EXCITON STATES IN QUASI-ZERO-DIMENSIONAL SEMICONDUCTOR SYSTEMS

S.I. POKUTNYI

Illichivs'k Educational and Scientific Center, I.I. Mechnikov Odesa National University
(17a, Danchenko Str., Illichivs'k 68001, Odesa region, Ukraine; e-mail: univer@ivt.ilyichevsk.odessa.ua)

UDC 535.34

For a semiconductor quantum dot (QD), the contributions made to the exciton energy spectrum by the electron and hole kinetic energies, the energy of Coulomb interaction between them, and the energy of their polarization interaction with the spherical interface between the QD and the dielectric medium have been analyzed. The limit transition from the energy spectrum of the exciton in the QD to that of the exciton in the infinite bulk has been traced.

1. Introduction

Optical properties of quasi-zero-dimensional semiconductor structures, which the semiconductor QDs of the spherical form with radii $a \approx 1 \div 100$ nm belong to, grown in a transparent dielectric media have been intensively studied recently [1–8]. Such heterostructures attract attention owing to their nonlinear optical properties and the prospects of their application in optoelectronics and quantum electronics, in particular, as novel materials perspective for the creation of elements which control optical signals in semiconductor injection lasers [1–11] and in optical bistable elements and transistors [4–6].

Since the energy gap in a semiconductor QD is essentially narrower than that in semiconductor (dielectric) matrices, the motion of charge carriers is confined to the QD volume in all three directions, i.e. charge carriers move in a three-dimensional spherical potential well. As a result, both an electron and a hole as well as an exciton have no quasi-momenta in a QD. Therefore, it is possible to speak only about quasiparticle states in a QD. Below, by an exciton in a QD, we understand such an exciton state which has no quasi-momentum.

In works [3, 12–14], the reconstruction of the exciton energy spectrum in a semiconductor under the influence of the surrounding dielectric medium was studied. The possibility for an exciton of large radius to be localized at a plane semiconductor–insulator interface by electrostatic image forces was shown in [12–14].

Optical and electrooptical properties of similar heterophase systems are determined to a great extent by the energy spectrum of a spatially-bounded electron-hole pair (the exciton) [3–11, 15–19]. The energy spectrum of the charge carriers in a QD will be completely discrete for the QD dimension a smaller than that of the order of the Bohr radii of an electron a_e and a hole a_h [20–27]. Therefore, such QDs are also called "superatoms" [28,29]. Under these conditions, the influence of the interface between the QD and the dielectric matrix can cause the dimensional quantization of the electron and hole energy spectra in the QD, which is connected to both the mere spatial confinement of a quantization region [15–19, 30–32] and the polarization interaction of charge carriers with the QD surface [20–27, 33–39].

The theory of exciton states in quasi-zero-dimensional structures has not yet been sufficiently developed so far. To fill in this blank, the contributions to the exciton energy spectrum, made by the electron and hole kinetic energies and the Coulomb interaction energies between them, and the energy of their polarization interaction with the spherical interface between the QD and the dielectric medium, have been analyzed in this work. In addition, the limit transition from the energy spectrum of the exciton in the QD to that of the exciton in the unlimited bulk has been traced.

The exciton, the structure (the effective mass, Bohr radius, and bond energy) of which in the QD does not

differ from that in an infinite semiconductor, will be called as the "bulk" exciton.

2. Exciton Energy Spectrum in a Quasi-Zero-Dimensional System

Following works [20–27, 33–37], let us consider a simple model of the quasi-zero-dimensional system: a neutral spherical semiconductor QD of radius a and dielectric permittivity (DP) ε_2 imbedded into a dielectric matrix with DP ε_1. In the bulk of such a QD move an electron e and a hole h with effective masses m_e and m_h, respectively. The variables r_e and r_h denote the distances of the electron and the hole, respectively, from the center of the QD (see Fig. 1). The electron and hole bands are supposed parabolic. The typical dimensions of the problem are the quantities a, a_e, a_h, and $a_{\rm ex}$, where

$$a_e = \varepsilon_2\hbar^2/m_e e^2, \quad a_h = \varepsilon_2\hbar^2/m_h e^2, \quad a_{\rm ex} = \varepsilon_2\hbar^2/\mu e^2 \quad (1)$$

are the Bohr radii of the electron, hole, and exciton, respectively, in an infinite semiconductor with DP ε_2, e is the electron charge, and $\mu = m_e m_h/(m_e + m_h)$ is the reduced effective mass of the exciton. The circumstance that all the typical dimensions of the problem are considerably larger than the interatomic distance a_0 [14],

$$a,\ a_e,\ a_h\ , a_{\rm ex}\ >>\ a_0\ , \quad (2)$$

allows us to consider the motions of the electron and the hole in the QD in the effective mass approximation.

In the model concerned, the Hamiltonian of the exciton in the QD, in the framework of the approximations stated above, looks like [33, 40, 41]

$$H = -\frac{\hbar^2}{2m_e}\,\Delta_e - \frac{\hbar^2}{2m_h}\Delta_h + $$

$$+E_g + V_{eh}(r_e, r_h) + U(r_e, r_h, a), \quad (3)$$

where the first two terms define the kinetic energies of the electron and the hole, and E_g is the energy gap width in an unconfined semiconductor with DP ε_2. In Eq. (3), the energy of the electron-hole Coulomb interaction $V_{eh}\,(r_e, r_h)$ is defined as

$$V_{eh}(r_e, r_h) = -\frac{e^2}{\varepsilon_2|r_h - r_e|}\ . \quad (4)$$

Provided that $\varepsilon_2 \gg \varepsilon_1$, the polarization interaction energy $U(r_e, r_h, a)$ in Eq. (3) can be written down as an algebraic sum of the energies of the hole and electron interactions with their own images, $V_{hh'}\,(r_h, a)$ and $V_{ee'}\,(r_e, a)$, respectively, and with the images of

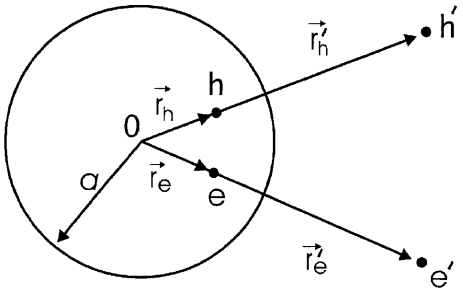

Fig. 1. Schematic image of an exciton in a spherical semiconductor nano-crystal of radius a. The radius-vectors $\vec{r}_e$ and $\vec{r}_h$ define the distances of the electron e and the holes h from the center of the nano-crystal. The point image charges of the electron, $e' = (a/r_e)e$, and the hole, $h' = -(a/r_h)e$, are situated at the distances $r_e' = a^2/r_e$ and $r_h' = a^2/r_h$, respectively, from the nano-crystal center O

"foreign" quasiparticle $V_{eh'}\,(r_e, r_h, a) = V_{he'}\,(r_e, r_h, a)$, [20, 33, 40, 41] (see Fig. 1):

$$U\,(r_e,\ r_h, a) = V_{hh'}\,(r_h, a) + V_{ee'}\,(r_e, a) +$$

$$+V_{eh'}\,(r_e, r_h, a) + V_{he'}\,(r_e, r_h, a)\,, \quad (5)$$

where

$$V_{hh'}\,(r_h, a) = \frac{e^2}{2\varepsilon_2 a}\left(\frac{a^2}{a^2 - r_h^2} + \frac{\varepsilon_2}{\varepsilon_1}\right), \quad (6)$$

$$V_{ee'}\,(r_e, a) = \frac{e^2}{2\varepsilon_2 a}\left(\frac{a^2}{a^2 - r_e^2} + \frac{\varepsilon_2}{\varepsilon_1}\right), \quad (7)$$

$$V_{eh'} = V_{he'} = -\frac{e^2}{2\varepsilon_2 a}\times$$

$$\times\frac{a}{\left[(r_e r_h/a)^2 - 2r_e r_h\cos\Theta + a^2\right]^{1/2}}, \quad \Theta = \widehat{\vec{r}_e\vec{r}_h}, \quad (8)$$

Although, in our model of the quasi-zero-dimensional system, the electron and the hole do not go beyond the space of the semiconductor QD, the potential energy of their interaction with the spherical interface of two media $U(r_e, r_h, a)$ (5) depends not only on the DP ε_2 of the QD, but also on the DP ε_1 of the matrix, into which the QD is imbedded [20–25, 33]. Such a dependence is connected to the penetration of the electrostatic field created by the electron and the hole beyond the boundaries of the QD.

The issue of revealing the effect of dimensional quantization in the QD spectra of excitonic and interband absorption was investigated theoretically for the first time in [30]. The energy spectrum of an exciton

in a QD with dimensions $a \leq a_{\rm ex}$ was obtained in the approximation, where the energy of the polarization interaction (5) of the electron and the hole with the QD surface in Hamiltonian (3) was neglected. Such an approximation was not quite justified, because, as was shown in [33, 42–47], the polarization interaction energy (5) in QDs with radii $a \leq a_{\rm ex}$ was comparable by value with the Coulomb attraction energy (4) between the electron and the hole.

The influence of the polarization interaction of an electron and a hole with the surface charge, induced by them on the plane interface semiconductor—insulator, on the reconstruction of the exciton spectrum in quantum structures was studied for the first time in [12–14,48–53].

In our works [33, 40, 41], when considering Hamiltonian (3) of the exciton in the QD, the polarization interaction (5) of charge carriers with the surface charge induced by them at the spherical interface "QD—dielectric matrix" was taken into account for the first time. Later on, such a polarization interaction was taken into account when calculating the exciton [34–36] and biexciton [35] energy spectra in the QD.

On the basis of works [33, 40, 41], we will obtain the energy spectrum of an exciton in a QD making use of the approximation, where the QD is an infinitely deep spherical potential well for an electron and a hole which move within its space. The radius a of the QD is taken as confined within the limits

$$a_h << a \leq a_e \approx a_{\rm ex}. \tag{9}$$

Then, the polarization interaction (5) plays a dominating role in the potential energy of Hamiltonian (3). Provided that condition (9) holds true, we use the adiabatic approximation, supposing the kinetic energy of an electron to have the largest value and considering the last two terms in Hamiltonian (3), as well as the operator of nonadiabaticity, in the framework of perturbation theory.

Confining ourselves to the first order of perturbation theory, we obtain the following expression for the exciton energy spectrum $E^{n_h,l_h,m_h=0}_{n_e,l_e=0,m_e=0}(S)$ in the state $(n_e, l_e = 0, m_e = 0; n_h, l_h, m_h = 0)$ in the QD with radius S [33, 40, 41]:

$$E^{n_h,l_h,0}_{n_e,0,0}(S) = E_g + T^e_{n_e,l_e=0}(S) + \bar{V}_{ee'}(S) + \lambda^{n_h,l_h,0}_{n_e,0,0}(S), \tag{10}$$

where

$$T^e_{n_e,o}(S) = E^e_{n_e,0}(S) = \frac{\pi^2 n_e^2}{S^2} \tag{11}$$

is the kinetic energy of an electron in the infinitely deep spherical well, $\bar{V}_{ee'}(S)$ is the average value of the interaction energy of an electron with its own image calculated using the wave functions of the electron in the infinitely deep spherical well of the QD,

$$\lambda^{t_h}_{n_e,0,0}(S) = \frac{P_{n_e,0}}{S} + \omega(S, n_e) \quad \left(t_h + \frac{3}{2}\right), \tag{12}$$

is the oscillator-type hole spectrum,

$$\frac{P_{n_e,o}}{S} = \bar{V}_{hh'}(S) + \left(\bar{V}^{n_e,o,o}_{eh}(S)\right)' +$$

$$+ \left(\bar{V}^{n_e,o,o}_{eh'}(S) + \bar{V}^{n_e,o,o}_{he'}(S)\right), \tag{13}$$

$$\omega(S, n_e) = 2\left(1 + \frac{2}{3}\pi^2 n_e^2\right)^{1/2}\left(\frac{m_e}{m_h}\right)^{1/2} S^{-3/2} \tag{14}$$

is the frequency of oscillations of the hole, $t_h = 2n_{r_h} + l_h = 0, 1, 2, \ldots$ is the main quantum number of the hole, and $n_{r_h} = 0, 1, 2, \ldots$ is the radial quantum number of the hole. In order the hole energy spectrum $\lambda^{t_h}_{n_e,0,0}$ (12) can be described by the spectrum of a three-dimensional harmonic oscillator, the requirement

$$S^{1/2} >> \left(\frac{m_e}{m_h}\right)^{1/2} \frac{t_h + 3/2}{\left(1 + \frac{2}{3}\pi^2 n_e^2\right)^{1/2}}. \tag{15}$$

must be fulfilled [33, 40, 41].

Let us write down the expressions for the average values of the energy of the electron interaction with its own image [33, 40, 41]

$$\bar{V}^{n_e,0,0}_{ee'}(S) = \frac{Z_{n_e,0}}{S}$$

$$\left(Z_{n_e,0} = \frac{\varepsilon_2}{\varepsilon_1} + 2\int\limits_0^1 \frac{dx \sin^2(\pi n_e x)}{1 - x^2}\right), \tag{16}$$

the energy of the hole interaction with its own image

$$\bar{V}_{hh'}(S) = \frac{1 + (\varepsilon_2/\varepsilon_1)}{S}, \tag{17}$$

the energies of the electron and hole interactions with the images of "foreign" quasiparticle

$$\bar{V}^{n_e,0,0}_{eh'}(S) + \bar{V}^{n_e,0,0}_{he'}(S) = -\frac{2}{S}, \tag{18}$$

and the electron-hole Coulomb interaction energy

$$\left(\bar{V}^{n_e,0,0}_{eh}(S)\right)' = -\frac{2}{S}\left[\ln(2\pi n_e) + \gamma - {\rm Ci}(2\pi n_e)\right],$$

$$\tilde{\bar{V}}_{eh}^{n_e,0,0;t_h}(S) = \left(\bar{V}_{eh}^{n_e,0,0}(S)\right)' + \omega(S,n_e)\left(t_h+\frac{3}{2}\right) =$$

$$= -\frac{2}{S}\left[\ln(2\pi n_e) + \gamma - \mathrm{Ci}(2\pi n_e)\right] + \omega(S,n_e)\left(t_h+\frac{3}{2}\right), \quad (19)$$

where $\mathrm{Ci}(y)$ is the cosine-integral function, $j = 0.577\ldots$ is the Euler constant.

It should be noted that formulae (12)–(19) were obtained by averaging the corresponding expressions (4), (6)–(8) using the wave functions of the infinitely deep spherical well of a QD [33, 40, 41].

The polarization interaction energy (5), averaged using the electron wave functions in the infinitely deep spherical well, looks like

$$\bar{U}_{\mathrm{pol}}^{n_e,0,0}(S) = \bar{V}_{hh'}(S) + \bar{V}_{ee'}^{n_e,0,0}(S) +$$

$$+ \left(\bar{V}_{eh'}^{n_e,0,0}(S) + \bar{V}_{he'}^{n_e,0,0}(S)\right) = \frac{Z_{n_e,0} + (\varepsilon_2/\varepsilon_1) - 1}{S}. \quad (20)$$

Hereafter, the energy is measured in terms of $\mathrm{Ry}_e = (\hbar^2/2m_e a_e^2)$, and the dimensionless variables $x = r_h/a$ and $S = a/a_e$ are used.

Taking into account Eqs. (12), (13) and (19), (20), we write down expression (10) for the exciton spectrum $E_{n_e,0,0}^{t_h}$ in the state $(n_e, 0, 0; t_h)$ in the QDs, the radii S of which satisfy conditions (9) and (15) simultaneously, as follows:

$$E_{n_e,0,0}^{t_h}(S) = E_g + T_{n_e,0}^{e}(S) \times$$

$$\times \left[1 + \frac{\bar{U}_{\mathrm{pol}}^{n_e,0,0}(S)}{T_{n_e,0}^{e}(S)} - \frac{\left|\tilde{\bar{V}}_{eh}^{n_e,0,0;t_h}(S)\right|}{T_{n_e,0}^{e}(S)}\right]. \quad (21)$$

It should be pointed out that the exciton spectrum (21) was obtained in the framework of the adiabatic approximation, where the kinetic energy of the electron $T_{n_e,0}^{e}(S)$ (11) was supposed to give the main contribution to the energy spectrum of the exciton in the QD. Therefore, formula (21) for the exciton energy spectrum $E_{n_e,0,0}^{t_h}(S)$ allows one to trace the contributions, given to the exciton spectrum by the electron-hole Coulomb interaction (19) and the polarization interaction (20) and to compare them with the contribution of the electron kinetic energy (11).

The obtained exciton spectrum (21) can be applied only to weakly excited exciton states $(n_e, 0, 0; t_h)$, for which the inequality

$$E_{n_e,0,0}^{t_h}(S) - E_g << \Delta V(S),$$

where $\Delta V(S)$ is the depth of the potential well for electrons in the QD, holds true (for example, in a CdS QD with dimensions obeying condition (9), the value of ΔV is $2.3 - 2.5$ eV [54]).

In [47], the spectrum of an exciton in a QD of radius a for a simple model of the quasi-zero-dimensional system (see Fig. 1), where the Hamiltonian of the exciton H is given by formula (3), was found within the variational method and not being restricted to the framework of the adiabatic approximation. Moreover, the radius a of the QD, contrary to [33, 40, 41], was not bounded by condition (9). The results of variational calculations of the energy spectrum of the exciton $E_0(a)$ in the QD of radius a are shown in Fig. 2. The relevant calculation parameters in work [47] corresponded to experimental conditions in works [17, 18, 54, 55].

3. Contributions of Kinetic, Polarization, and Coulomb Energies to the Spectra of Excitons in Quantum Dots

In works [17, 55], the peaks of interband absorption in spherical QDs with radius a within the interval of 1.2–30 nm, which were made of CdS with DP $\varepsilon_2 = 9.3$ and dispersed in a transparent matrix of silicate glass with DP $\varepsilon_1 = 2.25$ [31], were observed. The effective masses of the electron and the hole and the reduced mass of the exciton μ in CdS were $m_e/m_0 = 0.205$, $m_h/m_0 = 5$, and $\mu/m_0 = 0.197$, respectively [56]. In particular, the dependence of the positions of the adsorption band of QDs caused by interband transitions onto the dimensional quantization levels ($n_e = 1$, $l_e = 0$), ($n_e = 1$, $l_e = 1$), and ($n_e = 1$, $l_e = 2$) of the electron in the conduction band on the QD radius a was experimentally determined [17, 55].

In the experimental work [57], the peaks of brightening connected to the transitions between the dimensional quantization levels of the exciton were observed in the transmission spectra of the CdSe QDs with DP $\varepsilon_2 = 9.4$ and radius $a \approx 5$ mn, dispersed in matrices of silicate glass with DP $\varepsilon_1 = 2.25$ [31]. The effective masses of the electron and the hole and the reduced mass of the exciton μ in CdSe were $m_e/m_0 = 0.13$, $m_h/m_0 = 2.5$, and $\mu/m_0 = 0.124$, respectively [56], i.e. $m_e/m_h \ll 1$.

As was shown in [33, 40–47], formula (21) describes the exciton spectrum $E^{t_h}_{1,0,0}(S)$ as a function of the QD radius S with sufficient accuracy under the reported conditions of experiments in the CdS [17, 55] and CdSe [57] QDs. The parameters of the exciton spectrum $E^{t_h}_{1,0,0}(S)$ (21) under the experimental conditions [17, 55] for the CdS QDs with the radius $a = 1.5 - 3.0$ nm are listed in Tables 1 and 2.

According to formulae (20), (19), and (11), the ratios between the polarization interaction energy and the electron kinetic energy $\bar{U}^{1,0,0}_{\rm pol}(S)/T^e_{1,0}(S)$ and between the Coulomb interaction energy and the electron kinetic energy $\tilde{\bar{V}}^{1,0,0}_{eh}(S)/T^e_{1,0}(S)$ are proportional to S and $S^{1/2}$, respectively. Such a behavior of the ratios $\bar{U}_{\rm pol}(S)/T^e_{1,0}(S)$ (20) and $\tilde{\bar{V}}^{1,0,0;t_h}(S)/T^e_{1,0}(S)$ (19) is also confirmed by numerical data in Tables 1 and 2.

From Tables 1 and 2, it follows that the polarization interaction energy $\bar{U}^{1,0,0}_{\rm pol}(S)$ (20) makes the dominating contribution to the exciton energy spectrum (21), whereas the Coulomb interaction energy $\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)$ (19) makes a small negative one. Namely, the ratio $\bar{U}^{1,0,0}_{\rm pol}(S)/T^e_{1,0}(S)$ varies from 55.8% at $a = 1.5$ nm to 112% at $a = 3$ nm, whereas the absolute value of the ratio $\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)/T^e_{1,0}(S)$ from 8.5% at $a = 1.5$ nm to 30% at $a = 3$ nm. The data presented in Table 2 are also confirmed by the results of variational calculations of the spectrum $E_0(a)$ of the exciton in the QD of radius $a \leq 3a_{\rm ex}$, which were obtained in work [47] under the experimental conditions of works [17, 55] and beyond the adiabatic approximation.

The main contributions to the polarization interaction energy $\bar{U}^{1,0,0}_{\rm pol}(S)$ (20) are made by the interaction energies of the electron $\bar{V}^{1,0,0}_{ee'}(S)$ (16) (64.5%) and the hole $\bar{V}^{1,0,0}_{hh'}(S)$ (17) (58.2%) with their own images, whereas the interaction energy of the

Table 1. Parameters of the exciton energy spectrum $E^{t_h}_{1,0,0}(a)$ (10) and (21) for cadmium sulfide QDs with radii $a = 1.5 \div 3.0$ nm under the conditions of experiments in [17, 55]

a (nm) (S)	$T^e_{1,0}(S)$ (Ry$_e$)	$\left\lvert\bar{V}^{1,0,0}_{eh}(S)\right\rvert'$ (Ry$_e$)	$\omega(S)$ (Ry$_e$)	t_h	$\left\lvert\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)\right\rvert$ (Ry$_e$)	$\bar{V}^{1,0,0}_{ee'}(S)$ (Ry$_e$)	$\bar{V}^{1,0,0}_{hh'}(S)$ (Ry$_e$)	$\left\lvert\bar{V}^{1,0,0}_{eh'}(S)+\bar{V}^{1,0,0}_{he'}(S)\right\rvert$ (Ry$_e$)	$\bar{U}^{1,0,0}_{\rm pol}(S)$ (Ry$_e$)	$\left[E^{t_h}_{1,0,0}(S)-E_g\right]$ (Ry$_e$)
1.5				0	4.41	9.12	8.23	3.21	14.14	35.08
(0.624)	25.35	7.80	2.26	1	2.15					37.34
				2	0.11					39.61
2.0				0	3.65	6.84	6.17	2.40	10.61	21.21
(0.83)	14.26	5.85	1.47	1	2.18					22.68
				2	0.71					24.15
2.5				0	3.11	5.47	4.936	1.92	8.49	14.51
(1.04)	9.126	4.68	1.051	1	2.05					15.56
				2	1.00					16.61
3.0				0	2.70	4.56	4.11	1.60	7.07	10.71
(1.25)	6.338	3.90	0.8	1	1.90					11.51
				2	1.10					12.31

N o t e. The energies $\left(\bar{V}^{1,0,0}_{eh}(S)\right)'$ and $\bar{V}^{1,0,0}_{eh'}(S)+\bar{V}^{1,0,0}_{he'}(S)$ are negative. Ry$_e = 7.68 \times 10^{-1}$ eV.

Table 2. Contributions to the exciton spectrum $E^{t_h}_{1,0,0}(a)$ (10) and (21) made by the electron-hole Coulomb, $\left\lvert\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(a)\right\rvert$ (19), and polarization, $\bar{U}^{1,0,0}_{\rm pol}(a)$ (20), interaction energies in relation to the contribution of the electron kinetic energy $T^e_{1,0}(a)$ (11)

a (nm) (S)	$T^e_{1,0}(S)$ (Ry$_e$)	t_h	$\lvert\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)\rvert/T^e_{1,0}(S)$ (%)	$\bar{U}^{1,0,0}_{\rm pol}(S)/T^e_{1,0}(S)$ (%)	$\left[E^{t_h}_{1,0,0}(S)-E_g\right]$ (Ry$_e$)
1.5		0	17.4	55.8	35.08
(0.624)	25.35	1	8.5		37.34
2.0		0	25.6	74.4	21.21
(0.83)	14.26	1	15.3		22.68
2.5		0	34.0	93.0	14.51
(1.04)	9.13	1	22.5		15.56
3.0		0	42.6	111.5	10.71
(1.25)	6.34	1	30.0		11.51

N o t e. The ratio $\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(a)/T^e_{1,0}(a)$ is negative. The data are listed for the CdS QD with radii $a = 1.5 \div 3.0$ nm under the conditions of experiments in [17, 55]. Ry$_e = 7.68 \times 10^{-1}$ eV.

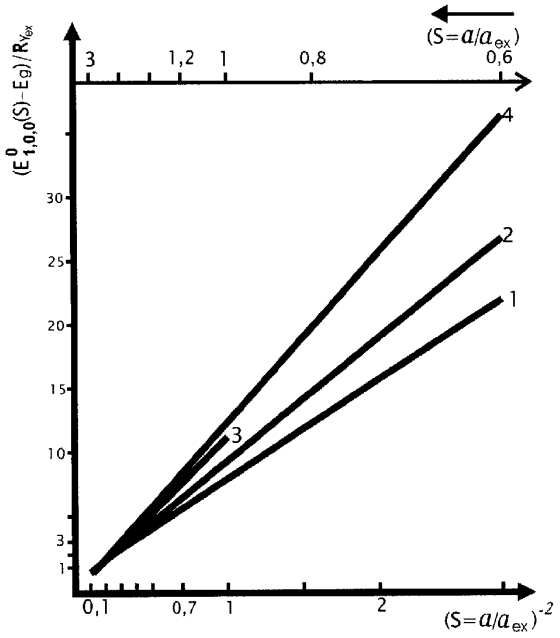

Fig. 2. The exciton energy spectra $E^0_{1,0,0}(S)$ as the functions of the nano-crystal dimension $S = a/a_{\rm ex}$: *1* — the experimental exciton spectrum [17, 55], *2* — the kinetic energy of the electron $T^e_{1,0}(S)$ (11), *3* – the exciton spectrum obtained by the variational method [47], and *4* — the exciton spectrum (10), (21) calculated in the framework of the adiabatic approximation

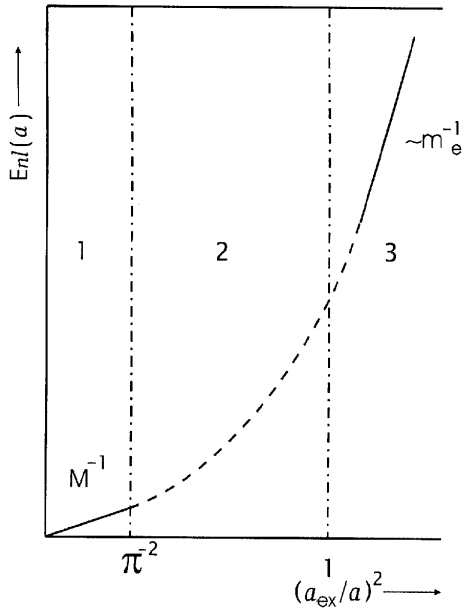

Fig. 3. Schematic dependence $E_{nl}(a)$ of the exciton energy spectrum on the radius of the nano-crystal. *1* — the range of radius which corresponds to the approximation of strong dimensional quantization $a \ll a_{\rm ex}$, *2* — the range of radius where $a \approx a_{\rm ex}$ (9), and *3* — the range of the large QD radius $a \gg a_{\rm ex}$. This figure is taken from work [19]

electron and the hole with the images of "others" $\bar{V}^{1,0,0}_{eh'}(S) + \bar{V}^{1,0,0}_{he'}(S)$ (18) gives a negative contribution, whose absolute value is 22.7% (see Table 3). It is essential that those contributions do not depend on the QD radius S.

The Coulomb interaction energy $\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)$ (19) makes a considerably smaller contribution to the exciton spectrum (10) and (21) in comparison with the polarization interaction energy $\bar{U}^{1,0,0}_{\rm pol}(S)$ (20). The ratio of these energies $\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)/\bar{U}^{1,0,0}_{\rm pol}(S)$ becomes negative

T a b l e 3. Contributions to the polarization interaction energy $\bar{U}^{1,0,0}_{\rm pol}(a)$ (20) made by the interaction of the electron with its own image, $\bar{V}^{1,0,0}_{ee'}(a)$ (16), by the interaction of the hole with its own image, $\bar{V}^{1,0,0}_{hh'}(a)$ (17), and by the interactions of the electron and the hole with the hole and electron image, respectively, $\left|\bar{V}^{1,0,0}_{eh'}(a) + \bar{V}^{1,0,0}_{he'}(a)\right|$ (18), as well as the ratio $\left|\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(a)/\bar{U}^{1,0,0}_{\rm pol}(a)\right|$ between the Coulomb and polarization interaction energies (19) and (20)

a(nm) (S)	$\bar{U}^{1,0,0}_{\rm pol}(S)$ (Ry$_e$)	$\bar{V}^{1,0,0}_{hh'}(S)/\bar{U}^{1,0,0}_{\rm pol}(S)$ (%)	$\bar{V}^{1,0,0}_{ee'}(S)/\bar{U}^{1,0,0}_{\rm pol}(S)$ (%)	$\left\|\bar{V}^{1,0,0}_{eh'}(S) + \bar{V}^{1,0,0}_{he'}(S)\right\|/U^{1,0,0}_{\rm pol}(S)$ (%)	t_h	$\lvert\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)\rvert/\bar{U}^{1,0,0}_{\rm pol}(S)$ (%)
1.5					0	31.2
(0.624)	14.14	64.5	58.2	22.7	1	15.2
2.0					0	34.4
(0.83)	10.61	64.5	58.2	22.7	1	20.5
2.5					0	36.6
(1.04)	8.49	64.5	58.2	22.7	1	24.2
3.0					0	38.2
(1.25)	7.07	64.5	58.2	22.7	1	26.9

N o t e. The ratios $\left(\bar{V}^{1,0,0}_{eh'}(S) + \bar{V}^{1,0,0}_{he'}(S)\right)/\bar{U}^{1,0,0}_{\rm pol}(S)$ and $\tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)/\bar{U}^{1,0,0}_{\rm pol}(S)$ are negative. The data are listed for the CdS QD with radii $a = 1.5 \div 3.0$ nm under the conditions of experiments in [17, 55].

(its absolute value changes from 31 and 15% at a = 1.5 nm to 38 and 27% at a = 3 nm for t_h = 0 and 1, respectively (see Table 3).

The experimental exciton spectrum was stated in works [17, 55] to be described with sufficient accuracy by the kinetic energy of the electron in the QD $T^e_{1,0}(a)$ (11) as the radius a of the CdS QD increases above 2.0 nm. Actually, as follows from Table 2, the ratio $\left|\bar{U}^{1,0,0}_{\rm pol}(S) + \tilde{\bar{V}}^{1,0,0;t_h}_{eh}(S)\right| / T^e_{1,0}(S)$ of the sum of the polarization and Coulomb interaction energies to the kinetic energy of the electron comprises a significant value of 0.49–0.69. Even for the QD with the smallest experimentally allowable radius a = 1.5 nm, such a ratio amounts to a substantial value of about 38% (see Fig. 2).

4. Emergence of the Bulk Exciton in a Quasi-Zero-Dimensional System

For the QD with a small radius $a \ll a_{\rm ex}$, the main contribution to the exciton spectrum (21) is given by the electron kinetic energy $T^e_{n_e,l_e}(S)$ (11), whereas the contributions of the terms $\bar{U}^{n_e,0,0}_{\rm pol}(S)$ and $\tilde{\bar{V}}^{n_e,0,0;t_h}_{eh}(S)$ are small: $\bar{U}^{n_e,0,0}_{\rm pol}(S)/T^e_{n_e,l_e}(S) \ll 1$, $\left|\tilde{\bar{V}}^{n_e,0,0;t_h}_{eh}(S)/T^e_{n_e,l_e}(S)\right| \ll 1$ [33, 40–47].

For the QD with a large radius $a \gg a_{\rm ex}$, the exciton is quantized as a whole, and its energy spectrum is determined as [30]

$$E_{nl}(a) = E_g - E_{\rm ex} + \frac{\hbar^2}{2M\,a^2}\varphi^2_{nl},$$

$$E_{\rm ex} = -{\rm Ry}_{\rm ex} = -\frac{\hbar^2}{2\mu\,a^2_{\rm ex}}, \qquad (22)$$

where M is the translational mass of the exciton, and φ_{nl} are the roots of the Bessel function $J_{l+\frac{1}{2}}(\varphi)$.

In work [58], an expression for the exciton spectrum was obtained by the variational method in the framework of the effective mass approximation but without regard for the polarization interaction energies of an electron and a hole with the surface of the QD, which made it possible to trace the limit transition to the spectrum of the bulk exciton (22), starting from the QD radius $S_{\rm ex} > S^0_{\rm ex} \geq 8$.

The spectrum of the exciton in the CdS QD, which was found by us in work [47] by the variational method in the framework of the effective mass approximation by taking into account the polarization interaction energy, turns into the spectrum of the bulk exciton (22) at $S_{\rm ex} > \tilde{S}^0_{\rm ex} \geq 9.44$ under the experimental conditions of works [17–19, 55]. In this case, the value of $\tilde{S}^0_{\rm ex}$ differs from that of $S^0_{\rm ex}$ by no more than 18%. Such a difference is connected to the fact that the account of the polarization interaction energy (it has not been done in work [58]) results in the exciton energy growth proportional to S^{-1}. In addition, the values of the QD radii $S^0_{\rm ex}$ and $\tilde{S}^0_{\rm ex}$ can be overestimated to a certain extent, because the variational calculations of the exciton spectrum yield the overestimated values of energy.

5. Conclusions

The schematic plot of the dependence $E_{nl}(a)$ of the exciton energy spectrum on the QD radius was built in work [19] (see Fig. 3). The expression for the exciton spectrum $E_{nl}(a)$ was obtained in work [30] in the framework of the adiabatic approximation. The relevant dependences for only two limit cases, the QDs with small ($a \ll a_{\rm ex}$) and large ($a \gg a_{\rm ex}$) radii, are depicted in Fig. 3. In these two limit cases, the exciton spectrum $E_{nl}(a)$ depends linearly on a^{-2}. In the case $a \ll a_{\rm ex}$, the slope of the linear dependence $E_{nl}(a^{-2})$, according to expression (11), is governed by the value of the effective electron mass m_e, i.e. $E_{nl}(a) \sim m_e^{-1}a^{-2}$, whereas, in the opposite limit case $a \gg a_{\rm ex}$, this slope, according to Eq. (22), was determined by the value of the translational mass of the exciton M, i.e. $E_{nl}(a) \sim M^{-1}a^{-2}$. For the QDs with radius $a \approx a_{\rm ex}$ (9), the dependence $E_{nl}(a)$ has not been determined.

Here, in the framework of the simple model of a quasi-zero-dimensional system, we have shown that, even for the QDs with the smallest experimentally allowable radii, the kinetic energy of the electron (11) makes a contribution to the exciton spectrum $E^{t_h}_{n_e,0,0}(a)$ (10) and (21) that is comparable by the order of magnitude with the contributions made to this spectrum by the polarization, $\bar{U}^{n_e,0,0}_{\rm pol}(a)$ (20), and Coulomb, $\tilde{\bar{V}}^{n_e,0,0;t_h}_{eh}(a)$ (19), interaction energies. In this connection, a description of the exciton spectrum in QDs with radii $a < a_{\rm ex}$ using only the expression for the electron kinetic energy $T^e_{nl}(a)$ (11), as it has been done in works [15–19], is not justified.

In the least studied case where the QD radius a is comparable by value with the Bohr radius of the exciton, we showed [33, 40–47] that the exciton spectrum $E^{t_h}_{n_e,0,0}(a)$ (10) and (21) can be described by the complicated dependence

$$E^{t_h}_{n_e,0,0}(a) = f\left(a^{-1},\ a^{-3/2},\ a^{-2},\ m_e^{-1},\ m_h^{-1}\right)$$

(see Fig. 2). In this case, the effective masses of the electron m_e and the exciton μ are the functions of the QD radius a [42–47].

The author is grateful to V.M. Agranovich, I.V. Blons'kyi, M.Ya. Valakh, M.O. Efremov, M.R. Kulish, D.V. Korbutyak, M.P. Lisitsa, V.G. Litovchenko, E.A. Pashitskii, V.I. Sugakov, M.V. Tkach, and P.M. Tomchuk for discussion of the results obtained.

1. *Alferov Zh.I.* // Fiz. Tekhn. Polupr. — 1998. — **32**, N 1. — P. 3—18.
2. *Yoffe A.D.* // Adv. Phys. — 1993. — **42**, N 1.— P. 173—185.
3. *Tkach M.* Quasiparticles in Nanoheterosystems. Quantum Dots and Wires. — Chernivtsi: Chernivtsi Nat. Univ., 2003 (in Ukrainian).
4. *Ledentsov N.N., Ustinov V.M., Shchukin V.A. et al.* // Fiz. Tekhn. Polupr. — 1998. — **32**, N 4. — P. 385—396.
5. *Banyai L., Koch S.W.* Semiconductor Quantum Dots. – Singapore: World Scientific, 1993.
6. *Kulish N.R., Kunets V.P., Lisitsa M.P.* // Kwant. elektronika. — 1994. — **75**. — P. 75—102; Ukr. Fiz. Zh. — 1990. — **35**, N 12. — P. 1817—1823; Ibid. — 1996. — **41**, N 11–12. — P. 1865—1871.
7. *Gaponenko S.V.* // Fiz. Tekhn. Polupr. — 1996. — **30**, N 4. — P. 577—601.
8. *Pokutnyi S.I.* Theory of Excitons in Quasi-zero-dimensional Semiconducting Systems. — Odesa: Astroprint, 2003 (in Russian).
9. *Ledentsov N.N., Ustinov V.M., Shchukin V.A.* // Fiz. Tekhn. Polupr. — 1998. — **32**, N 4. — P. 385—391.
10. *Evtikhiev V.P., Kudryashov I.V., Kotelnikov E.Yu.* // Ibid. — N 12. — P. 1482—1486.
11. *Tsatsulnikov A.F., Ledentsov N.N., Maksimov M.V.* // Ibid. — 1996. — **30**, N 10. — P. 1822—1827.
12. *Litovchenko V.G.* Fundamentals of Physics of Semiconducting Layered Systems. — Kyiv: Naukova Dumka, 1980 (in Russian).
13. *Dobrovolskii V.N., Litovchenko V.G.* Transport of Electrons and Holes near the Surface of Semiconductors. — Kyiv: Naukova Dumka, 1985 (in Russian).
14. *Agranovich V.M., Lozovik Yu.E.* // Pis'ma Zh. Eksp. Teor. Fiz. — 1973. — **17**, N 4. — P. 209—211.
15. *Ekimov A.I., Onushchenko A.A.* // Ibid. — 1981. — **34**, N 6. — P. 363—366.
16. *Ekimov A.I., Onushchenko A.A.* // Fiz. Tekhn. Polupr. — 1982. — **16**, N 7. — P. 1215—1219.
17. *Ekimov A.I., Onushchenko A.A.* // Pis'ma Zh. Eksp. Teor. Fiz. — 1984. — **40**, N 8. — P. 337—340.
18. *Ekimov A.I., Onushchenko A.A., Efros Al.L.* // Ibid. — 1986. — **43**, N 6. — P. 292—294.
19. *Ekimov A.I., Efros Al.L.* // Phys. status solidi (b). — 1988. — **150**, N 2. — 627—634.
20. *Efremov N.A., Pokutnyi S.I.* — Moscow, 1984. — (Preprint, Acad. Sci. USSR, Institute of Spectroscopy, N 1) (in Russian).
21. *Efremov N.A., Pokutnyi S.I.* // Fiz. Tverd. Tela. — 1985. — **27**, N 1. — P. 48—56.
22. *Efremov N.A., Pokutnyi S.I.* // Ibid. — 1990. — **32**, N 10. — P. 2921—2930.
23. *Efremov N.A., Pokutnyi S.I.* // Ibid. — 1991. — **33**, N 10. — P. 2845—2851.
24. *Pokutnyi S.I., Efremov N.A.* // Phys. status solidi (b). — 1991. — **165**, N 1. — 109—118.
25. *Pokutnyi S.I.* // Ibid. — 1992. — **172**, N 2. — 573—582.
26. *Pokutnyi S.I.* // Fiz. Tverd. Tela. — 1993. — **35**, N 2. — P. 257—264.
27. *Pokutnyi S.I.* // Fiz. Tekhn. Polupr. — 1997. — **31**, N 12. — P. 1443—1448.
28. *Andryushin E.A., Silin A.P.* // Fiz. Tverd. Tela. — 1991. — **33**, N 1. — P. 211–215.
29. *Watanabe H., Inoshita T.* // Optoelectron. Device Technol. — 1986. — **1**, N 1. — P. 33—38.
30. *Efros Al.L., Efros A.L.* // Fiz. Tekhn. Polupr. — 1982. – **16**, N 7. — P. 1209—1214.
31. *Ekimov A.I., Onushchenko A.A., Raikh M.E., Efros Al.L.* // Zh. Eksp. Teor. Fiz. — 1986. — **90**, N 5. — P. 1795—1807.
32. *Ekimov A.I., Onushchenko A.A., Plyukhin A.G., Efros Al.L.* // Ibid. — 1985. — **88**, N 4. — P. 1490—1501.
33. *Efremov N.A., Pokutnyi S.I.* // Fiz. Tverd. Tela. — 1990. — **32**, N 6. — P. 1637—1643.
34. *Tkach N.V., Golovatskii V.A.* // Ibid. — N 8. — P. 2512—2513.
35. *Grigoryan G.V., Rodina A.V., Efros Al.L.* // Ibid. — N 12. — P. 3512—3521.
36. *Banyai L., Gilliot P., Hu Y.Z., Koch. S.W.* // Phys. Rev. B. — 1992. — **45**, N 24. — P. 14136—14143.
37. *Shinojima H., Yumoto J., Uesugi N.* // Appl. Phys. Lett. – 1992. — **60**, N 3. — P. 298–301.
38. *Pokutnyi S.I., Salejda W., Jacak L., Misiewicz J.* // Optica Applic. — 2002. — **32**, N 1–2. — P. 147—156.
39. *Pokutnyi S.I.* // Phys. Low-Dim. Struct. — 2002. – **11–12**. — P. 67—76.
40. *Pokutnyi S.I.* // Fiz. Tekhn. Polupr. — 1991. – **25**, N 4. — P. 628—632.
41. *Pokutnyi S.I.* // Phys. Lett. A. — 1992. — **168**, N 5—6. — P. 433—436.
42. *Pokutnyi S.I.* // Ukr. Fiz. Zh. — 1995. — **40**, N 7. — P. 743—745.
43. *Pokutnyi S.I.* // Phys. Lett. A. — 1995. — **203**, N 5—6. — P. 388—394.
44. *Pokutnyi S.I.* // Fiz. Tverd. Tela. — 1996. — **38**, N 2. — P. 512—521.
45. *Pokutnyi S.I.* // Fiz. Tekhn. Polupr. — 1996. — **30**, N 11. — P. 1952—1959; Ukr. Fiz. Zh. — 1997. — **42**, N 1. — P. 111—114.
46. *Pokutnyi S.I.* // Fiz. Tekhn. Polupr. –.1996. — **30**, N 7. — P. 1320—1323.
47. *Pokutnyi S.I.* // Fiz. Tverd. Tela. — 1996. — **38**, N 9. — P. 2667—2672.

48. *Deigen M.F., Glinchuk M.D.* // Ibid. — 1963. — **5**, N 11. — P. 3250—3258.

49. *Litovchenko V.G.* // Thin Solid Films. — 1976. — **36**, N 1. — P. 205—215.

50. *Lozovik Yu.E., Nishanov V.N.* // Fiz. Tverd. Tela. — 1976. — **18**, N 11. — P. 3267—3272.

51. *Zuev V.A., Korbutyak D.V., Kurik M.V., Litovchenko V.G.* // Pis'ma Zh. Eksp. Teor. Fiz. — 1977. — **26**, N 6. — P. 455—459.

52. *Pokatilov E.P., Beril S.I., Fomin V.M. et al.* // Phys. status solidi (b). — 1988. — **145**, N 2. — P. 535–544.

53. *Litovchenko V.G., Beril S.I., Korbutyak D.V., Lashkevich E.G.* // Dopovidi AN UkrSSR, ser. A. — 1988. — **32**, N 2. — P. 57—61.

54. *Grabovskis V.Ya., Dzenis Ya.Ya., Ekimov A.I.* // Fiz. Tverd. Tela. — 1989. — **31**, N 1. — P. 272—275.

55. *Chepik D., Efros A., Ekimov A.* // J. Lumin. — 1990. – **47**, N 3. — P. 113—118.

56. *Gavrilenko V.I., Grekhov A.M., Korbutyak D.V., Litovchenko V.G.* Optical Properties of Semiconductors: A Handbook. — Kyiv: Naukova Dumka, 1987 (in Russian).

57. *Vandyshev Yu.V., Dneprovskii V.S., Klimov V.I.* // Zh. Eksp. Teor. Fiz. — 1992. — **101**, N 1. — P. 270—277.

58. *Tkach N.V., Golovatskii V.A.* — Kyiv, 1990. — (Preprint, Acad. Sci. UkrSSR, Institute of Theoretical Physics, N 90—59 R) (in Russian).

Received 28.05.04.
Translated from Ukrainian by O.I.Voitenko

ЕКСИТОННІ СТАНИ У НАПІВПРОВІДНИКОВИХ КВАЗІНУЛЬВИМІРНИХ СИСТЕМАХ

С.І. Покутній

Р е з ю м е

Проаналізовано внески в енергетичний спектр екситона в напівпровідниковій квантовій точці (КТ), які дають кінетична енергія електрона і дірки, енергія кулонівської взаємодії між ними та енергія поляризаційної взаємодії електрона і дірки зі сферичною поверхнею поділу КТ — діелектричне середовище. Прослідковано граничний перехід спектра екситона в КТ у спектр об'ємного екситона.