Quantum Electronics **43** (1) 76–78 (2013)

PACS numbers: 85.35.Be; 73.21.La
DOI: 10.1070/QE2013v043n01ABEH014965

Features of the electronic spectrum in a type-I core–shell quantum dot

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Abstract. **The model is proposed, which allows one to solve the problem of finding the energy spectrum and the wave function of an electron in a type-I core–shell quantum dot. It is shown that the size of the core and shell can serve as control parameters for the optimisation of the energy structure of the quantum dot in order to obtain the real structures with desired electrophysical and optical properties.**

Keywords: *type-I core–shell quantum dot, Schrödinger equation, energy spectrum of the wave function.*

Quantum dots (QDs) are finding wide application in opto- and nanoelectronic devices [1–3]. Among the variety of quantum dots there are several main types that are most frequently used in experimental studies and practical applications. First of all, these are nanocrystals in glasses and wideband dielectric matrices [4]. Another important type of quantum dots is so-called self-assembled quantum dots, which are grown by using the Volmer–Weber and Stranski–Krastanov techniques with the help of the methods of molecular beam and vapour-phase epitaxy [5]. This type of quantum dots is studied in many experimental and theoretical papers [6, 7]. Recent advances in nanotechnology suggest the appearance of a new class of quantum dots, i.e., colloidal nanocrystals.

In 1993 Bawendi et al. [8] described a method for the synthesis of high-quality nearly monodisperse SdSe semiconductor nanocrystals. These quantum dots had a high-quality crystal structure and a narrow size distribution; however, they were weakly fluorescent (the quantum yield was about 10%). A breakthrough was achieved after growing a shell of a wide-band-gap semiconductor (ZnS) around the core, which made it possible to ensure a fluorescence quantum yield (after optimising the technology) of over 80% at room temperature [9]. Such structures were called type-I core–shell quantum dots (or core/shell QDs). It should be noted that, despite the large amount of experimental work on the preparation and investigation of colloidal nanocrystals, the related theoretical research is sufficiently scarce. Describing core–shell quantum dots the authors of papers [10–12] consider the tunnelling of an electron from the QD core through the shell into the environment. Real colloidal nanocrystals are prepared as sols; in this case, tunnelling is not possible, since the agent stabilising the QD is often a dielectric [13].

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Received 7 July 2012
Kvantovaya Elektronika **43** (1) 76–78 (2013)
Translated by I.A. Ulitkin

The aim of this study is to develop a theory of the energy spectrum of the levels in a type-I core–shell quantum dot (Fig. 1). We will show that due to the presence of a shell made of a material with a band-gap that is much wider than that of the core, there appear additional possibilities of control over the position of the quantum levels.

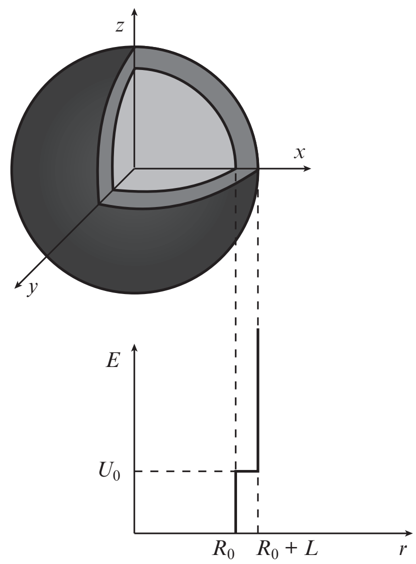

Figure 1. Scheme of a type-I core–shell quantum dot and type of the potential energy of an electron as a function of radius: U_0 is the height of the potential barrier; R_0 is the core radius; L is the shell thickness.

The energy spectrum and the wave functions of the electron in a QD are calculated within a model with hard walls. We write the stationary Schrödinger equation in the effective mass approximation:

$$-\frac{\hbar^2}{2m(r)}\nabla^2\psi + U(r)\psi = E\psi.$$

The electron potential $U(r)$ and effective mass $m(r)$ inside a quantum dot have the form

$$U(r) = \begin{cases} 0, & r \leqslant R_0, \\ U_0, & R_0 < r \leqslant R_0 + L, \\ \infty, & r > R_0 + L, \end{cases}$$

$$m(r) = \begin{cases} m_1^*, & R \leqslant R_0, \\ m_2^*, & R_0 < r \leqslant R_0 + L, \end{cases}$$

where U_0 is the height of the potential barrier; and m_1^* and m_2^* are the effective electron masses in the core and shell, respectively.

Taking into account the spherical symmetry and the type of the potential, we find the solution to the Schrödinger equation using the method of separation of variables:

$$\psi_{lm}^{(i)}(r,\theta,\phi) = R_l^{(i)}(r)\,Y_{lm}(\theta,\phi),$$

where $R_l^{(i)}(r)$ is the radial part of the wave function in the corresponding regions ($i = 1$ – core, and $i = 2$ – shell); $Y_{lm}(\theta, \phi)$ are the spherical harmonics; and $l = 0, 1, 2, \ldots$ and $m = 0, \pm 1, \pm 2, \ldots, \pm l$ are the orbital and magnetic quantum numbers.

The radial parts of $R_l^{(i)}(r)$ satisfy the equation for the Bessel function:

$$\frac{\partial^2 R_l^{(1)}(r)}{\partial r^2} + \frac{2}{r}\frac{\partial R_l^{(1)}(r)}{\partial r} + \left[k_1^2 - \frac{l(l+1)}{r^2}\right] R_l^{(1)}(r) = 0 \qquad (1)$$

inside the QD core,

$$\frac{\partial^2 R_l^{(2)}(r)}{\partial r^2} + \frac{2}{r}\frac{\partial R_l^{(2)}(r)}{\partial r} + \left[k_2^2 - \frac{l(l+1)}{r^2}\right] R_l^{(2)}(r) = 0 \qquad (2)$$

inside the QD shell, where

$$k_1^2 = \frac{2m_1^*}{\hbar^2}E, \quad k_2^2 = \frac{2m_2^*}{\hbar^2}(E - U_0)$$

are the squares of the wave numbers inside the QD core and shell, respectively.

Given the solutions to equations (1) and (2) we have

$$\psi_{lm}^{(i)} = \begin{cases} C_1 j_l(k_1 r)\,Y_{lm}(\theta,\phi), & r \leqslant R_0, \\ C_2 j_l(k_2 r)\,Y_{lm}(\theta,\phi), & R_0 < r \leqslant R_0 + L. \end{cases}$$

Here C_1 and C_2 are the normalisation factors determined from the condition that the wave functions are equal at the core – shell interface, and the normalisations by the discrete spectrum:

$$C_1 j_l(k_1 R_0) = C_2 j_l(k_2 R_0), \qquad (3)$$

$$m_2 C_1 \frac{\mathrm{d}j_l(k_1 r)}{\mathrm{d}r}\Big|_{r=R_0} = m_1 C_2 \frac{\mathrm{d}j_l(k_2 r)}{\mathrm{d}r}\Big|_{r=R_0}, \qquad (4)$$

$$\int_0^{R_0+L} R_l^{(i)}(r) r^2 \mathrm{d}r = 1.$$

Proceeding from the above reasoning, the wave function of an electron in the type-I core–shell quantum dot can be written in the form

$$\psi(r,\theta,\phi) = \begin{cases} C_1 j_l(k_1 r)\,Y_{lm}(\theta,\phi), & r \leqslant R_0, \\ C_1 \dfrac{j_l(k_1 R_0)}{j_l(k_2 R_0)} j_l(k_2 r)\,Y_{lm}(\theta,\phi), & R_0 < r \leqslant R_0 + L, \\ 0, & r > R_0 + L, \end{cases}$$

where

$$C_1 = \frac{j_l(k_2 R_0)\sqrt{2}}{\sqrt{R_0^3 j_l^2(k_2 R_0) a_l + j_l^2(k_1 R_0)[(R_0+L)^3 b_l - R_0^3 c_l]}};$$

$$a_l = j_l^2(k_1 R_0) - j_{l+1}(k_1 R_0) j_{l-1}(k_1 R_0);$$

$$b_l = j_l^2(k_2(R_0+L)) - j_{l+1}(k_2(R_0+L)) j_{l-1}(k_2(R_0+L));$$

$$c_l = j_l^2(k_2 R_0) - j_{l+1}(k_2 R_0) j_{l-1}(k_2 R_0).$$

The solvability condition of equations (3) and (4)

$$m_2 \frac{\mathrm{d}j_l(k_1 r)}{\mathrm{d}r}\Big|_{r=R_0} = m_1 \frac{j_l(k_1 R_0)}{j_l(k_2 R_0)} \frac{\mathrm{d}j_l(k_2 r)}{\mathrm{d}r}\Big|_{r=R_0} \qquad (5)$$

determines the energy spectrum of electrons with the energy $E^{(1)}$ less than U_0.

Let us analyse the evolution of quasi-stationary states in the framework of the above model. Figure 2 shows the results of the numerical analysis (5) for electrons with $E^{(1)} < U_0$ in the type-I core–shell CdSe/ZnS QD [14] (the effective electron mass $m_{\mathrm{CdSe}} = 0.13 m_0$, $m_{\mathrm{ZnS}} = 0.28 m_0$, where m_0 is the mass of a free electron; $U_0 = 0.70$ eV; and $l = 1$).

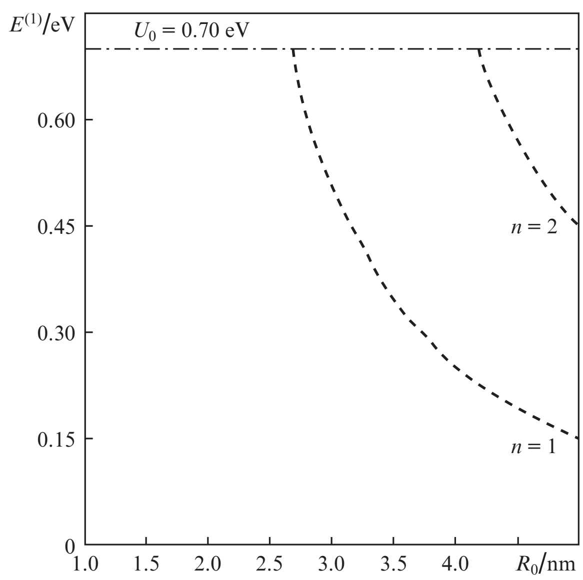

Figure 2. Energy spectrum of the electrons [$(E^{(1)} < U_0)$] as a function of the core radius of the type-I core–shell quantum dot.

The analysis shows that the number of discrete levels with $E^{(1)} < U_0$ is finite, and moreover, the discrete levels appear only when the radius of the quantum dot exceeds a minimum value $R_{\min}$. For a fixed value of the angular momentum l, equation (5) can have several solutions, corresponding to discrete energy levels with the principal quantum number n.

The condition that the wave function vanishes on the QD boundary,

$$R_l^{(i)}(R_0 + L) = 0,$$

determines the energy spectrum of the electrons with energy $E^{(2)} > U_0$:

$$E^{(2)} = \frac{\hbar^2 \xi_{nl}^2}{2m_2^*(R_0+L)^2} + U_0, \qquad (6)$$

where ξ is the nth root of the Bessel function of the order l.

Figure 3 shows the results of the numerical analysis (6) for the electrons with $E^{(2)} > U_0$ in the type-I CdSe(ZnS) core(shell) quantum dot ($l = 1$). The analysis shows that as the radius of the core decreases at a fixed shell thickness L the electron energy increases substantially due to the quantum size effect. One can see from Fig. 3 that the increase in the shell thickness from 2 to 3 nm leads to a decrease in the energy of charge carriers. Moreover, since the energy of the electrons in the QD is independent of the magnetic quantum number m, all the states with $l \neq 0$ are degenerate in energy with multiplicity $2l + 1$.

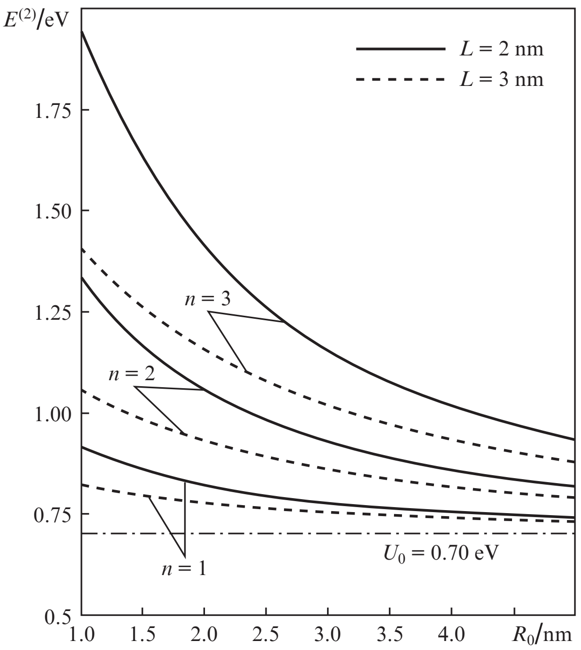

Figure 3. Energy spectrum of the electrons [($E^{(2)} > U_0$)] as a function of the core radius of the type-I core–shell quantum dot.

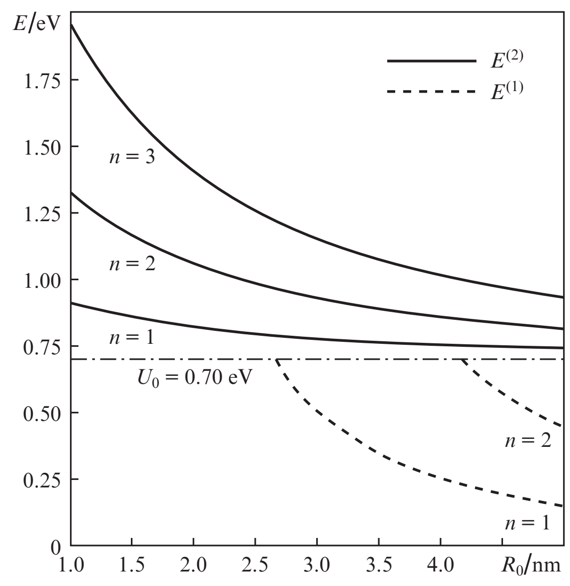

Figure 4. Energy spectrum of the electrons as a function of the core radius of the type-I core–shell quantum dot.

Figure 4 shows the generalised energy spectrum of electrons in the type-I CdSe(ZnS) core(shell) QD (l = 1). The analysis shows that at some radii of the QD core we can observe a jump in the energy of electrons, which is probably related to an additional quantum constraint on the charge carrier by the QD shell. It can be seen that as the size of the QD core increases, the energy levels converge, and at $R_0 >$ 10 nm the quantum size effects at room temperature become unobservable. Furthermore, the presence of discrete energy levels $E^{(1)} < U_0$ may lead to up-conversion of photons. This effect can be observed in the form of fluorescence upon excitation of a quantum dot by laser radiation with the energy that is lower than the band gap of the shell material [15].

Thus, this model provides a solution to the problem of finding the spectrum and wave functions of the electron in the type-I core–shell quantum dot. The results obtained can be used to grow QDs with specified electrical and optical properties for opto- and nanoelectronic devices of new generation.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant No. 12-02-97040).

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