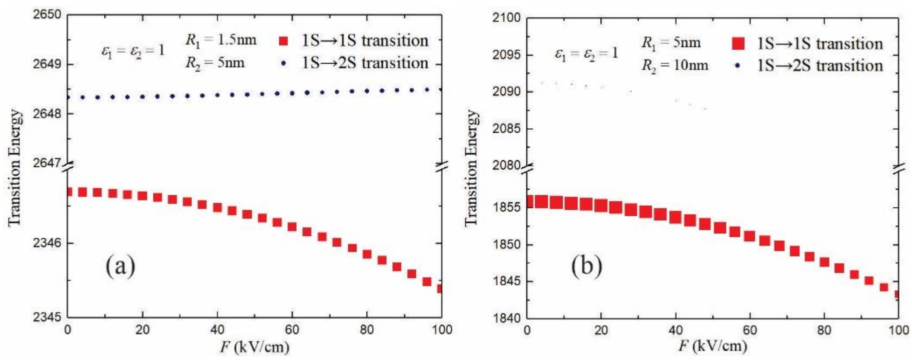

Figure 3 Dependences of the interband transition energies and intensities on the electric field strength. (a) CQD with smaller sizes, (b) CQD with larger sizes

As it can be seen from **Figure 3 (a)** for smaller CQD the transition energy from the heavy hole ground state to the electron ground state decreases with the increase of electric field strength, and the transition energy from the heavy hole ground state to the second $l = 0$ state increases. All other final states are dark. For the case of larger CQD (**Figure 3 (b)**) only the transition from hole ground state to electron ground state can be observed. For both cases the intensity of the transition only slightly changes with the increase of the electric field, which demonstrates the stability of such CQDs from the point of view of application in solar cells.

3.2 Ellipsoidal CQD

In order to model an ellipsoidal CQD we choose $\varepsilon_1 = 1.5$, $\varepsilon_2 = 1$ for the CQD stretched along the x axis, and $\varepsilon_1 = 1$, $\varepsilon_2 = 1.5$ for the CQD stretched along the y axis. In **Figure 4** the dependencies of the first few energy levels of an electron (**(a)** and **(b)**) and a heavy hole (**(c)** and **(d)**) on the electric field strength are presented for ellipsoidal CQDs stretched in x and y axis respectively.

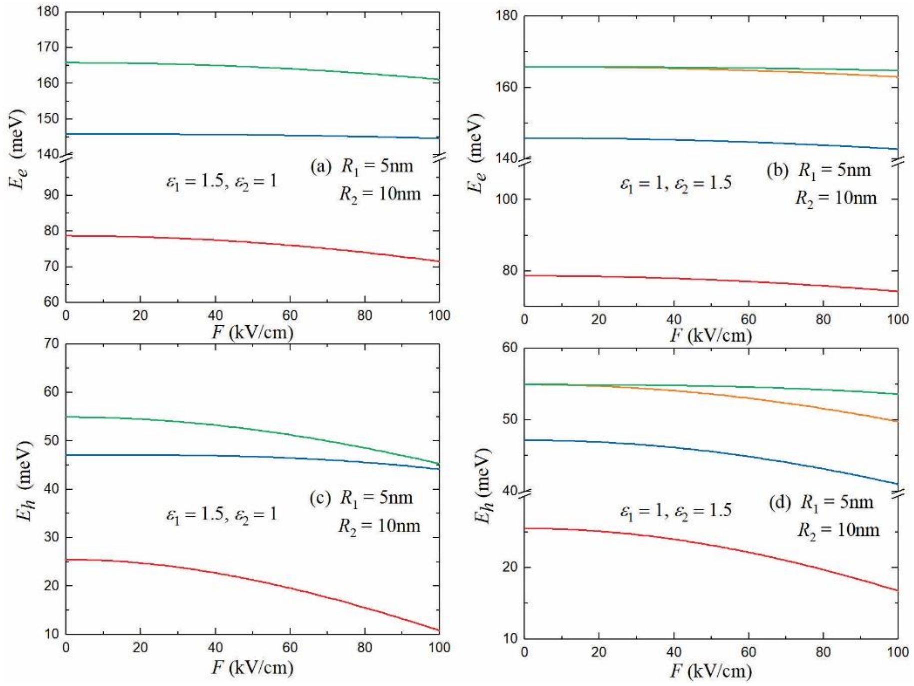

Figure 4 Dependences of the first few energy levels of an electron (a), (b) and a hole (c), (d) on the electric field strength

As we can see from the figures, for the case of ellipsoidal CQD the degeneracy of the first excited state is partially lifted even at 0 electric field, due to the symmetry breaking of the system (blue and green lines in **Figure 4 (a)** and **(b)**). With the increase of electric field strength all energies are decreasing. When the CQD is stretched in same direction as the electric field the green line remains doubly degenerated for all values of the field (**Figure 4 (a)** and **(c)**). When the field and stretched direction of CQD are perpendicular to each other (**Figure 4 (b)** and **(d)**), complete removal of the degeneracy is observed.

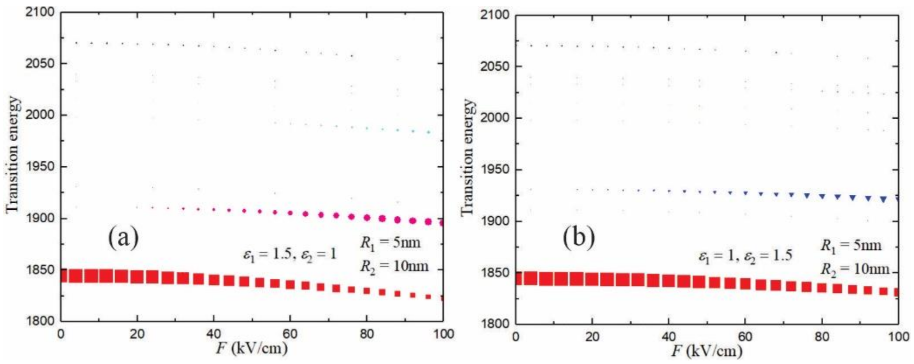

Figure 5 Dependences of the interband transition energies and intensities on the electric field strength. (a) CQD stretched along the x axis, (b) CQD stretched along the y axis

Figure 5 presents the dependences of the transition energies and intensities of interband transitions on the electric field strength for ellipsoidal CQDs stretched along the direction of the field **(a)** and perpendicular to it **(b)**. Here, as in the previous case, the size of the points indicates the intensity of the transition and the color indicates the final state of the transition. In this case new optical modes can be observed due to breaking symmetry of the system. But the transition to electron ground state has the highest intensity. Also both, the ground state transition energy and the transition intensity decrease with the increase of the electric field.

4. CONCLUSION

In this work, spherical and ellipsoidal CdSe/CdS core-shell CQDs, which are wildly used in solar cells, are theoretically studied. It has been shown that for small sizes of CQDs type I – quasi type II transition can be observed which means that the electron and the hole can be localized in different parts of the considered core-shell structure. This effect can change the optical characteristics of the dot. The dependences of the energy levels of the electron and the hole on the electric field for different sizes of the CQDs were obtained. Here we have considered also interband optical transitions between heavy hole ground state to various electron states. The effect of external electric field on electron and hole states and on transition intensities also have been investigated. We have demonstrated that for spherical CQDs the interband transition energies are changing with the increase of electric field strength, but the intensity of transitions remains almost constant, which shows the stability of considered system from point of view of their usage in solar cell technologies. For ellipsoidal CQDs the transition intensity for the electron ground state is decreasing with the increase of electric field, but new optical modes can be observed.

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