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Impurity states in non-concentric spherical core-shell quantum dot

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It was suggested the model of the non-concentric spherical core-shell quantum dot with hydrogenic impurity. It has been defined that the electron energy spectrum as a function of both an impurity and the core location. The splitting and degeneration of energy levels has been discussed. It is shown that displacing the core of a quantum dot or impurity in opposite directions can lead to alternate splitting and degeneracy of the energy levels of excited states. In certain configurations of arrangements, compensatory effects associated with the partial restoration of spherical symmetry in the field are observed.

Keywords: energy spectrum, core-shell quantum dot, shifted core, hydrogenic impurity.

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Introduction

At present, it is impossible to imagine modern electronics without semiconductor quantum dots (QDs). Their use in state-of-the-art optoelectronic devices leads to increased efficiency and reduced energy consumption. The application of QDs presents new opportunities and challenges. One such aspect involves the fundamental physical mechanisms of fluorescence blinking of individual quantum dots [1–6]. These blinking processes are often associated with the presence of additional charges in QDs or on their surfaces, significantly increasing the rate of non-radiative decay [7]. Therefore, to slow down non-radiative recombination, core-shell QDs with spatial separation of holes and electrons in different layers are employed. Other way is providing a carefully balancing confinement potential [8-9]. On the other hand, impurities can also affect blinking by trapping an electron and causing non-radiative transitions. Hence, multi-layered QDs with impurities can influence QD blinking.

One of the simpler types of multilayered quantum dots (QDs) are spherical core-shell QDs. Colloidal technologies for manufacturing such systems allow control over the thickness of QD layers; however, there is no 100% guarantee of obtaining perfectly concentric spherical core-shell QDs. Therefore, in most cases, we deal with non-concentric spherical core-shell quantum dots (NCSCSQDs). The theory of electronic and hole spectra of concentric spherical QDs has been developed in many works (as example [10-18]), taking into account electric [13, 14, 16, 17] and magnetic fields [11, 14], as well as the presence of impurities [10, 11, 17, 18] both inside and outside the QD center. Furthermore, the theory of electronic states of NCSCSQDs based on the plane wave expansion method has been developed [19]. NCSCSQDs have also been obtained experimentally [20], and their electronic states have been described using finite element methods.

As mentioned above, the introduction of impurities can influence the single-electron properties of QDs. Therefore, the presence of impurities in the NCSCSQD can lead to changes in electronic states as well. Particularly important is the question of the impurity's location in the NCSCSQD. In [21], it was demonstrated that photoluminescence and quantum yield strictly depend on the radial placement of impurities in core-shell QDs. Considering all this, the aim of this study is to determine the influence of impurity location and non-concentricity parameter on the single-electron states of the NCSCSQD.

I. Theory

A NCSCSQD is considered. The core radius is r_0, the shell radius is r_1. The NCSCSQD is characterized by effective electron mass: m_0 in the core, m_1 in the shell. The NCSCSQD are in the bulk matrix with electron effective mass m_2. We neglect both the polarization and deformation effects due to the close values of dielectric constants of materials and lattice constants for *GaAs/Al*$_{0.4}$*Ga*$_{0.6}$*As*. The QD core is displaced from the QD center by a distance D_{QD} in the *z*-direction (Fig.1), where $r_1 - r_0 < D_{QD}$. Also we assume the there is an hydrogenic impurity in the NCSCSQD. The impurity is located at the point $\vec{D}_{\text{im}}$ in the *z*-direction (Fig. 1).

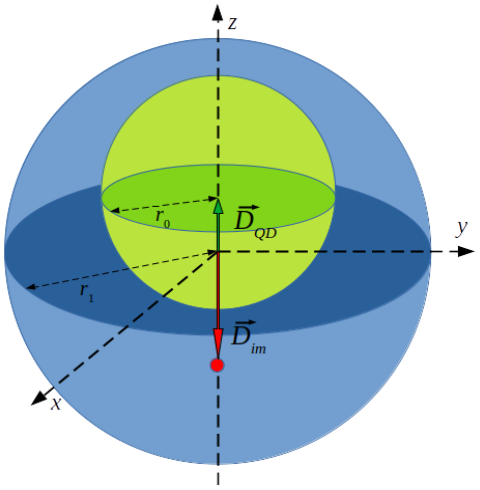

Fig.1. Geometric model of NCSCSQD with impurity.

The electron Hamiltonian of described system in units of effective Rydberg energy $Ry^* = \frac{\hbar^2}{2m_0 a_b^{*2}}$ and effective Bohr radius $a_b^* = \frac{\hbar^2 \varepsilon}{m_0 e^2}$ (ε is average dielectric permittivity, $\hbar$ is Planck constant, e is elementary charge) has form:

$$\hat{H} = -\vec{\nabla} \cdot \left(\frac{m_0}{m(\vec{r})}\vec{\nabla}\right) + U(\vec{r}) + V(\vec{r}), \tag{1}$$

where

$$m(\vec{r}) = \begin{cases} m_0, \vec{r} \in core, \\ m_1, \vec{r} \in shell, \\ m_2, \vec{r} \in matrix \end{cases} \tag{2}$$

is the electron effective mass,

$$U(\vec{r}) = \begin{cases} 0, \vec{r} \in core, \\ U_1, \vec{r} \in shell, \\ U_2, \vec{r} \in matrix \end{cases} \tag{3}$$

is confinement potential,

$$V(\vec{r}) = \frac{-2}{|\vec{r} - \vec{D}_{\text{im}}|} \tag{4}$$

is Coulomb potential energy.

In order to determine the energy spectrum and wave functions of electron in the NCSCSQD, the Schrödinger equation should be solved. In this case, exact solutions of the Schrödinger equation cannot be found. That is why we apply the plane wave method [19, 21-23]. According to the method the wave function can be represented in the following manner:

$$\psi(\vec{r}) = \sum_{n_x,n_y,n_z} C_{n_x,n_y,n_z} \psi^{(0)}_{n_x,n_y,n_z}(x,y,z), \tag{5}$$

where

$$\psi^{(0)}_{n_x,n_y,n_z}(x,y,z) = \frac{1}{\sqrt{L_x L_y L_z}} exp\{i\left[(k_x + n_x K_x)x + \left(k_y + n_y K_y\right)y + (k_z + n_z K_z)z\right]\}, \tag{6}$$

$L_x = L_y = L_z \equiv L$ are the edge lengths of the unit cell along the *x*, *y*, and *z* directions of the coordinate system,

$$K_x = K_y = K_z \equiv 2\pi/L, \tag{7}$$

$$n_x \in [-n_{max}, \ldots, n_{max}], n_y \in [-n_{max}, \ldots, n_{max}], n_z \in [-n_{max}, \ldots, n_{max}]. \tag{8}$$

References [19, 21-23] demonstrated that the results achieved convergence by considering $n_{max} = 7$ and $L = 2.5 + 2r_1$. Furthermore, it was substantiated that the obtained results are independent of the wave vector (k_x, k_y, k_z) when using those parameters. That is why, we get $k_x = k_y = k_z = 0$ in the following calculations.

Upon substituting equation (5) into the Schrödinger equation containing Hamiltonian (1), a system of linear homogeneous equations is obtained:

$$\sum_{n_x,n_y,n_z} \left(\underset{n_x,n_y,n_z}{T_{n_x',n_y',n_z'}} + \underset{n_x,n_y,n_z}{U_{n_x',n_y',n_z'}} + \underset{n_x,n_y,n_z}{V_{n_x',n_y',n_z'}} - E\,\underset{n_x,n_y,n_z}{\delta_{n_x',n_y',n_z'}} \right) C_{n_x,n_y,n_z} = 0. \tag{9}$$

Matrix elements $\underset{n_x,n_y,n_z}{T_{n_x',n_y',n_z'}}$ and $\underset{n_x,n_y,n_z}{U_{n_x',n_y',n_z'}}$ were presented and derived in our work [19]. The matrix element of the Coulomb potential (4) is derived in our work [24] for the case of $N = 1$ as well.

From the system of linear homogeneous equations (9) and normalize condition $\sum_{n_x,n_y,n_z} \left|C_{n_x,n_y,n_z}\right|^2 = 1$ the

energy E and all coefficients can be found. Therefore, the wave function (5) can be defined.

II. Result discussion

We performed the calculation for the NCSCSQD with an impurity. The heterostructure *GaAs/Al$_x$Ga$_{1-x}$As/matrix* parameters have been established in our previous works [19, 24]: $x = 0.4$, $m_0 = 0.067m_e$, $m_1 = 0.1m_e$, $m_2 = m_e$, $U_1 =$ 297 meV. We consider a matrix material where the band offset between the QD shell and the matrix is very large. Therefore, we assume $U_2 = 6000$ meV.

We considered two variants of the geometric dimensions of the core and shell:

I) $r_0 = 40$ Å, $r_1 = 60$ Å;

II) $r_0 = 40$ Å, $r_1 = 70$ Å.

For these variants, we calculated the energy dependencies of the ground 1s-state and lower excited 1p-states as functions of the impurity and core positions in the quantum dot (Fig. 2).

Overall, from the Fig. 2, it can be observed that the electron energy increases with the displacement of the core from the center of the QD. This effect is less noticeable for the ground state, while for the excited states, this effect is more pronounced. Specifically, the excited p-states split according to the value of $|m|$ due to the disruption of spherical symmetry. However, there are values of D_{im} for which a restoration of degeneracy is observed, leading to a change in the order of levels. This dependence arises because the displacement of the QD core can be compensated by an opposite displacement of the impurity. The interplay between these parameters results in the alternation of split p-levels, when $D_{QD} \neq 0$. When $D_{QD} = 0$ (Fig1. A) p-levels only split but level order does no change. The similar level order changing also has been disused in [19] in the NCSCSQD without impurity. Similar calculation (Fig. 3) has been done for NCSCSQD for larger shell (case II).

For a comprehensive analysis, we also determined the electron energy for fixed impurity positions while varying the location of the donor nucleus. These dependencies are presented in Figure 4. From Figure 4, it is evident that the displacement of the QD core also results in the splitting of excited p-levels. However, the alternation of levels occurs with significant changes in impurity positions, and there is no oscillatory pattern in the energy dependence of the excited state on the QD core location. This is because the change in the position of the QD core has a stronger impact than the variation in the impurity position. In other words, the Coulomb interaction energy between the impurity and the electron is smaller than the potential confinement of the QD. This is indeed confirmed by the large value of the effective Bohr radius for an electron in the QD. A large effective Bohr radius indicates that the interaction of the electron with the nucleus of the quantum dot significantly influences the electronic structure compared to the interaction of the electron with the impurity. This underscores the importance of the quantum dot nucleus location in determining the energy levels and properties of electrons in the system. However, opposite displacements of the QD core and the impurity can lead to partial compensation of their mutual influences. As a result, points of degeneracy restoration in the energy states are observed in all the figures (when $D_{QD} \neq 0$ and $D_{\text{im}} \neq 0$).

Another interesting case (Fig. 5) is when the impurity is located at the center of the quantum dot core, which, together with the impurity, can be outside the center of the core-shell QD (when $D_{QD} = D_{\text{im}}$). From Fig. 5, it is clear that simultaneous displacement of the QD core and the impurity (assuming the impurity is at the center of the QD core) results in the splitting of levels.

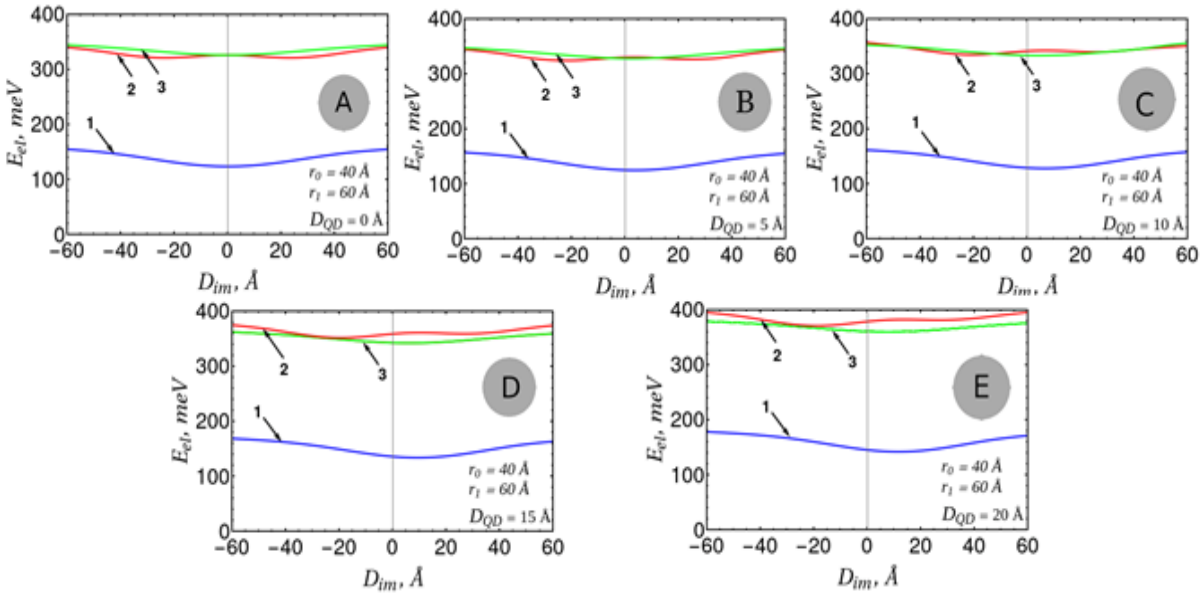

Fig. 2. The dependence of the electron energy on the impurity position for various configurations of the core position (D_{QD}) in the NCSCSQD is illustrated. Curves 1 represent the energy of the ground state, red curves 2 correspond to the energy of the p-state (where $|m| = 0$), and green curves 3 depict the energy of the p-state ($|m| = 1$). QD radii are printed in the plot.

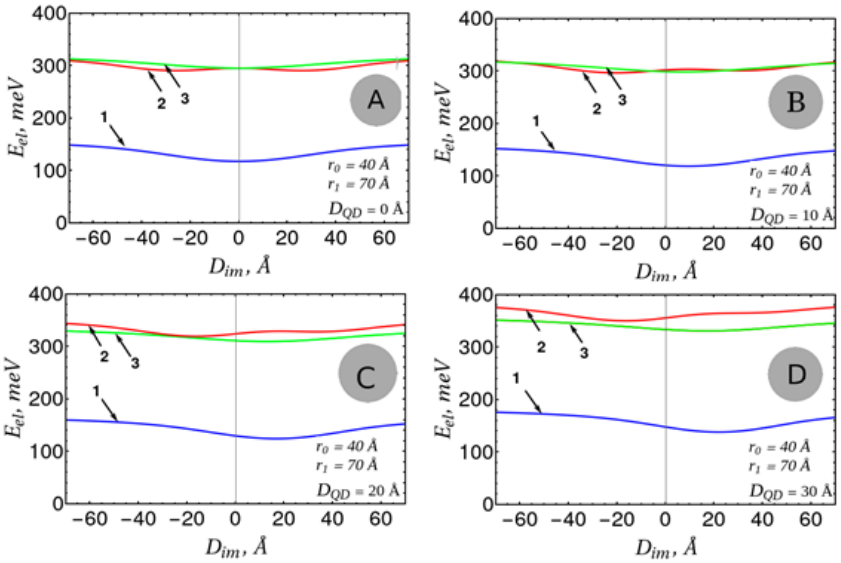

Fig.3. The dependence of the electron energy on the impurity position for various configurations of the core position (D_{QD}) in the NCSCSQD is illustrated. Curves 1 represent the energy of the ground state, red curves 2 correspond to the energy of the p-state (where $|m| = 0$), and green curves 3 depict the energy of the p-state ($|m| = 1$). QD radii are printed in the plot.

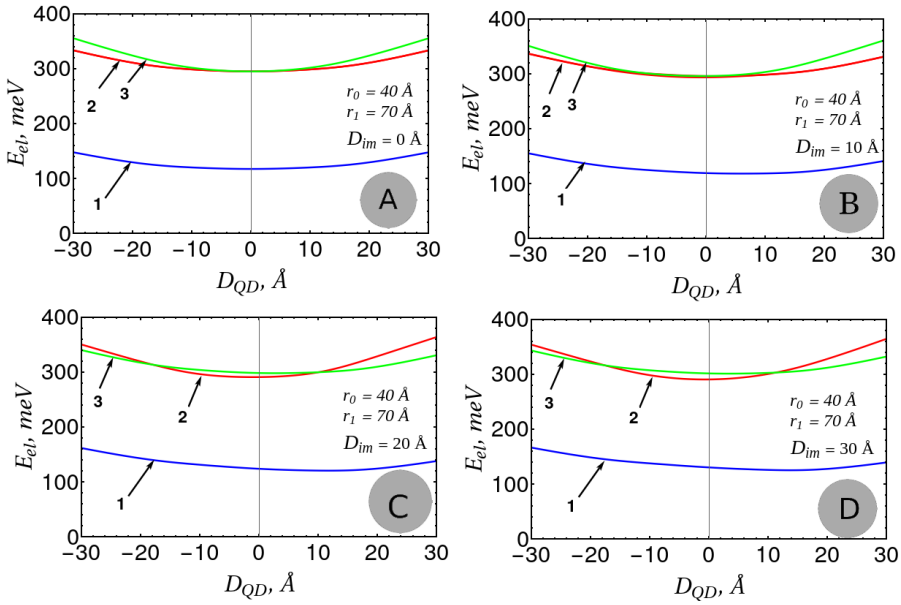

Fig. 4. The dependence of the electron energy on the core position for various configurations of the impurity position (D_{im}) in the NCSCSQD is illustrated. Curves 1 represent the energy of the ground state, red curves 2 correspond to the energy of the p-state (where $|m| = 0$), and green curves 3 depict the energy of the p-state ($|m| = 1$). QD radii are printed in the plot.

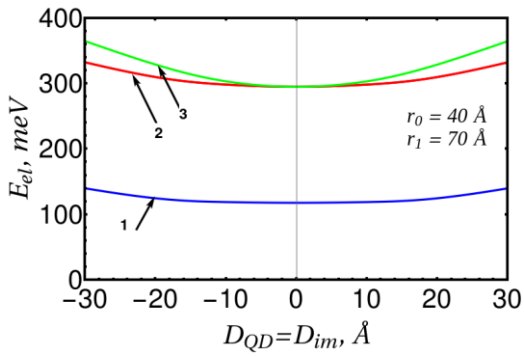

Fig. 5. The dependence of the electron energy on the core position when the impurity is the core center. Curves 1 represent the energy of the ground state, red curves 2 correspond to the energy of the p-state (where $|m| = 0$), and green curves 3 depict the energy of the p-state ($|m|$=1). QD radii are printed in the plot.

Both the impurity and QD core displacements enhance the splitting effect. For both the ground and excited energy levels, this displacement leads to a monotonic increase in the electron energy.

Conclusions

Therefore, this work proposes a method for determining the electron energy in the NCSCSQD in the presence of an hydrogenic impurity. The model takes into account the intentional placement of the impurity and the QD core along the z-axis. Calculations for the heterosystem revealed that the confinement potential has a stronger impact on the electron than the Coulomb potential energy of the electron-ion interaction. As a result, the displacement of the QD core affects the electron spectrum more significantly than the variation in the impurity position. It was also identified that the competition between these two factors leads to partial degeneracy restoration of excited p-states for specific configurations of nucleus and impurity positions. Both factors contribute to an increase in electron energy when the spherical symmetry is disrupted. The obtained results can be utilized for the calculation and interpretation of absorption bands (caused by impurities) in the core-shell QDs with account the shifting QD core from common center.

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Домішкові стани у неконцентричній сферичній квантовій точці типу ядро-оболонка

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Запропоновано модель неконцентричної сферичної квантової точки з водневоподібною домішкою. Визначено енергетичний спектр електрона як функцію розташування домішки та ядра квантової точки. Проаналізовано розщеплення і виродження енергетичних рівнів. Показано, що зміщення ядра квантової точки чи домішки у протилежних напрямках може призвести до чергування виродження та розщеплення енергетичних рівнів збуджених станів. При певних конфігураціях у розташуванні ядра квантової точки і домішки спостерігаються ефекти компенсації, що зумовлюються часткове відновлення сферичного розподілу електронної густини.

Ключові слова: енергетичний спектр, квантова точка типу ядро-оболонка, зміщене ядро, домішка