INFLUENCE OF POLARIZATION INTERACTION ON THE EXCITON ENERGY SPECTRUM IN SEMICONDUCTOR NANOCRYSTALS

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A theory of the exciton energy spectrum in a semiconductor spherical nanocrystal (SN) is developed under the conditions where the dominant role is played by polarization interaction of an electron and a hole with the SN-dielectric matrix interface. A new modified effective mass approximation used for the description of the exciton energy spectrum in a semiconductor SN with radii a comparable to the Bohr radius of the exciton $a_{\rm ex}^0$ is proposed. It is shown that, in the framework of the model simulating SN as an infinite-depth potential well, the effective mass approximation can be used for the description of exciton states in SNs with radii $a \approx a_{\rm ex}^0$ considering that the reduced mass of the exciton μ represents a function of the SN radius a.

1. Introduction

Progress in solid-state technology allows one to obtain semiconductor quasizero-dimensional structures such as a semiconductor SN with radii $a \approx 1 \div 10$ nm grown in transparent dielectric (or semiconductor) matrices [1–10]. Such linear dimensions a of SNs are comparable to the de Broglie wavelength of an electron and a hole and (or) to their Bohr radii. This results in the fact that the phenomena of space dimensional quantization of charge carriers play a dominant role in optical and electrooptical processes in such nanosystems [8–18].

As the energy gap of a semiconductor material that contains SNs in its bulk is essentially lower than that in dielectric (semiconductor) matrices, the motion of charge carriers in an SN is limited by its volume in all three dimensions. That is, charge carriers move in a three-dimensional spherical potential well. This results in the fact that quasiparticles (electron, hole, and exciton) in an SN have no quasimomentum. Thus, one can consider only states of quasiparticles in SNs. In what follows, we'll understand by an exciton in SNs such an exciton state that has no quasimomentum [11–14].

Within the framework of the adiabatic approximation (in which $m_e \ll m_h$, where m_e and m_h denote effective masses of an electron and a hole in an SN) and the effective mass approximation, with regard for the electron-hole Coulomb interaction in the exciton Hamiltonian as well as the polarization interaction of an electron and a hole with the SN surface, the energy spectrum of the exciton in SN was obtained in [19] as a function of the SN radius a using only the first order of perturbation theory for the wave functions of an electron in a spherical potential well of infinite depth. In [19], the value of the critical radius a_c was found, starting from which a bulk exciton appears in an SN with the radius $a \geq a_c$. An exciton, whose structure (effective mass, Bohr radius, and binding energy) in an SN doesn't differ from that in an unlimited semiconductor material, will be called a bulk exciton.

In [20, 21] in the framework of the adiabatic and effective mass approximations, the energy spectrum of an exciton in an SN as a function of the SN radius a and the potential well depth, $\Delta V(a)$, was obtained within the model, in which an SN was simulated by a finite-depth potential well. In these papers, the value of the SN critical radius a_c was also obtained. In [22], not restricting to the adiabatic approximation, the energy spectrum of an exciton in SN was derived as a function of the SN radius a with the help of the variational method within the effective mass approximation.

The majority of approaches to the description of physical properties of a semiconductor SN can be conventionally divided into two groups [8–13,23]: 1) description from the position of a solid body in the context of the band theory in its one-electron approximation [1–24], and 2) description from the position of a separate atom in the context of the quantum chemical cluster approach, where an SN is considered as a large molecule [25].

In the framework of the former approach, an SN was considered as a nanocrystal that has periodic crystal structure. Quasiparticles (electron, hole, and exciton) that moved in the SN considered to possess a certain effective mass in the same way as in a massive

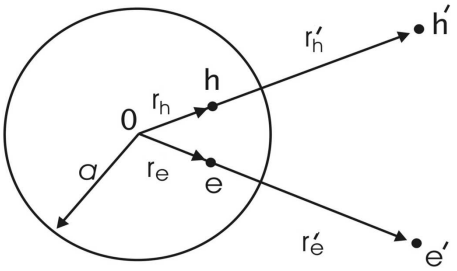

Fig. 1. Diagram of an exciton in a semiconductor SN. The radius-vectors r_e and r_h denote the distance of the electron e and the hole h from the center of an SN with radius a. The charges of the images $e' = (a/r_e)\, e$ and $h' = (a/r_h)\, e$ are located at the distances $r_e = a^2/r_e$ and $r_h = a^2/r_h$ from the SN center *0* and represent the point charges of the electron and hole images, respectively

monocrystal. In this case, the effect of dimensional quantization was explained by the motion of a quasiparticle in a potential well of infinite depth (to which an SN was like) [1–7]. The problem of correctness of such an approach, the domain of its applicability for small SN dimensions a, and the change of parameters of a monocrystal in the case of the transition to dimensions a of the quantum scale remain incompletely solved [9–14, 23].

In the majority of theoretical models, where the energy spectra of quasiparticles in SNs were obtained, the authors used the approximation of effective mass that was ascribed to an SN in the same way as to massive monocrystals [9–24]. In this case, the question appeared: which are the minimal SN dimensions a, where the effective mass approximation is still valid? A partial answer to this question was given in [26]. In that paper, the results of calculations of the energy gap width E_g of Si nanocrystals in vacuum (porous silicon) obtained in the effective mass approximation were compared with the results of quantum chemical calculations which didn't use parameters of massive monocrystals [27–30].

The calculation of the quantity E_g in an SN with small radius $a < a^0_{\rm ex}$ (where $a^0_{\rm ex}$ is the Bohr radius of an exciton in a semiconductor material contained in the SN bulk) performed in [26] in the effective mass approximation provided a strongly overstated value of E_g as compared with the magnitude of E^0_g of a massive silicon monocrystal. In this case, in order to calculate E_g in a silicon SN, it's necessary to use quantum chemical cluster methods, as well as those based on the microscopic-statistical approach [27–30].

Large-radius SNs ($a \gg a^0_{\rm ex}$) were described to a satisfactory accuracy by macroscopic optical parameters (energy gap width, effective masses of quasiparticles, and permittivity) that characterized the corresponding massive semiconductor monocrystals [1–7, 11–13, 23, 26].

The least investigated SNs are those having radii a comparable with the Bohr radius of an exciton $a^0_{\rm ex}$. The problem of applicability of the effective mass approximation to the description of such SNs remains unsolved till now [9–14, 23].

In the present paper, the theory of the exciton energy spectrum in a semiconductor SN is developed under conditions where the polarization interaction of an electron and a hole with the spherical SN-dielectric matrix interface plays a dominant role. A new modified effective mass approximation is proposed and is used for the description of the exciton energy spectrum in semiconductor SNs with radii $a \approx a^0_{\rm ex}$. It is demonstrated that, in the framework of the SN model, in which an SN is simulated with the help of an infinitely deep potential well, the effective mass approximation can be applied to the description of exciton states in an SN with radii a comparable with the Bohr radius $a^0_{\rm ex}$ of an exciton taking into account that the reduced effective mass of an exciton $\mu = \mu(a)$ represents a function of the SN radius a.

2. Exciton Hamiltonian in a Semiconductor Nanocrystal

Following [12–14, 17, 19–22], we consider the following simple model of a quasizero-dimensional system: a neutral semiconductor SN with radius a. In its bulk, a semiconductor material with permittivity ε_2 is immersed into the dielectric (semiconductor) matrix with permittivity ε_1. An electron e and a hole h with the effective masses m_e and m_h move in the bulk of such an SN ($\mathbf{r}_e$ and $\mathbf{r}_h$ are the distances of the electron and the hole from the SN center) (see Fig. 1). We assume that the bands of electrons and holes have parabolic form. The characteristic dimensions of the problem are the quantities : a, a_e, a_h, and $a^0_{\rm ex}$, where

$$a_e = \frac{\varepsilon_2 \hbar^2}{m^0_e e^2}, \quad a_h = \frac{\varepsilon_2 \hbar^2}{m^0_h e^2}, \quad a^0_{\rm ex} = \frac{\varepsilon_2 \hbar^2}{\mu_0 e^2} \tag{1}$$

are the Bohr radii of the electron, hole, and exciton, respectively, in the unlimited semiconductor with permittivity ε_2 (e is the electron charge), m^0_e, m^0_h, and $\mu_0 = m^0_e m^0_h/(m^0_e + m^0_h)$ are the effective masses of the electron and the hole and the reduced effective mass of the exciton, respectively, in the unlimited semiconductor with permittivity ε_2.

The conditions of localization of a charge carrier in the neighborhood of a spherical dielectric nanoparticle were analyzed by us in [31–35], where the problem concerning the field induced by a charge carrier in the neighborhood of a dielectric nanoparticle immersed into the dielectric medium was completely solved analytically, and the analytic expressions for the potential energy of interaction of a charge carrier with the spherical interface of two media were given.

In the investigated simple model of a quasizero-dimensional system, the energy of interaction of the electron e and the hole h located in the bulk of an SN at the points $\mathbf{r}_e$ and $\mathbf{r}_h$, respectively, with the polarization field induced by these quasiparticles can be presented as follows [36]:

$$U(\mathbf{r}_e,\mathbf{r}_h,a)=$$

$$=-\frac{e^2\beta}{\varepsilon_2 a}[(r_e r_h/a^2)^2-2(r_e r_h/a^2)\cos\theta+1]^{-1/2}-$$

$$-\frac{e^2\beta}{2(\varepsilon_2+\varepsilon_1)a}\int\limits_0^\infty \frac{dy(a^2/r_h y)^\alpha\Theta(y-(a^2/r_h))}{|\mathbf{r}_e-y(\mathbf{r}_h/r_h)|}-$$

$$-\frac{e^2\beta}{2(\varepsilon_2+\varepsilon_1)a}\int\limits_0^\infty \frac{dy(a^2/r_e y)^\alpha\Theta(y-(a^2/r_e))}{|\mathbf{r}_h-y(\mathbf{r}_e/r_e)|}, \qquad (2)$$

where the parameter $\beta=(\varepsilon_2-\varepsilon_1)/(\varepsilon_2+\varepsilon_1)$, the angle $\theta=\widehat{\mathbf{r}_e,\mathbf{r}_h}$, while $\Theta(x)$ stands for the Heaviside function.

The energy of polarization interaction $U(\mathbf{r}_e,\mathbf{r}_h,a)$ (2) at the relative permittivity $\varepsilon=(\varepsilon_2/\varepsilon_1)\gg 1$ can be presented in the form of the algebraic sum of the interaction energies of the electron and the hole with the own $V_{hh'}(r_h,a)$, $V_{ee'}(r_e,a)$ and "extraneous" $V_{eh'}(r_e,r_h,a)=V_{he'}(r_e,r_h,a)$ images, respectively, [37–39] (see Fig. 1):

$$U(\mathbf{r}_e,\mathbf{r}_h,a)=V_{hh'}(r_h,a)+$$

$$+V_{ee'}(r_e,a)+V_{eh'}(\mathbf{r}_e,\mathbf{r}_h,a)+V_{he'}(\mathbf{r}_e,\mathbf{r}_h,a), \qquad (3)$$

where

$$V_{hh'}(r_h,a)=\frac{e^2}{2\varepsilon_2 a}\left(\frac{a^2}{a^2-r_h^2}+\frac{\varepsilon_2}{\varepsilon_1}\right), \qquad (4)$$

$$V_{ee'}(r_e,a)=\frac{e^2}{2\varepsilon_2 a}\left(\frac{a^2}{a^2-r_e^2}+\frac{\varepsilon_2}{\varepsilon_1}\right), \qquad (5)$$

$$V_{eh'}(\mathbf{r}_e,\mathbf{r}_h,a)=V_{he'}(\mathbf{r}_e,\mathbf{r}_h,a)=$$

$$=-\frac{e^2}{2\varepsilon_2 a}\frac{a}{\left[(r_e r_h/a)^2-2r_e r_h\cos\theta+a^2\right]^{1/2}}. \qquad (6)$$

In the investigated model of a quasizero-dimensional system in the framework of the above-stated approximations and in the effective mass approximation with the use of the triangular coordinate system [40,41] $r_e=|\mathbf{r}_e|$, $r_h=|\mathbf{r}_h|$, $r=|\mathbf{r}_e-\mathbf{r}_h|$ having the origin at the SN center, the Hamiltonian of an exciton that moves in the SN bulk reads [22]

$$H(\mathbf{r}_e,\mathbf{r}_h,\mathbf{r},a)=$$

$$=-\frac{\hbar^2}{2m_e^0}\left(\frac{\partial^2}{\partial r_e^2}+\frac{2}{r_e}\cdot\frac{\partial}{\partial r_e}+\frac{r_e^2-r_h^2+r^2}{r_e r}\frac{\partial^2}{\partial r_e\,\partial r}\right)-$$

$$-\frac{\hbar^2}{2m_h^0}\left(\frac{\partial^2}{\partial r_h^2}+\frac{2}{r_h}\frac{\partial}{\partial r_h}+\frac{r_h^2-r_e^2+r^2}{r_h r}\frac{\partial^2}{\partial r_h\,\partial r}\right)-$$

$$-\frac{\hbar^2}{2\mu_0}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+$$

$$+V_{eh}(\mathbf{r})+U(\mathbf{r}_e,\mathbf{r}_h,a)+V(\mathbf{r}_e,\mathbf{r}_h)+E_g^0. \qquad (7)$$

Here, the first three terms represent the operators for the kinetic energies of the electron, hole, and exciton, E_g^0 is the energy gap width in the unlimited semiconductor with permittivity ε_2. In the exciton Hamiltonian, the energy of polarization interaction $U(\mathbf{r}_e,\mathbf{r}_h,a)$ is determined with the help of formulas (3)–(6), while the energy of electron-hole Coulomb interaction $V_{eh}(\boldsymbol{r})$ is described by the formula

$$V_{eh}(\mathbf{r})=-\frac{e^2}{\varepsilon_2 r}. \qquad (8)$$

In the exciton Hamiltonian (7), the potential

$$V(r_e,r_h)=\begin{cases}0, & r_e,r_h\le a,\\ \infty, & r_e,r_h>a\end{cases} \qquad (9)$$

describes the motion of quasiparticles in the SN bulk with the help of the model of infinitely deep potential well.

3. Variational Calculation of the Exciton Energy Spectrum in a Semiconductor Nanocrystal

Choosing the variational wave function of an exciton in an SN, we use the approach similar to that developed in [22,40,41]. The variational radial wave function of the ground state of an exciton ($1s$ state of the electron and $1s$ state of the hole) in an SN with radius a can be presented in the following form:

$$\Psi_0\left(r_e, r_h, r\right) = A \exp\left(-\frac{\mu(a)}{\mu_0}\frac{r}{a_{\rm ex}^0}\right) \times$$

$$\times \frac{\sin\ (\pi\ r_e/a)}{r_e} \frac{\sin\ (\pi\ r_h/a)}{r_h} \frac{\left(a^2 - r_e^2\right)}{a^2} \times$$

$$\times \frac{\left(a^2 - r_h^2\right)}{a^2} \frac{r}{a} \frac{\left|r_e - (a/r_h)^2\, r_h\right|}{a}. \qquad (10)$$

Here, the coefficient A was determined from the normalization condition for the exciton wave function (10)

$$\int\limits_0^a r_e\, dr_e \int\limits_0^a r_h\, dr_h \int\limits_r^{r_e+r_h} \Psi_0^2\left(r_e, r_h, r\right)\ r\, dr = 1,$$

while the effective reduced mass $\mu(a)$ of the exciton represents a variational parameter.

It's worth noting that, in the exciton Hamiltonian (7), the operators for the kinetic energies of the electron, hole, and exciton are presented by analogy with the corresponding operators for the kinetic energies of quasiparticles with a constant effective mass. This is related to the fact that the expression for the kinetic energy of quasiparticles with mass $m(r)$,

$$\hat{T} = \frac{\hbar^2}{2m(r)}\nabla_r^2, \qquad (11)$$

is not proper, because operator (11) isn't Hermitian and, hence, cannot correspond to a real physical quantity – the kinetic energy of a quasiparticle.

At $a \ll a_{\rm ex}^0$, the space quantization energy of the electron (hole) in an SN ($\sim \hbar^2/2m_{e(h)}a^2$) will be large as compared with the energy of electron-hole Coulomb interaction $|V_{eh}(\mathbf{r})|$ (8) and the energy of the polarization interaction $U(\mathbf{r}_e, \mathbf{r}_h, a)$ (3) of the electron and the hole with the SN surface which amount to ($\sim e^2/\varepsilon_2 a$) by the order of magnitude. That's why, in the first approximation, the Coulomb and polarization interactions can be neglected. In this case, the main contribution to the exciton Hamiltonian (7) in a low-radius SN ($a \ll a_{\rm ex}^0$) is made by the kinetic energy of the noninteracting electron and hole. Moreover, the variational wave function (10) of the exciton includes the wave functions of the noninteracting electron and hole that move in the spherical infinite-depth potential well $V\left(r_e, r_h\right)$ (9) of an SN.

With increase in the SN radius a ($a > a_{\rm ex}^0$), there appeared a bulk exciton in it [19–22]. This results in that the exciton variational wave function (10) contains the proper wave function of the Wannier–Mott exciton. In addition, the exciton variational wave function (10) includes the polynomials in r_e and r_h, which gives a possibility to eliminate the singularities in the functional $E_0\left(a, \mu\left(a\right)\right)$ of the ground state of the exciton in an SN and obtain the expression for the functional $E_0\left(a, \mu\left(a\right)\right)$ in the final analytic form.

In order to determine the energy $E_0\left(a\right)$ of the ground state of an exciton in an SN with radius a with the help of the variational method, we write down the average value of the exciton Hamiltonian (7) for the wave functions (10) as

$$E_0\ \left(a,\ \mu\left(a\right)\right) = \left\langle \Psi_0\left(r_e, r_h, r\right)\right| \times$$

$$\times H(\mathbf{r}_e, \mathbf{r}_h, \mathbf{r}, a) \left|\Psi_0\left(r_e, r_h, r\right)\right\rangle =$$

$$= \int\limits_0^a dr_e \int\limits_0^a dr_h \int\limits_r^{r_e+r_h} dr\ r_e\ r_h\ r\ \Psi_0\left(r_e, r_h, r\right) \times$$

$$\times H(\mathbf{r}_e, \mathbf{r}_h, \mathbf{r}, a) \Psi_0\left(r_e, r_h, r\right). \qquad (12)$$

The expression for the energy spectrum $E_{1,0,0;1,0,0}\left(a\right)$ of the exciton ground state ($n_e = 1,\ l_e = m_e = 0$; $n_h = 1,\ l_h = m_h = 0$, where $n_e,\ l_e,\ m_e$ i $n_h,\ l_h,\ m_h$ are the principal, orbital, and magnetic quantum numbers of the electron and the hole, respectively) as a function of the SN radius a can be obtained by means of the minimization of the functional $E_0\left(a, \mu\left(a\right)\right)$ (12):

$$\frac{\partial\ E_0\left(a, \mu\left(a\right)\right)}{\partial\ \mu\left(a\right)} \equiv F\left(\mu\left(a\right), a\right) = 0. \qquad (13)$$

Without adducing the cumbersome expressions for the first derivative of the functional $\left(\partial E_0\left(a, \mu\left(a\right)\right)/\partial\mu(a)\right) \equiv F(\mu(a), a)$, we give the numerical solution of the equation $F\left(\ \mu\left(a\right), a\ \right) = 0$ in

a tabular form. The data of the Table indicate that the solution of this equation is presented by the function $\mu(a)$ that monotonously weakly changes within the limits

$$0.40 \leq (\mu(a)/m_0) \leq 0.197 \tag{14}$$

as the SN radius a changes in the range

$$2.5 \leq a \leq 8.5 \text{ nm}, \tag{15}$$

where m_0 is the electron mass in vacuum. The substitution of the value of the variational parameter $\mu(a)$ (14) taken from the Table together with the corresponding values of the SN radius a from interval (15) into the functional $E_0(a, \mu(a))$ (12) gives the energy of the exciton ground state $E_{1,0,0;1,0,0}(a)$ (12) as a function of the SN radius a. The results of variational calculations of the exciton energy spectrum $E_{1,0,0;1,0,0}(a)$ (12) in SN with the radius a are presented in Fig. 2 (see curve *2*). The value of the function $\mu(a)$ (14) and the results of variational calculations of the exciton spectrum $E_{1,0,0;1,0,0}(a)$ (12) in an SN, whose radius is determined by inequality (15), are obtained here with regard for the conditions of experiments [2–5].

Figure 2 (curve *3*) also gives the dependence of the exciton energy spectrum $E_{1,0,0;1,0,0}(a)$ on the radius a of a cadmium sulfide SN obtained in [13,14] without regard for the polarization interaction energy $U(\mathbf{r}_e, \mathbf{r}_h, a)$ (2) of an electron and a hole with the SN surface. From the comparison of curves *2* and *3* in Fig. 2, it appears that, under the conditions of experiments [2–5], the highest contribution to the exciton spectrum $E_{1,0,0;1,0,0}(a)$ is made by the polarization interaction energy. With increase in the radius a of a cadmium sulfide SN from $a = 2.5$ nm to $a = 5.0$ nm, the ratio of the polarization interaction energy to $E_{1,0,0;1,0,0}(a)$ increases from 61% to 93%, respectively [13,14].

Values of the variational parameter $\mu(a)$ as a function of the radius a of a cadmium sulfide SN

a, nm	$\mu(a)/m_0$	$m_e(a)/m_0$
2.5	0.40	0.42
3.0	0.37	0.39
4.0	0.32	0.33
5.0	0.28	0.29
6.0	0.23	0.24
7.0	0.21	0.22
8.0	0.20	0.208
8.5	0.197	0.205

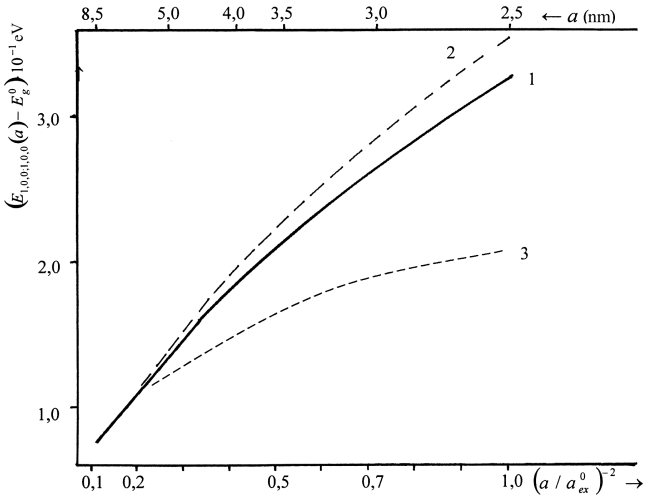

Fig. 2. Exciton energy spectrum $E_{1,0,0;1,0,0}(a)$ as a function of the SN radius a. The curves correspond to: *1* – exciton spectrum taken from experiments [2,5]; *2* – exciton spectrum $E_{1,0,0;1,0,0}(a)$ obtained using the variational procedure; *3* – exciton spectrum $E_{1,0,0;1,0,0}(a)$ obtained in [13,14] without regard for the polarization interaction energy $U(\mathbf{r}_e, \mathbf{r}_h, a)$ (2) of the electron and the hole with the SN surface

The obtained exciton spectrum $E_{1,0,0;1,0,0}(a)$ can be applied only to the exciton ground state ($n_e = 1$, $l_e = m_e = 0$; $n_h = 1$, $l_h = m_h = 0$), for which the inequality

$$(E_{1,0,0;1,0,0}(a) - E_g) \ll \Delta V(a),$$

is satisfied, where $\Delta V(a)$ is the depth of the potential well for electrons in an SN (for example, in a CdS SN, $\Delta V(a) = (2.3 \breve{} 2.5)$ eV in the range of dimensions $a \geq a_{\text{ex}}^0$ [7]).

The experimental dependence of the positions of exciton absorption lines for cadmium sulfide SNs (with the permittivity $\varepsilon_2 = 9.3$ and the size $a \leq 30$ nm) dispersed in the transparent dielectric matrix of silicate glass (with the permittivity $\varepsilon_1 \approx 2.25$), that were caused by interband transitions into the levels of dimensional quantization of the electron ($n_e = 1$, $l_e \leq 2$, where n_e and l_e are the principal and orbital quantum numbers of the electron) in the conduction band, on the SN radius a was obtained in [2–5]. In this case, the dispersion laws for charge carriers in the neighborhood of the conduction band bottom and the valence band top can be considered parabolic in a good approximation [2–5].

In the experimental papers [1–7], it was discovered with the help of the methods of optical spectroscopy that the energy spectra of excitons and electrons moving in the bulk of an SN depend on the SN radius a. Such

a dependence is mainly conditioned by the following reasons. For the same number of charge carriers in an SN, the decrease of its size a results in the increase of the concentration of charge carriers in the SN at the expense of the reduction of the SN volume. This is accompanied by the decrease of the SN permittivity as a function of the coordinate $\varepsilon_2(r)$, which results in the rise of the energy of electron-hole Coulomb interaction and the increase of the energy of polarization interaction of the electron and hole with the spherical SN-dielectric matrix interface [11–13,31–37]. In this case, the energy of polarization interaction also rises with decrease in the SN permittivity $\varepsilon_2(r)$.

In addition, the influence of the spherical SN-dielectric matrix interface can cause the dimensional quantization of the energy spectrum of quasiparticles in SNs related to both the purely spatial restriction of a quantization domain [2,24] and the polarization interaction of the electron and the hole with the SN surface [11–13,31–39,41–44].

In the given paper, the contribution to the exciton energy spectrum in SN conditioned by a decrease of the quantity $\varepsilon_2(r)$ wasn't taken into account, as the problem of correct consideration of the smooth variation of $\varepsilon_2(r)$ under the transition through the spherical SN-dielectric matrix interface remains actual and requires further theoretical investigations [11–13, 23].

In an unbounded semiconductor material (semiconductor monocrystal), a large-radius exciton appears due to the Coulomb attraction $V_{eh}(\mathbf{r})$ (8) between the electron and the hole. In addition, the contribution to the Hamiltonian $H(\mathbf{r}_e, \mathbf{r}_h, \mathbf{r}, a)$ (7) of the exciton moving in the SN bulk will be also made by some additional effective attraction between the electron and the hole conditioned by the repulsion of the electron $V_{hh'}(r_h, a)$ (5) and the hole $V_{ee'}(r_e, a)$ (4) from their images (see Fig. 1). Moreover, the effective repulsion energy between the electron and the hole described by the terms $V_{eh'}(\mathbf{r}_e, \mathbf{r}_h, a)$ and $V_{he'}(\mathbf{r}_e, \mathbf{r}_h, a)$ (6) which correspond to the attraction of quasiparticles to the SN surface (to "extraneous" images, see Fig. 1) will be lower than the energy of additional effective attraction [19–22, 43, 44].

As a result, with decrease in the SN radius a up to the value $a \leq a^0_{\text{ex}}$, this additional effective attraction between the electron and the hole will increase as a^{-1} [19–22, 43, 44]. This effective polarization attraction results in that the electron and the hole move in the SN bulk with the effective masses $m_e(a)$ and $m_h(a)$ larger than the effective masses of the quasiparticles ina monocrystal $m^0_e(a)$ and $m^0_h(a)$, respectively [19–22, 43, 44]. In this case, the exciton also moves in the SN bulk with the effective mass $\mu(a)$ larger than its mass μ_0 in a semiconductor monocrystal.

We assume that the decrease of the radius a of a cadmium sulfide SN up to a value of the order of the Bohr radius of a bulk exciton $a_{\text{ex}} = 2.5$ nm results only in the change of the effective electron mass $m_e(a)$ in a CdS monocrystal (together with the effective mass $\mu(a)$ of the exciton) that will depend on both a and the position the exciton energy level $(n_e,\ l_e,\ m_e;\ n_h,\ l_h,\ m_h)$ in SN, that is, $m_e = m_e(a;\ n_e,\ l_e,\ m_e;\ n_h,\ l_h,\ m_h)$ and $\mu = \mu(a;\ n_e,\ l_e,\ m_e;\ n_h,\ l_h,\ m_h)$ [19–22, 43, 44] (the hole in a cadmium sulfide monocrystal is heavy $(m^0_h/m^0_e \approx 25)$. That's why we consider that its effective mass m_h in an SN is not changed, that is, $m_h = m^0_h)$).

Thus, the new modified effective mass method used in finding the exciton energy spectrum $E_{1,0,0;1,0,0}(a)$ (12) in an SN with radius a with the help of the variational procedure allows one to describe the exciton spectrum taken from experiments [2–5] to a sufficient accuracy. The difference between these spectra didn't exceed 10% (see Fig. 2).

The Table gives the numerical values of the functions $\mu = \mu(a)$ and $m_e = m_e(a)$. The behavior of these functions indicates that, as the SN radius increases $(a > a^0_{\text{ex}})$, the effective mass of the exciton $\mu = \mu(a)$ (electron $m_e = m_e(a)$) decreases approaching, at $a = a_c \approx 3.40 a^0_{\text{ex}} \approx 8.5$ nm, the value of the effective mass of the exciton $\mu_0 = 0.197\ m_0$ (electron $m^0_e(a) = 0.205 m_0$) in unbounded cadmium sulfide (see the Table).

In [19–22], the critical dimension of a cadmium sulfide SN was obtained for the same experimental conditions [2–5] in the framework of the adiabatic approximation $(a^{(1)}_c = 2.8 a^0_{\text{ex}})$ and by means of the variational method not restricting to the adiabatic approximation $(a^{(2)}_c = 3.48 a^0_{\text{ex}})$. The critical radii of CdS SNs $a^{(3)}_c = 3.48 a^0_{\text{ex}}$ [22], $a^{(1)}_c = 2.8 a^0_{\text{ex}}$ [19], and $a_c = 3.40 r_h$ differ weakly (to within 18%). Such a difference is most likely conditioned by that the variational methods of calculations of the exciton spectrum $E_{1,0,0;1,0,0}(a)$ (12) and the exciton spectrum in [22] can give overstated values of the energy, which results, in turn, in the overstated value of the critical radii of SNs $a_c = 3.40 a^0_{\text{ex}}$ and $a^{(3)}_c = 3.48 a^0_{\text{ex}}$ [22].

Thus, in the given paper, a new modified effective mass approximation, which is used for the description of the exciton energy spectrum in semiconductor SNs with radii $a \approx a^0_{\text{ex}}$, is proposed. It is shown that, in the

framework of the model presenting an SN as an infinitely deep potential well, the effective mass approximation can be used for the description of exciton states in an SN with radius a comparable with the Bohr radius of the exciton $a_{\rm ex}^0$, the reduced mass of the exciton $\mu = \mu(a)$ being considered as a function of the SN radius a.

1. N.P. Kulish, V.P. Kunets, and M.P. Lisitsa, Ukr. Fiz. Zh. **35**, 1141 (1990).
2. A.I. Ekimov and A.A. Onushchenko, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 337 (1984).
3. N.P. Kulish, V.P. Kunets, and M.P. Lisitsa, Fiz. Tverd. Tela **39**, 1865 (1997).
4. V.P. Kunets, N.P. Kulish, and M.P. Lisitsa, Fiz. Tekhn. Polupr. **36**, 227 (2002).
5. D. Chepik, A. Efros, and A. Ekimov, J. Luminesc. **47**, 113 (1990).
6. V.P. Kunets, N.R. Kulish, and M.P. Lisitsa, Semicond. **38**, 447 (2004).
7. V. Ya. Grabovskis, Ya.Ya. Dzenis, and A.I. Elimov, Fiz. Tverd. Tela **31**, 272 (1989).
8. Zh.I. Alferov, Fiz. Tekhn. Polupr. **32**, 3 (1998).
9. A.D. Yoffe, Advanc. Phys. **42**, 173 (1993)
10. L. Banyai and S. Koch, *Semiconductor Quantum Dots* (World Sci. Publ., Singapore, 1993).
11. S.I. Pokutnyi, *Theory of Excitons in Quasizero-Dimensional Semiconductor Systems* (Astroprint, Odessa, 2003) (in Russian).
12. A.P. Shpak, S.I. Pokutnyi, Progr. Phys. Metal. **6**, 105 (2005).
13. S.I. Pokutnyi, Ukr. J. Phys. Rev. **3**, 46 (2006).
14. S.I. Pokutnyi, Fiz. Tekhn. Polupr. **39**, 1101 (2005).
15. S.I. Pokutnyi, J. Appl. Phys. **96**, 1115 (2004).
16. S.I. Pokutnyi, Fiz. Tekhn. Polupr. **40**, 223 (2006).
17. S.I. Pokutnyi, Phys. Lett. A **342**, 347 (2005).
18. S.I. Pokutnyi, J. Appl. Phys. **99**, 323 (2007).
19. S.I. Pokutnyi, Fiz. Tekhn. Polupr. **30**, 1952 (1996).
20. S.I. Pokutnyi, Phys. Lett. A **203**, 388 (1995).
21. S.I. Pokutnyi, Fiz. Tverd. Tela **38**, 512 (1996).
22. S.I. Pokutnyi, Fiz. Tverd. Tela **38**, 2667 (1996).
23. A.P. Shpak and S.I. Pokutnyi, *Spectroscopy of Electron and Exciton States in Low-Dimensional Systems* (Akademperiodika, Kyiv, 2005) (in Russian).
24. Al.L. Efros and A.L. Efros, Fiz. Tekhn. Polupr. **16**, 1209 (1982).
25. V.N. Soloviev, A. Eeichofer, and D. Frenske, Phys. Status Solidi B **224**, 285 (2001).
26. R.T. Collins, P.M. Eauchet, and M.A. Tischler, Phys. Today **50**, 24 (1997).
27. C.Y. Yeh, S.B. Zhang, and A. Zunger, Phys. Rev. B **50**, 14405 (1994).
28. C. Delerue, G. Allan, and M. Lanno, Phys. Rev. B **48**, 11024 (1993).
29. A.J. Read, R.J. Needs, and K.J. Nash, Phys. Rev. Lett. **69**, 1232 (1992).
30. F. Buda, J. Kohanoff, and M. Rarrinello, Phys. Rev. B **69**, 1272 (1992).
31. N.A. Efremov and S.I. Pokutnyi, Fiz. Tverd. Tela **27**, 48 (1985).
32. N.A. Efremov and S.I. Pokutnyi, Fiz. Tverd. Tela **32**, 2921 (1990).
33. S.I. Pokutnyi, Phys. Status Solidi B **172**, 573 (1992).
34. S.I. Pokutnyi, Fiz. Tverd. Tela **35**, 257 (1993).
35. S.I. Pokutnyi, Fiz. Tekhn. Polupr. **31**, 1443 (1997).
36. S.I. Pokutnyi, Phys. Low-Dim. Struct. **78**, 39 (2002).
37. N.A. Efremov and S.I. Pokutnyi, Fiz. Tverd. Tela **32**, 1637 (1990).
38. S.I. Pokutnyi, Fiz. Tekhn. Polupr. **25**, 628 (1991).
39. S.I. Pokutnyi, Phys. Lett. A **168**, 433 (1992).
40. Y. Kayanuma, Sol. Stat. Commun. **59**, 405 (1986).
41. N.V. Tkach and V.A. Golovatskii, Fiz. Tverd. Tela **32**, 2512 (1990).
42. S.I. Pokutnyi, Phys. Stat. Sol. B **173**, 607 (1992).
43. S.I. Pokutnyi, Fiz. Tverd. Tela **34**, 2386 (1992).
44. S.I. Pokutnyi, Ukr. Fiz. Zh. **42**, 111 (1997).

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ВПЛИВ ПОЛЯРИЗАЦІЙНОЇ ВЗАЄМОДІЇ НА ЕНЕРГЕТИЧНИЙ СПЕКТР ЕКСИТОНА У НАПІВПРОВІДНИКОВИХ НАНОКРИСТАЛАХ

С.І. Покутний

Р е з ю м е

Розвинуто теорію енергетичного спектра екситона у напівпровідниковому сферичному нанокристалі (СН) в умовах, коли поляризаційна взаємодія електрона і дірки зі сферичною поверхнею поділу "СН – діелектрична матриця" відіграє домінуючу роль. Запропоновано нове модифіковане наближення ефективної маси, за допомогою якого описується енергетичний спектр екситона у напівпровідникових СН з радіусами a, сумірними з борівським радіусом екситона $a_{\rm ex}^0$. Показано, що у рамках моделі СН, в якій СН моделювався нескінченно глибокою потенціальною ямою, наближення ефективної маси можна застосовувати для опису екситонних станів в СН з радіусами $a \approx a_{\rm ex}^0$, вважаючи, що зведена ефективна маса екситона μ є функцією радіуса a СН.