

PERMANENT ELECTRIC DIPOLE MOMENT EFFECT ON THE ELECTRONIC STATES IN CdSe/ZnS CORE-SHELL QUANTUM DOTS UNDER ELECTRIC FIELD

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The effect of the permanent electric dipole moment on the electron energy states in a CdSe/ZnS quantum structure under applied electric field was studied. Single particle Schrödinger equation was solved in the effective mass approximation by using the finite element method. We found that the CdSe/ZnS related energy states are differently influenced by the relative orientation between the electric field and electric dipole moment. If the two vectors are parallel, the energy level variation is significant. These allow tuning the characteristics and properties of optoelectronic systems. It is shown that the applied electric field and the permanent electric dipole moment decrease the quantum degeneracy degree.

Keywords: core-shell nanodot, permanent electric dipole moment, electronic states.

1. Introduction

In the low-dimensional semiconductor structures, like quantum dots (QDs), quantum wells (QW) or quantum well wires (QWW), the energy levels control can be tuned through variation of external parameters. This has made possible many practical applications in various fields like as: light emitting diodes [1], video displays [2], solar and photovoltaic cells [3], nanotags in biological imaging labeling [4] and sensing [5].

Many theoretical and experimental studies on the QDs have been made. Lately, nanostructures consisting of combinations II-VI or IV-VI semiconductors were created [6]. Due to its remarkable optical properties, a particular attention has been accorded to study of the Cadmium Selenide (CdSe) structure. By changing of the dot size, the CdSe emission can cover almost whole visible spectrum. Coating the QD with a thin layer of Cadmium Sulfide (CdS) or Zinc Sulfide (ZnS) led to an interesting heterostructures emergence. The ZnS coverage increase the quantum yield [7] and the CdSe coating led to enhanced the average emission rate [8] by reducing the intermittent emission. A lot of theoretical or experimental works have been allocated to study of these structures [9-11].

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Dielectric spectroscopy and optical birefringence measurements [12, 13] was revealed a permanent electric dipole moment (PEDM) in CdSe crystal. Nann & Schneider [14] have explained this dipole as originating in the noncentrosymmetric wurtzite crystalline structure of CdSe where the z-axis is not equivalent to the other two axes. This asymmetry was used to grow the nanorods structures [15]. Li and Alivisatos have established a linear dependence between the size dipole and nanocrystallite volume with $n = 0.65$ factor [13], while Nann finds $n = 1.27$ [14].

The PEDM change the crystal Hamiltonian and as consequence, the energy levels are changed. The theoretical model proposed in this work take in to consideration the effects of the PEDM on the electronic states in CdSe/ZnS core-shell nanocrystal subjected to an external electric field. The relative orientation between applied electric field and permanent electric dipole moment allows an adjustable tuning of the electron energy levels.

The paper is structured as follows. In Section 2 the theoretical background is given. Section 3 is devoted to discussions on the theoretical results obtained by solving the Schrödinger equation. Conclusions are summarized in Section 4.

2. Theory

We assume a spherical CdSe nanodot surrounded by a ZnS insulating medium with a very large gap considered as an infinite wall. The CdSe core is of radius R_1 , and the ZnS shell is of thickness $d = R_2 - R_1$ (See Fig. 1). The image charge effect on the confining potential is ignored. The potential has an infinite leap at the medium core-shell nanodot interface.

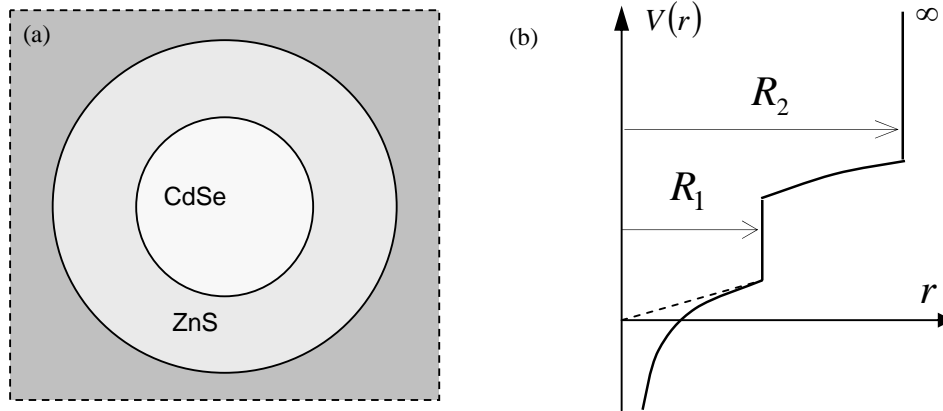


Fig. 1. Schematic of a CdSe/ZnS core shell quantum dot (a), and the electron interaction potential under electric field and PEDM (b).

In the effective mass approximation, the electron Hamiltonian in the presence of an electric field and a PEDM is given by the equation:

$$\hat{H} = -\frac{\hbar^2}{2m^*} \nabla^2 + V + q\vec{F} \cdot \vec{r} - \vec{\mu} \cdot \vec{F} + \frac{q\vec{\mu} \cdot \vec{r}}{4\pi\epsilon_0\epsilon_r r^3} \quad (1)$$

The vector \vec{F} stands for the electric field strength and $\vec{\mu}$ is the permanent dipole moment in wurtzite crystal, oriented along the z-axis.

The effective mass of the electron is:

$$m^* = \begin{cases} m_{core}^*, & r \leq R_1 \\ m_{shell}^*, & R_1 < r \leq R_2 \end{cases} \quad (2)$$

The confinement spherical potentials V are given by:

$$V = \begin{cases} 0, & r \leq R_1 \\ V_0, & R_1 < r \leq R_2 \\ \infty, & r > R_2 \end{cases} \quad (3)$$

The term $-\vec{\mu} \cdot \vec{F}$ represents the interaction of the PEDM with electric field. This term is constant for fixed field strength, so it does not change the wave functions of the electron and the interband transition energies. Only the origin value of the energy is modified.

3. Numerical results and discussion

The time-independent Schrödinger equation (eigenvalue problem) with the Hamiltonian given by equation (1) was solved through 3D finite element method. The domain was divided in tetrahedrons called mesh elements. The domain boundaries (2D dimension variety) was divided in curved triangular boundary elements. The number of the mesh elements is determined by the shape geometry. Usually it start by 10 points along one direction, which means 1000 elements in 3D. A zero value for wavefunction was imposed on the external frontier (ZnS). On the internal surface (between CdSe core and ZnS shell) a Neumann condition ensure the continuity of the wave function and his derivatives.

The initial number of iterations is fixed to be maximum 300. After each iteration the energy eigenvalue was compared with the previously value. If the difference of the energy values became smaller than a fixed value (0.001 meV) the iterations were stopped. If the difference exceed the imposed value and the number of iteration reach 300, the mesh grid was refined. A regular refinement method which divide each segment into two element of the same shape was used.

The accuracy of the solution was increased by restarting the numerical procedure and initializing with the solution obtained previously.

The CdSe quantum dots radius was chosen $R_1 = 2$ nm. The thicknesses of the ZnS shell take values between 0 and 3 nm. The parameters used in numerical simulations are presented in Table I.

Table 1

Parameters used in the numerical simulations [16].

Material	m^* / m_0	$\varepsilon / \varepsilon_0$	V_0 (eV)
CdSe	0.13	9.3	0
ZnS	0.28	8.1	0.982

In Figure 2 are shown the dependence of the electron ground state energy of the electric field strength for a CdSe/ZnS QDs with radii $R_1 = 2$ nm and $R_2 = 3$ nm (a, b), and $R_1 = 2$ nm and $R_2 = 4$ nm (c, d) respectively. Are presented the cases when \vec{F} is parallel to PEDM (a, c) and \vec{F} is perpendicular to PEDM (b, d). The curves labeled (2) and (3) are for the dipole moment values of 21.8 Debye and 42.5 Debye, calculated for a volume scale factor of 0.65 [13], respectively 1.27 [14].

For comparison, the fundamental energy level calculated without electric dipole moment is given with black line and is labeled by (1). Can be observed that the ground state energy decreases with increasing electric field strength. For a nanocrystal without PEDM subjected to an electric field, the electron ground state energy have a red shift.

Consider now a PEDM in the core-shell nanostructure.

Even in the absence of the electric field, the electron-PEDM interaction pushes the electron toward $z < 0$ area near the dot center (See also Fig 3).

Applying an electric field oriented along negative direction of z-axis, the electron is pushed near to the middle of CdSe spheres; so, for the negative electric field, the electron energy is little affected in comparison with (1), as shown the curves labeled of (2) and (3) in Fig. 2 a) and Fig 2c).

To a certain electric field value, the electron ground state energy become bigger than the electron energy without PEDM at zero electric field. This is the blue shift of the energy. Corelated with the hole dynamics on the valence band, this involve an increase of the total energy, and a blue shift in the photoluminescence emission.

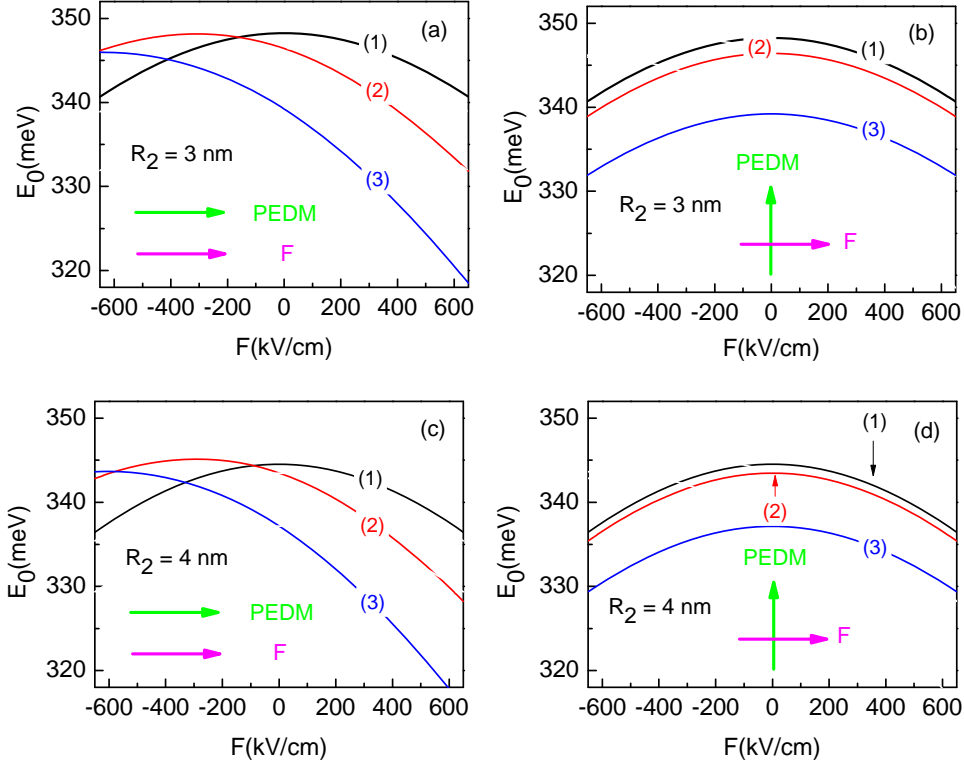


Fig. 2. Electron ground state energy versus electric field intensity for applied electric field \vec{F} parallel with the permanent electric dipole moment $\vec{\mu}$ (a, c) and perpendicular to the electric dipole moment $\vec{\mu}$ (b, d). The ZnS thickness is 1 nm (a, b), respectively 2 nm (c, d). Notation (1), (2) and (3) stands for $|\vec{\mu}| = 0$, $|\vec{\mu}| = 21.8$ Debye and $|\vec{\mu}| = 42.5$ Debye.

But if the applied field is in the positive direction of the z -axis (parallel to the electric dipole), the electron is more pushed toward $z < 0$ zone by the electric field and by the permanent dipole. As a result, the wave function is not solely localized in CdSe region, but also the wave function has significant values in the $z < 0$ area of the shell (see Fig. 3a). A large space wave function expansion leads to a decrease of the electron energy (red shift).

This blinking (red shift-blue shift-red shift) of the CdSe/ZnS QD light emission at the applied electric field orientation changing was observed experimentally by Zang *et al.* [17]. They have applied a triangular wave voltage signal with a periodicity of 10 s on a capacitor-like device architecture in which a CdSe/ZnS quantum dot was placed. The blinking was considered as an indirect evidence of the permanent electric dipole moment of a CdSe wurtzite structure

and was explained in terms of the electron and hole probability density distribution.

It can be seen in Fig. 2 (b and d) that in the case when the applied electric field and dipole moment are orthogonal to one another, the electric field effect remains symmetrically with respect to the field orientation. Also, the energy level decreases when the electric field strength grows. In this case only the red shift of the ground state energy appear.

In Fig. 3 are presented the cross section (at $y = 0$ plane) of the electron ground state wave functions for a CdSe/ZnS QD with a core radius of 2 nm and the shell thickness of 1 nm. The PEDM value is of 42.5 Debye.

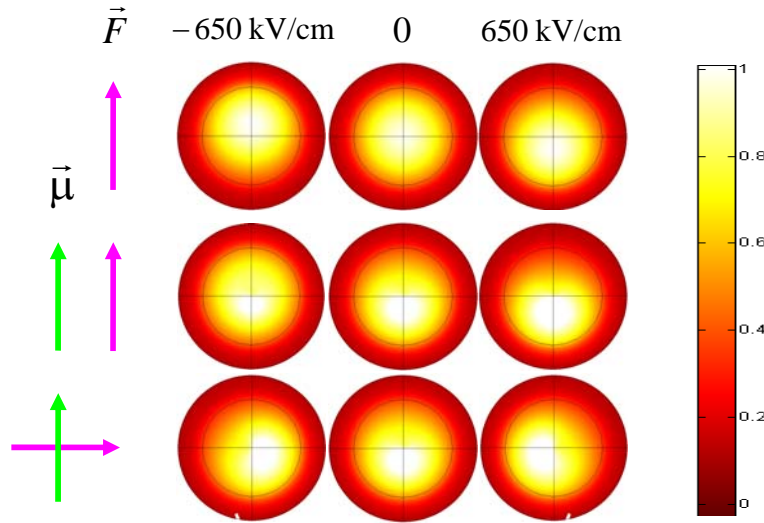


Fig. 3. The cross section (at $y = 0$ plane) of the electron ground state wave functions for a CdSe/ZnS QD with a core radius of 2 nm and the shell thickness of 1 nm.

If the coating thickness increases, a red shift energy is found for both situations of relative orientation of the applied electric field and PEDM. The red shift dependence on the shell thickness for applied electric field \vec{F} parallel with PEDM is shown in Figure 4 (a). Can be seen that the red shift is sensitive to the dipole magnitude and to the electric field orientation.

Not the same can be said for the situation when the electric field is perpendicular to the PEDM. The red shift is similar for both electric field polarization. The result is in accordance with the Fig. 2 (a) and (d). The red shift energy is less sensitive to the PEDM magnitude. A detail view is shown in the inset of Fig. 4(b).

A significant ground state energy variation is for ZnS coated thickness less than 1 nm. For bigger thickness the energy is almost constant (and the red shift is quasi zero).

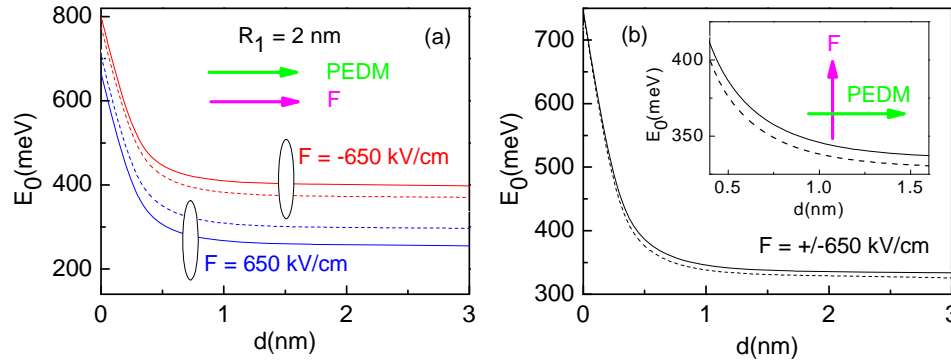


Fig. 4. Ground state energy decrease (red shift) versus ZnS coated thickness increase for applied electric field \vec{F} parallel with permanent electric dipole moment (a) and perpendicular to the permanent electric dipole moment (b). The CdSe/ZnS core radius its of 2 nm. Solide lines stand for PEDM of 42.5 Debye, and dashed line for 21.8 Debye.

The first excited state of the electron is represented in Figure 5.

Figure 5(a) represents the case without PEDM for both heterostructures with radius R_2 of 3 nm and 4 nm respectively. As can be seen, in the absence of electric field the first excited state is triple degenerate. The applied electric field decreases the degeneracy degree at 2 (the levels $2p_+$ and $2p_-$ remain degenerate).

The permanent electric dipole moment reduces degeneracy degree.

In the case of parallelism between the two vectors, the degeneracy degree is diminished only if the electric field orientation is in opposite side of the electric dipole one. For positive values of the electric field the degeneracy is partially raised. Actually, the positive electric field orientation move the electron in the same sense that is moved by the dipole. For certain values of electric field the PEDM effect is drowned, the separation of the energy levels being very low.

The degeneracy is fully removed if the applied electric field is perpendicular to the dipole moment (Fig. 5. (d)).

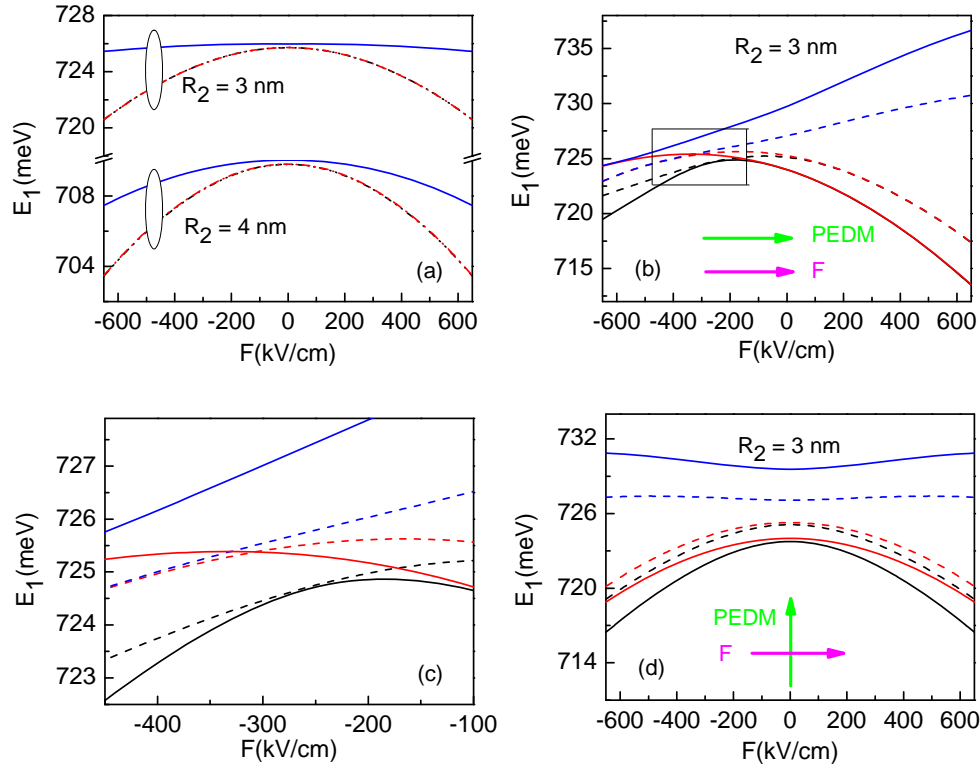


Fig. 5. First electron excited states energy versus electric field strength for $|\vec{\mu}| = 0$ (a), for applied electric field \vec{F} parallel with the permanent electric dipole moment $\vec{\mu}$ (b) and perpendicular to the electric dipole moment $\vec{\mu}$ (d), respectively. Subplot (c) represents a detail of subplot (b).

Dashed line is for $|\vec{\mu}| = 21.8$ Debye and solid line stand for $|\vec{\mu}| = 42.5$ Debye.

An overview in zOx plan section of the first excited wave functions can be seen in Figure 6. The shell thickness is of 1 nm and the PEDM values is of 42.5 Debye.

The ground state and the first excited states are located in CdSe core for both of studied configuration. In the case when the electric field and the PEDM rise completely the degeneracy degree, the CdSe core can contain no more than four quantum energy levels.

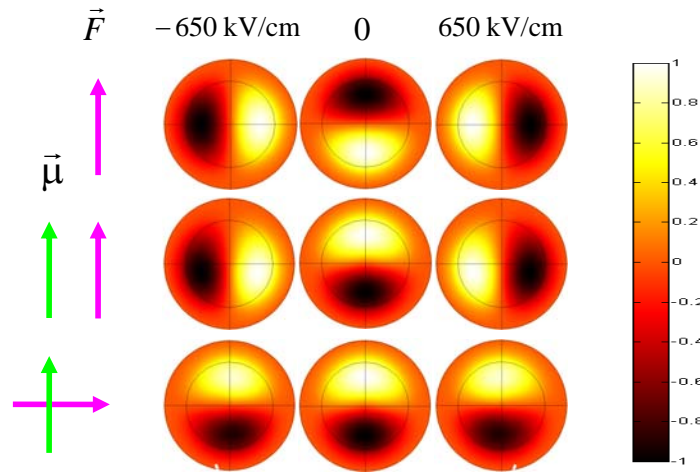


Fig. 6. The cross section (at $y = 0$ plane) of the electron first excited state wave functions for a CdSe/ZnS QD with a core radius of 2 nm and the shell thickness of 1 nm.

The upper excited states are specific of the ZnS quantum well, the wave functions stretching the CdSe/ZnS heterostructure. In the Figure 7 few density probabilities of electron localization are exemplified for CdSe/ZnS structures with ratio R_1 / R_2 of 2/3 and 2/4. It can be seen that even at zero electric field the electron has a significant probability value to be localized in the shell. Applying of an electric field increases the probability of the electron localization outside of the CdSe core.

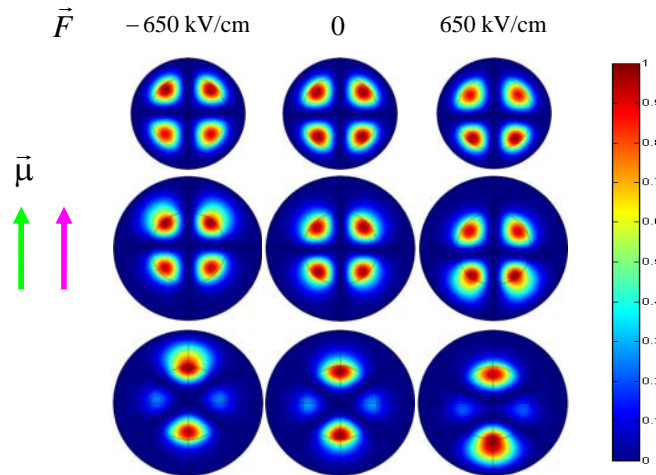


Fig. 7. Densities of the electron localization probability in the third excited state.

It should be noted that the PEDM influence is significant for the ground state and the influence decreases for higher energy levels.

4. Conclusions

In this work it was studied the PEDM effect on the electron energy states in a core-shell quantum structures subjected to an electric field.

It was found:

- i) the ground state is more affected, and the PEDM effect is diminished with increasing of quantum state order;
- ii) for the configurations analyzed only the first two energy levels is in the CdSe well. The upper wave functions cover all CdSe/ZnS heterostructure;
- iii) the most important effects are obtained in the case where the applied electric field and PEDM have the same orientation.
- iv) the combination of electric field and permanent electric dipole moment reduce totally the degeneracy degree of the first excited state.

In addition, a similar study must be done for heavy holes from valence band. We hope that this theoretical study opens new perspectives and directions for the experimental researches.

The results are useful in making optoelectronic devices by controlling energy levels through suitable choice of the core-shell nanostructure geometry, by an appropriate relative orientation of the electric field and dipole moment and by the choice of their magnitude.

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