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SEMICONDUCTOR STRUCTURES, LOW-DIMENSIONAL SYSTEMS, AND QUANTUM PHENOMENA

Biexcitons Formed from Spatially Separated Electrons and Holes in Quasi-Zero-Dimensional Semiconductor Nanosystems

S. I. Pokutnyi

Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, Kyiv, 03680 Ukraine
e-mail: Pokutnyi_Sergey@inbox.ru

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Abstract—A theory of biexcitons (formed from spatially separated electron and holes) in nanosystems that consist of zinc-selenide quantum dots synthesized in borosilicate glassy matrices is developed. The dependences of the total energy and the binding energy of the singlet ground biexciton state in such a system on the spacing between the quantum-dot surfaces and the quantum-dot radius are derived by the variational method. It is shown that biexciton formation is of the threshold character and possible in nanosystems, in which the spacing between the quantum-dot surfaces is larger than a certain critical spacing.

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1. INTRODUCTION

The optical properties of quasi-zero-dimensional semiconductor nanosystems that consist of spherically shaped semiconductor quantum dots (QDs) grown to a radius of $a \approx 1–10$ nm in transparent insulator matrices are defined to a large extent by the energy spectra of charge carriers localized close to the QD surface [1–11]. In [6, 7], the optical properties of borosilicate glassy samples containing ZnSe QDs were studied experimentally. The average radii of such QDs were in the range of $\bar{a} \approx 2.0–4.8$ nm. At a small QD content ($x = 0.003$ and 0.03%), at which the optical properties of the samples were determined mainly by those of the individual QDs, it was found [6, 7] that the maxima (peaks) of the absorption and low-temperature luminescence spectra were shifted to shorter wavelengths (with respect to the band gap E_g of the ZnSe single crystal). In [8] (and [6, 7]), it was found that an electron could be localized in a polarization well near the external QD surface, while a hole was in motion within the QD. It was theoretically established [12] that the shift of the low-temperature luminescence spectral peak in such a nanosystem was due to quantum confinement of the energy of the exciton ground state (formed from a spatially separated hole and electron).

In [6, 7], a shift of the spectral peak of the low-temperature luminescence was observed also for samples with a QD content of $x \approx 0.6\%$. It was noted [6, 7] that, at such a QD content in the samples, one must take into account the interaction between charge carriers localized above the QD surfaces. Therefore, in this study, we develop the theory of a biexciton (formed from spatially separated electrons and holes) in a nanosystem that consists of ZnSe QDs synthesized in a borosilicate glassy matrix. Using the variational method, we obtain the total energy and the binding energy of the biexciton singlet ground state in such system as functions of the spacing between the QD surfaces and of the QD radius. We show that the biexciton formation is of the threshold character and possible in a nanosystem, in which the spacing between the QD surfaces exceeds a certain critical spacing. It is established that the spectral shift of the low-temperature luminescence peak [6, 7] in such a nanosystem is due to quantum confinement of the energy of the biexciton ground state.

2. HAMILTONIAN OF A BIEXCITON IN A QUASI-ZERO-DIMENSIONAL NANOSYSTEM

We consider a model nanosystem that consists of two spherical semiconductor QDs, A and B, synthesized in a borosilicate glassy matrix with the permittivity ε_1. Let the QD radii be a, the spacing between the QD centers be L, and the spacing between the spherical QD surfaces be D. Each QD is formed from a semiconductor material with the permittivity ε_2. For simplicity, without loss of generality, we assume that the holes $h(\mathrm{A})$ and $h(\mathrm{B})$ with the effective masses m_h are in the QD (A) and QD (B) centers and the electrons $e(1)$ and $e(2)$ with the effective masses $m_e^{(1)}$ are localized near the spherical QD (A) and QD (B) surfaces, respectively ($r_{\mathrm{A}(1)}$ is the distance of the electron $e(1)$ from the QD (A) center; $r_{\mathrm{B}(2)}$ is the distance of the electron $e(2)$ from the QD (B) center; $r_{\mathrm{A}(2)}$ is the distance of the electron $e(2)$ from the QD (A) center; $r_{\mathrm{B}(1)}$ is the distance of the electron $e(1)$ from the QD (B) center; r_{12} is the distance between the electrons $e(1)$ and $e(2)$ (see Fig. 1)). The above assumption is reasonable, since the ratio between the effective masses of the electron and hole in the nanosystem is much smaller than unity: $m_e^{(1)}/m_h \ll 1$. Let us assume that there is an infinitely high potential barrier at the spherical QD–matrix interface. Therefore, in the nanosystem, holes do not leave the QD bulk, whereas electrons do not penetrate into the QDs.

For such a nanosystem model, we study the possibility of the formation of a biexciton from spatially separated electrons and holes. (Holes are located in the QD (A) and QD (B) centers, and electrons are localized near the spherical QD (A) and QD (B) surfaces.) The characteristic lengths of the problem are determined by the quantities

$$a_h = \frac{\varepsilon_2\hbar^2}{m_h e^2}, \quad a_e^{(1)} = \frac{\varepsilon_1\hbar^2}{m_e^{(1)}e^2}, \tag{1}$$

$$a_{\text{ex}}^0 = \frac{2\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\frac{\hbar^2}{\mu_0 e^2}. \tag{2}$$

Here, a_h and $a_e^{(1)}$ are the Bohr radii of holes and electrons, correspondingly, in the semiconductor with the permittivity ε_2 and in the matrix with the permittivity ε_1; a_{ex}^0 is the Bohr radius of a two-dimensional (2D) exciton localized above the planar interface between a semiconductor with the permittivity ε_2 and a matrix with the permittivity ε_1 (the hole is in motion within the semiconductor, whereas the electron is in the matrix), e is the electron charge, $\mu_0 = \frac{m_e^{(1)}}{(m_e^{(1)}+m_h)}$ is the reduced 2D-exciton effective mass. The fact that all of the characteristic lengths of the problem

$$a,\ L,\ D,\ a_e^{(1)},\ a_h,\ a_{\text{ex}}^0 \gg a_0 \tag{3}$$

are much larger than the interatomic spacing a_0 allows us to consider the motion of electrons and holes in the nanosystem in the effective mass approximation [1, 9].

In the context of the adiabatic approximation and effective mass approximation, the Hamiltonian of a biexciton (formed from spatially separated electrons and holes) in the center-of-mass system can be written as

$$\hat{H} = \hat{H}_{\text{A}(1)} + \hat{H}_{\text{B}(2)} + \hat{H}_{\text{int}}. \tag{4}$$

Here $\hat{H}_{\text{A}(1)}$ describes the Hamiltonian of an exciton formed from an electron and a hole spatially separated from the electron (the hole h(A) is in the QD (A) center and the electron e(1) is localized above the QD (A) surface) [12]:

$$\begin{aligned}\hat{H}_{\text{A}(1)} = {} & -\frac{\hbar^2}{2\mu}\Delta_{(1)} + V_{e(1)h(\text{A})}(\mathbf{r}_{\text{A}(1)}, \mathbf{r}_{h(\text{A})}) \\ & + U(\mathbf{r}_{\text{A}(1)}, \mathbf{r}_{h(\text{A})}, a) + V_{e(1)}(r_{\text{A}(1)}) + V_{h(\text{A})}(r_{h(\text{A})}) + E_g.\end{aligned} \tag{5}$$

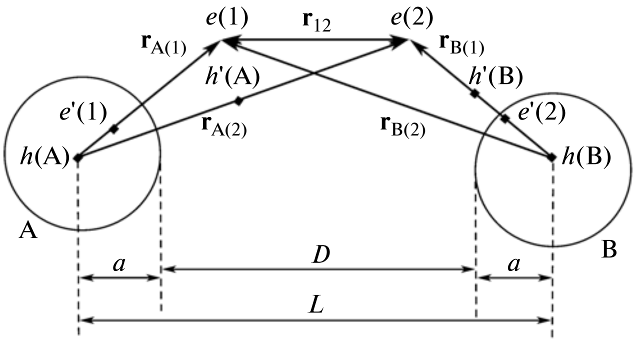

Fig. 1. Schematic representation of a nanosystem consisting of two spherical ZnSe QDs, QD (A) and QD (B) of radii a. The holes h(A) and h(B) are located in the QD (A) and QD (B) centers, and the electrons e(1) and e(2) are localized near the QD (A) and QD (B) surfaces ($\mathbf{r}_{\text{A}(1)}$ is the distance of the electron e(1) from the QD (A) center; $\mathbf{r}_{\text{B}(2)}$ is the distance of the electron e(2) from the QD (B) center; $\mathbf{r}_{\text{A}(2)}$ is the distance of the electron e(2) from the QD (A) center; $\mathbf{r}_{\text{B}(1)}$ is the distance of the electron e(1) from the QD (B) center; $\mathbf{r}_{12}$ is the spacing between the electrons e(1) and e(2); L is the spacing between the QD centers; D is the spacing between the QD surfaces; e'(1), e'(2) and h'(A), h'(B) are the image charges of the electrons and holes).

In (5), the first term is the kinetic energy operator of the exciton; the energy of Coulomb interaction $V_{e(1)h(\text{A})}$ between the electron e(1) and the hole h(A) is described by the formula

$$V_{e(1)h(\text{A})} = -\frac{1}{2}\left(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2}\right)\frac{e^2}{|\mathbf{r}_{e(1)} - \mathbf{r}_{h(\text{A})}|}; \tag{6}$$

the potentials

$$V_{h(\text{A})}(r_{h(\text{A})}) = \begin{cases} 0, & r_{h(\text{A})} \le a \\ \infty, & r_{h(\text{A})} > a, \end{cases} \tag{7}$$

$$V_{e(1)}(r_{\text{A}(1)}) = \infty, \quad r_{e(1)} \le a \tag{8}$$

describe the motion of quasiparticles in the nanosystem in the model of an infinitely deep potential well; and E_g is the band gap in the semiconductor with the permittivity ε_2.

In [12], in the context of the modified effective mass method [9], the theory of an exciton formed from an electron and a hole spatially separated from the electron was developed (the hole was in motion within the QD and the electron was localized on the outer side of the spherical QD–matrix interface). In [12], the energy of the polarization interaction of the electron and hole with the spherical interface with the relative permittivity $\varepsilon = \varepsilon_1/\varepsilon_2 \gg 1$, $U(\mathbf{r}_{\text{A}(1)}, \mathbf{r}_{h(\text{A})}, a)$, is represented as the algebraic sum of the energies of interaction of the hole h(A) and the electron e(1) with their own ($V_{h(\mathrm{A})h'(\mathrm{A})}$, $V_{e(1)e''(1)}$) and foreign ($V_{e(1)h'(\mathrm{A})}$, $V_{h(\mathrm{A})e''(1)}$) images:

$$\begin{gathered}U(r_{\mathrm{A}(1)}, r_{h(\mathrm{A})}, a) = V_{h(\mathrm{A})h'(\mathrm{A})}(r_{h(\mathrm{A})h'(\mathrm{A})}, a)\\ + V_{e(1)e'(1)}(r_{\mathrm{A}(1)}, a) + V_{h(\mathrm{A})e'(1)}(r_{h(\mathrm{A})}, r_{\mathrm{A}(1)}, a)\\ + V_{e(1)h'(\mathrm{A})}(r_{\mathrm{A}(1)}, r_{h(\mathrm{A})}, a),\end{gathered} \tag{9}$$

$$V_{h(\mathrm{A})h'(\mathrm{A})} = \frac{e^2\beta}{2\varepsilon_2 a}\left(\frac{a^2}{a^2 - r_{h(\mathrm{A})}^2} + \varepsilon\right), \tag{10}$$

$$V_{e(1)e'(1)} = -\frac{e^2\beta}{2\varepsilon_1 a}\frac{a^4}{r_{\mathrm{A}(1)}^2(r_{\mathrm{A}(1)}^2 - a^2)}, \tag{11}$$

$$V_{h(\mathrm{A})e'(1)} = \frac{e^2\beta}{2\varepsilon_2 a}\frac{a^2}{r_{\mathrm{A}(1)}\left|\mathbf{r}_{h(\mathrm{A})} - [(a/r_{\mathrm{A}(1)})^2]/r_{\mathrm{A}(1)}\right|}, \tag{12}$$

$$V_{e(1)h'(\mathrm{A})} = -\frac{e^2\beta}{2\varepsilon_1 a}\frac{a^2}{r_{h(\mathrm{A})}^2\left|r_{\mathrm{A}(1)} - (a/r_{h(\mathrm{A})})^2 r_{h(\mathrm{A})}\right|}. \tag{13}$$

Here $r_{h(\mathrm{A})}$ is the distance of the hole from the QD (A) center.

In the biexciton Hamiltonian (4), $\hat{H}_{\mathrm{B}(2)}$ is the Hamiltonian of an exciton formed from an electron and a hole spaced from the electron (the hole h(B) is located in the QD (B) center and the electron e(2) is localized above the QD (B) surface). The Hamiltonian $\hat{H}_{\mathrm{B}(2)}$ has a form similar to that of the Hamiltonian $\hat{H}_{\mathrm{A}(1)}$ in (5):

$$\begin{gathered}\hat{H}_{\mathrm{B}(2)} = -\frac{\hbar^2}{2\mu}\Delta_{(2)} + V_{e(2)h(\mathrm{B})}(r_{\mathrm{B}(2)}, r_{h(\mathrm{B})})\\ + U(r_{\mathrm{B}(2)}, r_{h(\mathrm{B})}, a) + V_{e(2)}(r_{\mathrm{B}(2)}) + V_{h(\mathrm{B})}(r_{h(\mathrm{B})}) + E_g.\end{gathered} \tag{14}$$

The terms entering into the Hamiltonian (14) are expressed by formulas similar to the corresponding formulas in the Hamiltonian (5). Let us write the expression for the Hamiltonian $\hat{H}_{\mathrm{int}}$:

$$\begin{gathered}\hat{H}_{\mathrm{int}} = V_{\mathrm{AB}}(D, a) + V_{e(1)h(\mathrm{B})}(r_{\mathrm{B}(1)}, r_{h(\mathrm{B})})\\ + V_{e(2)h(\mathrm{A})}(r_{\mathrm{A}(2)}, r_{h(\mathrm{A})}) + V_{e(1)e(2)}(r_{12}).\end{gathered} \tag{15}$$

Here, $V_{\mathrm{AB}}(D, a)$ is the energy of the interaction of charge carriers (the electrons e(1) and e(2) and the holes h(A) and h(B)) with polarization fields induced by these charge carriers at the QD (A) and QD (B) surfaces,

$$\begin{gathered}V_{\mathrm{AB}}(D, a) = V_{h(\mathrm{A})h(\mathrm{B})}(D, a) + V_{h(\mathrm{A})h'(\mathrm{B})}(D, a)\\ + V_{h(\mathrm{A})e'(2)}(r_{\mathrm{B}(2)}, a) + V_{e(1)e'(2)}(r_{\mathrm{A}(1)}, r_{\mathrm{B}(2)}, a)\\ + V_{e(1)h'(\mathrm{B})}(r_{\mathrm{B}(1)}, a) + V_{h(\mathrm{B})h'(\mathrm{A})}(D, a)\\ + V_{h(\mathrm{B})e'(1)}(r_{\mathrm{B}(1)}, a) + V_{e(2)e'(1)}(r_{\mathrm{B}(2)}, r_{\mathrm{A}(1)}, a)\\ + V_{e(2)h'(\mathrm{A})}(r_{\mathrm{A}(2)}, a);\end{gathered} \tag{16}$$

$V_{e(1)h(\mathrm{B})}$ is the energy of interaction of the electron e(1) with the hole h(B); and $V_{e(2)h(\mathrm{A})}$ is the energy of interaction of the electron e(2) with the hole h(A). The last-mentioned energies are described by the expressions

$$V_{e(1)h(\mathrm{B})}(r_{\mathrm{B}(1)}) = -\frac{e^2}{\varepsilon_1 r_{\mathrm{B}(1)}}, \tag{17}$$

$$V_{e(2)h(\mathrm{A})}(r_{\mathrm{A}(2)}) = -\frac{e^2}{\varepsilon_1 r_{\mathrm{A}(2)}}. \tag{18}$$

The energy of Coulomb interaction between the electrons e(1) and e(2), $V_{e(1)e(2)}(r_{12})$, is determined by the formula

$$V_{e(1)e(2)}(r_{12}) = -\frac{e^2}{\varepsilon_1 r_{12}}, \tag{19}$$

and the energy of interaction between the holes h(A) and h(B) is described by the expression

$$V_{h(\mathrm{A})h(\mathrm{B})}(D, a) = -\frac{e^2}{\varepsilon_1(D + 2a)}. \tag{20}$$

According to [12], the major contribution to the energy of the ground state of the exciton (formed by an electron and a hole spatially separated from the electron) is made by the average energy of the Coulomb interaction between the electron and hole $\langle R_0(r_{\mathrm{A}(1)}, \tilde{a})|V_{e(1)h(\mathrm{A})}(r_{\mathrm{A}(1)})|R_0(r_{\mathrm{A}(1)}, \tilde{a})\rangle$ (or $\langle R_0(r_{\mathrm{B}(2)}, \tilde{a})|V_{e(2)h(\mathrm{B})}(r_{\mathrm{B}(2)})|R_0(r_{\mathrm{B}(2)}, \tilde{a})\rangle$) on the basis of the Coulomb-shaped variational wavefunctions $R_0(r_{\mathrm{A}(1)}, a)$:

$$R_0(r_{\mathrm{A}(1)}, \tilde{a}) = \tilde{A}\exp(-\bar{\mu}(\tilde{a})(r_{\mathrm{A}(1)}/a_{\mathrm{ex}}^0)). \tag{21}$$

Here, $\bar{\mu}(\tilde{a}) = (\tilde{\mu}(\tilde{a})/m_0)$ is the variational parameter ($\tilde{\mu}(\tilde{a})$ is the reduced exciton effective mass, m_0 is the electron mass in vacuum) and the normalization constant is

$$\begin{gathered}\tilde{A} = \pi^{-1/2}(a_{\mathrm{ex}}^0)^{-3/2}\mu^{-3/2}\\ \times \exp(\bar{\mu}\tilde{a})[2(\bar{\mu}\tilde{a})^2 + 2(\bar{\mu}\tilde{a}) + 1]^{-1/2},\end{gathered} \tag{22}$$

where $\tilde{a} = (a/a_{\mathrm{ex}}^0)$ is the dimensionless QD radius. The above-mentioned feature allows us to retain only the energies of the Coulomb interaction between the electron and hole $V_{e(1)h(\mathrm{A})}(r_{\mathrm{A}(1)})$ (6) and $V_{e(2)h(\mathrm{B})}(r_{\mathrm{B}(2)})$ determined by a formula similar to (6), correspondingly, in the Hamiltonians $\hat{H}_{\mathrm{A}(1)}$ (5) and $\hat{H}_{\mathrm{B}(2)}$ (14) and to retain only the energy of the interaction between the holes h(A) and h(B) $V_{h(\mathrm{A})h(\mathrm{B})}(D, a)$ (20) in the interaction energy $V_{\mathrm{AB}}(D, a)$ (16). At the same time, the energy $V_{\mathrm{AB}}(D, a)$ is determined by the formula (20):

$$V_{\mathrm{AB}}(D, a) = V_{h(\mathrm{A})h(\mathrm{B})}(D, a) = -\frac{e^2}{\varepsilon_1(D + 2a)}. \tag{23}$$

With the above assumptions, the exciton Hamiltonians $\hat{H}_{A(1)}$ (5) and $\hat{H}_{B(2)}$ (14) take the form

$$\hat{H}_{A(1)} = -\frac{\hbar^2}{2\mu}\Delta_{(1)} + V_{e(1)h(A)}(r_{A(1)}) + E_g, \tag{24}$$

$$\hat{H}_{B(2)} = -\frac{\hbar^2}{2\mu}\Delta_{(2)} + V_{e(2)h(B)}(r_{B(2)}) + E_g. \tag{25}$$

In this case, the biexciton Hamiltonian $\hat{H}$ (4) involves the exciton Hamiltonians $\hat{H}_{A(1)}$ (24) and $\hat{H}_{B(2)}$ (25) as well as the Hamiltonian $\hat{H}_{\text{int}}$ (15), in which the interaction energy $V_{AB}(D, a)$ is determined by formula (23).

3. ENERGY OF THE BIEXCITON GROUND STATE IN THE NANOSYSTEM

On the assumption that the spins of the electrons $e(1)$ and $e(2)$ are antiparallel, we write the normalized wavefunction of the biexciton singlet ground state as a symmetric linear combination of the wavefunctions $\Psi_1(r_{A(1)}, r_{B(2)})$ and $\Psi_2(r_{A(2)}, r_{B(1)})$ [13–15]:

$$\begin{aligned}\Psi_s(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)}) &= [2(1 + S^2(D, a))]^{-1/2} \\ &\times [\Psi_1(r_{A(1)}, r_{B(2)}) + \Psi_2(r_{A(2)}, r_{B(1)})].\end{aligned} \tag{26}$$

Assuming that the electrons $e(1)$ and $e(2)$ move independently of each other, we represent the wavefunctions $\Psi_1(r_{A(1)}, r_{B(2)})$ and $\Psi_2(r_{A(2)}, r_{B(1)})$ as a product of the one-electron wavefunctions $\varphi_{A(1)}(r_{A(1)})$ and $\varphi_{B(2)}(r_{B(2)})$ and a product of $\varphi_{A(2)}(r_{A(2)})$ and $\varphi_{B(1)}(r_{B(1)})$ [13–15]:

$$\Psi_1(r_{A(1)}, r_{B(2)}) = \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)}), \tag{27}$$

$$\Psi_2(r_{A(2)}, r_{B(1)}) = \varphi_{A(2)}(r_{A(2)})\varphi_{B(1)}(r_{B(1)}). \tag{28}$$

We represent the one-electron wavefunctions $\varphi_{A(1)}(r_{A(1)})$ and $\varphi_{B(2)}(r_{B(2)})$ that describe, correspondingly, the electron $e(1)$ localized above the QD (A) surface and the electron $e(2)$ localized above the QD (B) surface and the wavefunctions $\varphi_{A(2)}(r_{A(2)})$ and $\varphi_{B(1)}(r_{B(1)})$ that describe, correspondingly, the electron $e(2)$ localized above the QD (A) surface and the electron $e(1)$ localized above the QD (B) surface as variational Coulomb-shaped wavefunctions (21):

$$\varphi_{A(1)}(r_{A(1)}) = \tilde{A}\exp(-\bar{\mu}(\tilde{a})(r_{A(1)}/a_{\text{ex}}^0)), \tag{29}$$

$$\varphi_{B(2)}(r_{B(2)}) = \tilde{A}\exp(-\bar{\mu}(\tilde{a})(r_{B(2)}/a_{\text{ex}}^0)), \tag{30}$$

$$\varphi_{A(2)}(r_{A(2)}) = \tilde{A}\exp(-\bar{\mu}(\tilde{a})(r_{A(2)}/a_{\text{ex}}^0)), \tag{31}$$

$$\varphi_{B(1)}(r_{B(1)}) = \tilde{A}\exp(-\bar{\mu}(\tilde{a})(r_{B(1)}/a_{\text{ex}}^0)). \tag{32}$$

Because of the identity of the electrons, the wavefunction $\Psi_2(r_{A(2)}, r_{B(1)})$ (28) is equivalent to the wavefunction $\Psi_1(r_{A(1)}, r_{B(2)})$ (27). In (26), the overlapping integral $S(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ is determined by the formula

$$S(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) = \int d\tau_1 \varphi_{A(1)}(r_{A(1)})\varphi_{B(1)}(r_{B(1)}), \tag{33}$$

where $d\tau_1$ is the volume element of the electron $e(1)$, $\tilde{D} = (D/a_{\text{ex}}^0)$ is the dimensionless spacing between the QD (A) and QD (B) surfaces.

In the first approximation, the energy of the biexciton singlet ground state is defined by the average value of the Hamiltonian $\hat{H}$ (4) on the basis of states described by the zero-approximation wavefunctions Ψ_s (26) [14, 15]:

$$\begin{aligned}E(D, \bar{\mu}(a, D), a) &= \langle\Psi_s(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)}) \\ &\times |\hat{H}|\Psi_s(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)})\rangle.\end{aligned} \tag{34}$$

With the explicit form of the wavefunctions (26)–(32), the energy functional of the biexciton singlet ground state takes the form

$$\begin{aligned}E_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= 2E_{\text{ex}}(\tilde{a}, \bar{\mu}(\tilde{a})) \\ &+ \frac{J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) + K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}{1 + S^2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}.\end{aligned} \tag{35}$$

Here, $E_{\text{ex}}(\tilde{a}, \bar{\mu}(\tilde{a}))$ is the energy functional of the exciton ground state (for the exciton formed from an electron and a hole spatially separated from the electron):

$$E_{\text{ex}}(\tilde{a}, \bar{\mu}(\tilde{a})) = \langle\psi_{A(1)}(r_{A(1)})|\hat{H}_{A(1)}|\psi_{A(1)}(r_{A(1)})\rangle. \tag{36}$$

In the functional determined by formula (35), $J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ is determined by the expression

$$\begin{aligned}J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= \langle\psi_{A(1)}(r_{A(1)})\psi_{B(2)}(r_{B(2)}) \\ &\times |\hat{H}_{\text{int}}|\psi_{A(1)}(r_{A(1)})\psi_{B(2)}(r_{B(2)})\rangle.\end{aligned} \tag{37}$$

The functional $J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ (37) can be represented as the algebraic sum of the functionals of the average energies of Coulomb interaction:

$$J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) = \sum_{i=1}^{4} J_i(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}). \tag{38}$$

With formulas (15) and (23), the functionals J_i take the form

$$\begin{aligned}J_1 &= \langle\varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})|V_{h(A)h(B)}| \\ &\times \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})\rangle \\ &= \frac{\varepsilon_2}{2(\varepsilon_1 + \varepsilon_2)}\frac{E_{\text{ex}}^0}{\tilde{a}(1 + (\tilde{D}/2\tilde{a}))},\end{aligned} \tag{39}$$

$$\begin{aligned} J_2 &= \langle \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})|V_{e(1)h(B)}| \\ &\quad\times \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})\rangle \qquad (40) \\ &= \langle \psi_{A(1)}(r_{A(1)})|V_{e(1)h(B)}(r_{e(1)h(B)})|\varphi_{A(1)}(r_{A(1)})\rangle, \end{aligned}$$

$$\begin{aligned} J_3 &= \langle \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})|V_{e(2)h(A)}| \\ &\quad\times \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})\rangle \qquad (41) \\ &= \langle \varphi_{B(2)}(r_{B(2)})|V_{e(2)h(A)}(r_{e(2)h(A)})|\varphi_{B(2)}(r_{B(2)})\rangle, \end{aligned}$$

$$\begin{aligned} J_4 &= \langle \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})|V_{e(1)e(2)}(r_{12})| \\ &\quad\times \varphi_{A(1)}(r_{A(1)})\bar{\varphi}_{B(2)}(r_{B(2)})\rangle. \end{aligned} \qquad (42)$$

In the sum (38), expression (39) for J_1 defines the functional of the average energy of Coulomb interaction between the holes h(A) and h(B); expression (40) for J_2 describes the functional of the average energy of Coulomb interaction between the electron e(1) and the hole h(B); expression (41) for J_3 describes the functional of the average energy of Coulomb interaction between the electron e(2) and the hole h(A); and expression (42) for J_4 describes the functional of the average energy of Coulomb interaction between the electrons e(1) and e(2).

Because of the identity of the electrons e(1) and e(2), we have the equality

$$\begin{aligned} J_2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= J_3(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) \\ &= J_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}). \end{aligned} \qquad (43)$$

With (43) taken into account, the functional $J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ (38) takes the form

$$\begin{aligned} J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= J_1(\tilde{D}, \tilde{a}) + 2J_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) \\ &\quad + J_4(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}). \end{aligned} \qquad (44)$$

In the functional described by (35), $K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ is determined by the formula

$$\begin{aligned} K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= \langle \varphi_{B(1)}(r_{B(1)})\varphi_{A(2)}(r_{A(2)})|\hat{H}_{\text{int}}| \\ &\quad\times \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})\rangle. \end{aligned} \qquad (45)$$

The functional $K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ (45) can be represented as the algebraic sum of the functionals of the average energies of the exchange interaction:

$$K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) = \sum_{i=1}^{4} K_i(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}). \qquad (46)$$

Taking into consideration formulas (15) and (23), we write the functionals K_i as

$$\begin{aligned} K_1(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= \langle \varphi_{B(1)}\varphi_{A(2)}|V_{h(A)h(B)}|\varphi_{A(1)}\varphi_{B(2)}\rangle \\ &= \frac{\varepsilon_2}{2(\varepsilon_1 + \varepsilon_2)} \frac{S^2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})E_{\text{ex}}^0}{\tilde{a}(1 + (\tilde{D}/2\tilde{a}))}, \end{aligned} \qquad (47)$$

$$\begin{aligned} &K_2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) \\ &= \langle \varphi_{B(1)}\varphi_{A(2)}|V_{e(1)h(B)}|\varphi_{A(1)}\varphi_{B(2)}\rangle, \end{aligned} \qquad (48)$$

$$\begin{aligned} &K_3(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) \\ &= \langle \varphi_{B(1)}\varphi_{A(2)}|V_{e(2)h(A)}|\varphi_{A(1)}\varphi_{B(2)}\rangle, \end{aligned} \qquad (49)$$

$$\begin{aligned} &K_4(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) \\ &= \langle \varphi_{B(1)}\varphi_{A(2)}|V_{e(1)e(2)}(r_{12})|\varphi_{A(1)}\varphi_{B(2)}\rangle. \end{aligned} \qquad (50)$$

In the sum in (46), expression (47) for K_1 describes the functional of the average energy of exchange the interaction between the holes h(A) and h(B) and the electrons e(1) and e(2); expression (48) for K_2 describes the functional of the average energy of the exchange interaction between the electron e(1) (which simultaneously is partially in the state $\varphi_{A(1)}(r_{A(1)})$ (29) and partially in the state $\varphi_{B(1)}(r_{B(1)})$ (32)) and the hole h(B); expression (49) for K_3 describes the functional of the average energy of the exchange interaction between the electron e(2) (which simultaneously is partially in the state $\varphi_{A(2)}(r_{A(2)})$ (31) and partially in the state $\varphi_{B(2)}(r_{B(2)})$ (30)) and the hole h(A); and expression (50) for K_4 describes the functional of the average energy of the exchange interaction between the electrons e(1) and e(2).

Because of the identity of the electrons e(1) and e(2), we have the equality for the functionals

$$\begin{aligned} K_2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= K_3(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) \\ &= K_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}). \end{aligned} \qquad (51)$$

With (51) taken into account, the functional $K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ takes the form

$$\begin{aligned} K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= K_1(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) \\ &\quad + 2K_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) + K_4(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}). \end{aligned} \qquad (52)$$

Taking into consideration formulas (44) and (52), we can write the functional of the energy of the biexciton ground state $E_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ as

$$\begin{aligned} E_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) &= 2E_{\text{ex}}(\tilde{a}, \bar{\mu}(\tilde{a})) + \frac{J_1(\tilde{D}, \tilde{a}) + 2J_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) + J_4(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}{1 + S^2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})} \\ &\quad + \frac{K_1(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) + 2K_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) + K_4(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}{1 + S^2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}. \end{aligned} \qquad (53)$$

With the explicit form of the electron functions (29) and (32) taken into account, the overlapping integral (33) takes the form

$$S(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) = \frac{[(\bar{\mu}(\tilde{a}, \tilde{D})\tilde{D})^2/3 + (\bar{\mu}(\tilde{a}, \tilde{D})\tilde{D}) + 1]}{2(\bar{\mu}(\tilde{a}, \tilde{D})\tilde{a})^2 + 2(\bar{\mu}(\tilde{a}, \tilde{D})\tilde{a}) + 1} \times \exp(-\bar{\mu}(\tilde{a}, \tilde{D})\tilde{D}). \tag{54}$$

The dependence of the energy $E_0(\tilde{D}, \tilde{a})$ of the biexciton ground state on the spacing between the QD (A) and QD (B) surfaces can be calculated by minimizing the functional (35):

$$\frac{\partial E_0(\bar{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}{\partial \bar{\mu}(\tilde{a}, \tilde{D})} = 0. \tag{55}$$

Omittingthe cumbersome expressions for the first derivative of the functional, we present the numerical solution of Eq. (55) in the form of a table. From the table, it follows that the solution of Eq. (55) is the function $\bar{\mu}(\tilde{a}, \tilde{D})$, which slightly steadily varies within the limits defined by the inequality

$$0.27 \le \bar{\mu}(\tilde{a}_1, \tilde{D}) \le 0.33 \tag{56}$$

(for a QD of radius $a = a_1 = 3.88$ nm ($\tilde{a}_1 = 6.77$)), as the spacing $\tilde{D}$ varies in the range defined as

$$5.24 \le \tilde{D} \le 28.6 \quad \text{or} \quad 3\ \text{nm} \le D \le 16.4\ \text{nm}. \tag{57}$$

As the spacing D between the QD surfaces is increased (so that $D \gg a_{\text{ex}}^0$ or $\tilde{D} \gg 1$), the function $\bar{\mu}(\tilde{a}_1, \tilde{D})$ takes the value $\bar{\mu}(\tilde{a}_1, \tilde{D}) = 0.33$ (at $\tilde{D} = 28.6$) (see table). The reduced exciton effective mass $\bar{\mu}(\tilde{a}_1, \tilde{D})$ (56) in the nanosystem only slightly differs from the reduced exciton effective mass (for the exciton formed of an electron and a hole spatially separated from the electron) $(\mu_0/m_0) = 0.304$ [12]. As $\tilde{D}$ is varied in the range defined by (57), the relative difference is $(|\bar{\mu}(a_1, \tilde{D}) - (\mu_0/m_0)|/(\mu_0/m_0) \le 0.11$.

As the spacing $\tilde{D}$ between the QD (A) and QD (B) surfaces in the nanosystem under consideration is increased (so that $D \gg a_{\text{ex}}^0$), the electrons $e(1)$ and $e(2)$ become localized above the QD (A) and QD (B) surfaces, respectively. Thus, in this case, excitons (formed from spatially separated electrons and holes) become localized above the QD (A) and QD(B) surfaces. In this case, the interaction between the excitons and the interaction of the excitons with the polarization fields induced by these excitons at the QD (A) and QD (B) surfaces can be disregarded. Then the functional (53) of the energy of the ground state of the nanosystem takes the form

$$E_0^0(\tilde{a}, \bar{\mu}(\tilde{a})) = 2E_{\text{ex}}(\tilde{a}, \bar{\mu}(\tilde{a})), \tag{58}$$

where the functional $E_{\text{ex}}(\tilde{a}, \bar{\mu}(\tilde{a}))$ of the energy of the ground state of the exciton localized above the QD (A) (or QD (B)) surface is determined by formula (36) (see also [12]).

The variational parameter $\bar{\mu}(\tilde{a}, \tilde{D})$ as a function of the spacing $\tilde{D} = (D/a_{\text{ex}}^0)$ between the QD (A) and QD (B) surfaces at a QD radius of $a_1 = 3.88$ nm (D, nm is the spacing between the QD surfaces, $a_{\text{ex}}^0 = 0.573$ nm is the Bohr radius of a 2D exciton (2))

$\tilde{D}$	$\bar{\mu}(\tilde{a}, \tilde{D})$
5.24	0.27
6.0	0.282
7.0	0.292
8.0	0.30
10.0	0.312
12.0	0.319
15.0	0.323
20.0	0.327
25.0	0.329
28.6	0.330

As the spacing $\tilde{D}$ between the QD (A) and QD (B) surfaces is decreased, the overlapping integral $S(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ (54) of the electron wavefunctions (29) and (32) and the energy of the exchange interaction of the electrons $e(1)$ and $e(2)$ with the holes $h(\text{A})$ and $h(\text{B})$ substantially increase. Therefore, a coupled state of two excitons is formed in the nanosystem; i.e., a biexciton (composed of spatially separated electrons and holes) is formed. With formulas (35), (36), and (58), the functional of the biexciton binding energy is determined by the expression

$$E_b(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) = E_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) - E_0^0(\tilde{a}, \bar{\mu}(\tilde{a})) = \frac{J(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a}) + K(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}{1 + S^2(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})}. \tag{59}$$

Substituting the values of the variational parameter $\bar{\mu}(\tilde{a}, \tilde{D})$ (56) from the table (for a QT of radius $a = a_1 = 3.88$ nm) and the corresponding values of $\tilde{D}$ from the range defined by (57) into the functionals $E_0(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ (35) and $E_b(\tilde{D}, \bar{\mu}(\tilde{a}, \tilde{D}), \tilde{a})$ (59), we obtain the energy $E_0(\tilde{D}, \tilde{a})$ of the biexciton ground

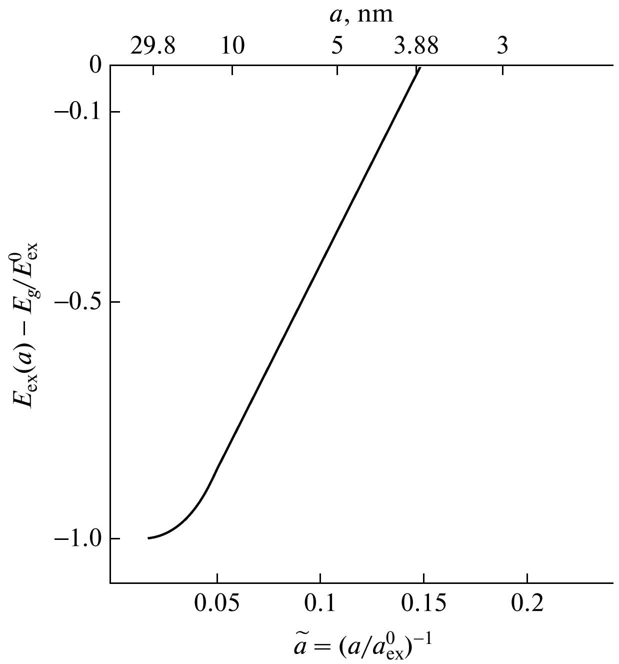

Fig. 2. Dependence of the binding energy ($E_{ex}(a) - E_g$) of the ground state of an exciton (formed by an electron and a hole spatially separated from the electron) localized above the QD surface on the ZnSe QD radius a [12]. Here $E_g = 2.823$ eV is the band gap of the ZnSe single crystal, $E^0_{ex} = 1.5296$ eV and $a^0_{ex} = 0.573$ nm (2) are, correspondingly, the binding energy of the ground state and the Bohr radius of a 2D exciton (formed by an electron and a hole spatially separated from the electron) [12].

state and the binding energy $E_b(\tilde{D}, \tilde{a})$ of the biexciton ground state in the nanosystem as functions of the spacing $\tilde{D}$ between the QD (A) and QD (B) surfaces and of the QD radius $\tilde{a}$:

$$E_0(\tilde{D}, \tilde{a}) = 2E_{ex}(\tilde{a}) + E_{\mathrm{b}}(\tilde{D}, \tilde{a}). \qquad (60)$$

Here, the binding energy $E_{ex}(\tilde{a})$ of the ground state of the exciton (formed from an electron and a hole spatially separated from the electron) localized above the QD (A) (or QD (B)) surface is determined by the functional (36). For the nanosystem under study, the values of the binding energies $E_{ex}(\tilde{a})$ are calculated in [12] for the experimental conditions of [6, 7] (Fig. 2). In this case, the values of the binding energy $E_{ex}(\tilde{a})$ of the exciton ground state in the nanosystem satisfy the inequality

$$(E_{ex} - E_g) \ll \Delta V(a) \qquad (3a)$$

under variations in the QD radius a in the range defined as 3.84 nm ≤ a ≤ 4.4 nm (Fig. 2). In (3a), $\Delta V(a)$ is the depth of the potential well for an electron in the QD. For a wide class of II–VI semiconductors and for QD dimensions a no larger than 30 nm, the value of $\Delta V(a)$ is (2.3–2.5) eV [8]. In the derivation of the binding energy of the exciton ground state in the nanosystem in [12], the condition (3a) presumably enables us to disregard the effect of the complex structure of the QD valence band on the binding energy of the exciton ground state in the nanosystem and to describe the motion of a hole within the QD in the model of an infinitely deep potential well.

With consideration for formula (59), we write the biexciton binding energy $E_b(\tilde{D}, \tilde{a})$ as

$$E_b(\tilde{D}, \tilde{a}) = \frac{J(\tilde{D}, \tilde{a}) + K(\tilde{D}, \tilde{a})}{1 + S^2(\tilde{D}, \tilde{a})}. \qquad (61)$$

Here, in accordance with formulas (44) and (52), the energies $J(\tilde{D}, \tilde{a})$ and $K(\tilde{D}, \tilde{a})$ are

$$J(\tilde{D}, \tilde{a}) = J_1(\tilde{D}, \tilde{a}) + 2J_0(\tilde{D}, \tilde{a}) + J_4(\tilde{D}, \tilde{a}), \qquad (62)$$

$$K(\tilde{D}, \tilde{a}) = K_1(\tilde{D}, \tilde{a}) + 2K_0(\tilde{D}, \tilde{a}) + K_4(\tilde{D}, \tilde{a}), \qquad (63)$$

In expressions (62) and (63), the energies $J_1(\tilde{D}, \tilde{a})$, $J_0(\tilde{D}, \tilde{a})$, and $J_4(\tilde{D}, \tilde{a})$ are defined by the corresponding functionals (39), (43), and (42), and the energies $K_1(\tilde{D}, \tilde{a})$, $K_0(\tilde{D}, \tilde{a})$, and $K_4(\tilde{D}, \tilde{a})$ by the functionals (47), (51), and (50).

The variational method used here for the calculating the binding energy $E_b(\tilde{D}, \tilde{a})$ (61) of the biexciton ground state in the nanosystem is appropriate, if the biexciton binding energy $E_b(\tilde{D}, \tilde{a})$ is small compared to the binding energy $E_{ex}(\tilde{a})$ of the exciton ground state [12] (Fig. 2). In other words, the inequality

$$E_b(\tilde{D}, \tilde{a})/E_{ex}(\tilde{a}) \ll 1 \qquad (64)$$

must be satisfied. The validity of this approach is justified by the results of variational calculation.

The results of variational calculation of the binding energy $E_b(\tilde{D}, \tilde{a})$ of the biexciton ground state in the nanosystem of ZnSe QDs with average radii of a_1 = 3.88 nm synthesized in a borosilicate matrix are shown in Fig. 3. Such a nanosystem was experimentally studied in [6, 7]. In [6, 7], the borosilicate glassy samples doped with ZnSe to the content x from $x = 0.003$ to 1% were produced by the sol–gel technique. At a QD content of $x \simeq 0.6\%$, one must take into account the interaction of charge carriers localized above the QD surfaces.

The binding energy $E_b(\tilde{D}, \tilde{a})$ of the biexciton ground state in the nanosystem containing ZnSe QDs with average radii of $\bar{a}_1 = 3.88$ nm has a minimum of $E_b^{(1)}(\tilde{D}_1, \bar{a}_1) \approx -4.2$ meV (at the spacing $D_1 \cong 3.2$ nm)

(Fig. 3). (The value of $E_b^{(1)}$ corresponds to the temperature $T_1 \approx 49$ K.) From Fig. 3, it follows that a biexciton is formed in the nanosystem, starting from a spacing between the QD surfaces of $D \geq D_c^{(1)} \approx 2.4$ nm. The formation of such a biexciton is of the threshold character and possible only in a nanosystem with QDs with average radii $\bar{a}_1$ such that the spacing between the QD surfaces D exceeds a certain critical spacing $D_c^{(1)}$. Moreover, the biexciton can exist only at temperatures below a certain critical temperature: $T_1 = 49$ K.

As follows from the results of variational calculation ([12], see also Fig. 2), the binding energy of an exciton (formed from an electron and a hole spatially separated from the electron) localized above the surface of the QD (A) (or a QD (B)) with an average radius of $\bar{a}_1 = 3.88$ nm is $E_{ex}(\bar{a}_1) \approx -53.9$ eV. In this case the energy of the biexciton ground state $E_0(\tilde{D}, \tilde{a})$ (60) takes the value $E_0(\tilde{D}, \bar{a}_1) \approx -112$ meV. It should be emphasized that the criterion (64) of the applicability of the variational method used here for calculating the biexciton binding energy $E_b(\tilde{D}, \tilde{a})$ (61) is satisfied (the corresponding ratio is $E_b(\tilde{D}, \tilde{a})/E_{ex}(\tilde{a}) \ll 1$).

From the results of variational calculation of the biexciton binding energy $E_b(\tilde{D}, \tilde{a})$ (61), it follows that the major contribution to the binding energy (61) is made by the average energy $|K(\tilde{D}, \tilde{a})|$ (63) of the exchange interaction of the electrons $e(1)$ and $e(2)$ with the holes h(A) and h(B). At the same time, the energy of Coulomb interaction (62) makes a much smaller contribution to the exciton binding energy $E_b(\tilde{D}, \tilde{a})$ (61) (i.e., the corresponding ratio is $|J(\tilde{D}, \tilde{a})/K(\tilde{D}, \tilde{a})| \leq 0.18$).

The major contribution to the exchange-interaction energy $|K(\tilde{D}, \tilde{a})|$ (63) is made by the energy $|2K_0(\tilde{D}, \tilde{a})|$ of the exchange interaction of the electron $e(1)$ with the hole h(B), as well as of the electron $e(2)$ with the hole h(A). In this case, the energies $|K_1(\tilde{D}, \tilde{a})|$ and $|K_4(\tilde{D}, \tilde{a})|$ provide only small additions to the energy $|K(\tilde{D}, \tilde{a})|$ (63) (i.e., the corresponding ratios are $|K_1/2K_0| \ll 1$ and $|K_4/2K_0| \ll 1$).

The major contribution to the Coulomb-interaction energy $|J(\tilde{D}, \tilde{a})|$ (62) is made by the energy $|2J_0(\tilde{D}, \tilde{a})|$ of Coulomb interaction of the electron $e(1)$ with the hole h(B) as well as of the electron $e(2)$ with the hole h(A). In this case, the energies $|J_1(\tilde{D}, \tilde{a})|$ and $|J_4(\tilde{D}, \tilde{a})|$ provide only small additions to the energy $|J(\tilde{D}, \tilde{a})|$ (63) (i.e., the corresponding ratios are $|J_1/2J_0| \ll 1$ and $|J_4/2J_0| \ll 1$).

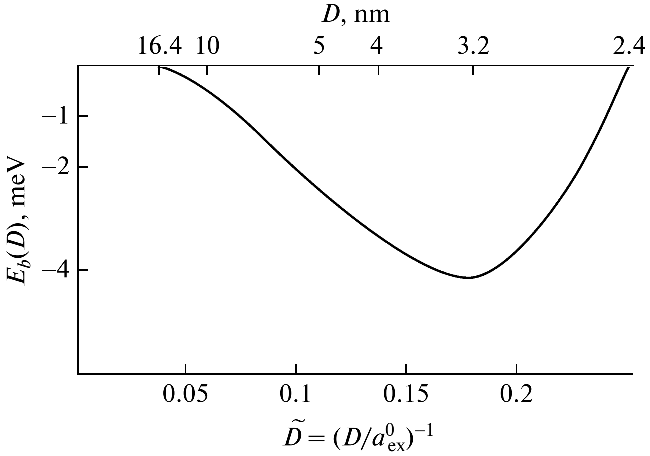

Fig. 3. Dependence of the binding energy $E_b(D)$ (61) of the singlet ground state of a biexciton (formed from spatially separated electrons and holes) in the nanosystem consisting of two spherical ZnSe QDs, QD (A) and QD (B), of average radii $\bar{a}_1 = 3.88$ nm on the spacing D between the QD (A) and QD (B) surfaces. Here, $a_{ex}^0 = 0.573$ nm (2) is the Bohr radius of a 2D exciton (formed by an electron and a hole spaced from the electron).

The contribution of the energy $|2J_0(\tilde{D}, \tilde{a})|$ to the average Coulomb-interaction energy $|J(\tilde{D}, \tilde{a})|$ (62) is approximately the same as the contribution of the energy $|2K_0(\tilde{D}, \tilde{a})|$ to the average exchange interaction energy $|K(\tilde{D}, \tilde{a})|$ (63). However, in the Coulomb interaction $|J(\tilde{D}, \tilde{a})|$ (62), the energy $J_4(\tilde{D}, \tilde{a})$, which is the energy of Coulomb interaction between the electrons $e(1)$ and $e(2)$, is substantially larger than the energy $K_4(\tilde{D}, \tilde{a})$ of the exchange interaction between the electrons $e(1)$ and $e(2)$. In addition, the energy $J_1(\tilde{D}, \tilde{a})$ of Coulomb interaction between the holes h(A) and h(B) is substantially larger than the exchange interaction energy $K_1(\tilde{D}, \tilde{a})$ (since according to (47), the energy $K_1(\tilde{D}, \tilde{a})$ involves the squared overlapping integral $S^2(\tilde{D}, \tilde{a})$ (54) which is much smaller than unity). Thus, the average energy $|K_4(\tilde{D}, \tilde{a})|$ (63) of the exchange interaction of the electrons $e(1)$ and $e(2)$ with the holes h(A) and h(B) is substantially larger than the average energy $|J(\tilde{D}, \tilde{a})|$ (62) of Coulomb interaction of the electrons $e(1)$ and $e(2)$ with the holes h(A) and h(B).

As the spacing D between the QD (A) and QD (B) surfaces is increased, starting from $D \geq D_c^{(2)} \approx 16.4$ nm (Fig. 3), the average Coulomb-interaction energy $J(\tilde{D}, \tilde{a})$ (62) substantially decreases. In addition, because of the decrease in the overlapping of the electron wavefunctions (29) and (32), the average exchange interaction energy $K(\tilde{D}, \tilde{a})$ (63) substantially decreases as well. As a consequence, the average Coulomb-interaction energy $J(\tilde{D}, \tilde{a})$ (62) and the average energy $|K(\tilde{D}, \tilde{a})|$ (63) of the exchange interaction of the electrons $e(1)$ and $e(2)$ with the holes h(A) and h(B) sharply decrease in comparison with the exciton binding energy $E_{\text{ex}}(a)$ [12] (i.e., the corresponding ratios are $|J(\tilde{D}, \tilde{a})/E_{\text{ex}}(\tilde{a})| \ll 1$ and $|K(\tilde{D}, \tilde{a})/E_{\text{ex}}(\tilde{a})| \ll 1$), resulting in decomposition of the biexciton in the nanosystem into two excitons (formed of spatially separated electrons and holes) localized above the QD (A) and QD (B) surfaces (Fig. 3).

Thus, in a nanosystem composed of ZnSe QDs with the average radii $\bar{a}_1$, the formation of a biexciton is of the threshold character and possible in a nanosystem, in which the spacing D between the QD surfaces is defined by the condition $D_c^{(1)} \leq D \leq D_c^{(2)}$. Moreover, the biexciton can exist only at temperatures below a certain critical temperature $T_1 = 49$ K.

4. CORRELATION OF THE THEORY WITH EXPERIMENTS

Bondar and Brodyn [6, 7] observed a low-temperature luminescence peak at $\bar{E} \approx 2.716$ eV (at a temperature of $T = 4.5$ K) in samples with a ZnSe QD content of $x \approx 0.6\%$; this peak was below the band gap ($E_g = 2.823$ eV) of the ZnS single crystal. The shift of the $\bar{E}$ low-temperature luminescence peak with respect to the band gap of the ZnSe single crystal was $\Delta\bar{E} = \bar{E} - E_g \cong -103$ eV.

Comparing the energy $E_0(\tilde{D}, \tilde{a})$ (60) of the biexciton ground state with the shift $\Delta\bar{E} = -103$ eV of the luminescence spectral peak, we obtain the average spacing $\bar{D}_0 \approx 4.48$ nm between the QD (A) and QD (B) surfaces (at an average QD radius of $\bar{a}_1 = 3.88$ nm). In this case, the biexciton binding energy is $E_b^{(2)}(\bar{D}, \bar{a}_1) \cong -3$ meV (corresponding to a temperature of $T_2 \approx 35$ K), and the value of $\bar{a}_1 = 3.88$ nm is in the range of the average ZnSe QD radii ($\bar{a} = 2.0$–4.8 nm) studied in the experimental conditions of [6, 7].

Thus, the experimentally observed shift $\Delta\bar{E}$ of the low-temperature luminescence peak in the samples containing ZnSe QDs with a content of $x \approx 0.6\%$ [6, 7] is due to the dependence of the energy $E_b(D, a)$ (60) of the singlet ground state of a biexciton (formed from spatially separated electrons and holes) on the spacing D between the QD surfaces and on the QD radius a.

It should be noted that the calculations of the binding energy $|E_b(\tilde{D}, \tilde{a})|$ (61) of the biexciton ground state in the nanosystem are variational, and therefore, can apparently yield understated estimates of the biexciton binding energy $|E_b(\tilde{D}, \tilde{a})|$ (61). It seems likely that the calculated maximum value of the biexciton binding energy $|E_b^{(1)}|$ is underestimated as well.

5. CONCLUSIONS

In this study, the theory of biexcitons (formed from spatially separated electrons and holes) in a nanosystem that consists of ZnSe QDs synthesized in a borosilicate glassy matrix is developed within the context of the modified effective mass approximation.

The dependences of the total energy and the binding energy of the biexciton singlet ground state in the nanosystem on the spacing D between the QD surfaces and on the QD radius are derived by the variational method. It is shown that the major contribution to the biexciton binding energy is made by the energy of the exchange interaction of electrons with holes and this contribution is much more substantial than the contribution of the energy of Coulomb interaction between the electrons and holes.

It is established that, in a nanosystem composed of ZnSe QDs of an average radii of $\bar{a}_1$, the formation of a biexciton is of the threshold character and possible in a nanosystem, in which the spacing D between the QD surfaces is larger than a certain critical spacing $D_c^{(1)}$. It is shown that an increase in the spacing D between the QD surfaces from $D \geq D_c^{(2)}$ yields decomposition of the biexciton into two excitons (formed from spatially separated electrons and holes) localized above the QD surfaces. Thus, a biexciton can be formed in the nanosystem under the condition $D_c^{(1)} \leq D \leq D_c^{(2)}$. In addition, the biexciton can exist only at temperatures below a certain critical temperature $T_1 = 49$ K. In the ZnSe single crystal, the biexciton is formed with the binding energy $E_b = 0.45$ meV corresponding to the temperature 5.2 K [16]. At the same time, the exciton binding energy $E_b^{(1)}$ in the nanosystem is about an order of magnitude higher than E_b.

It is established that the experimentally observed shift of the low-temperature luminescence spectral peak in the samples with the ZnSe QD content $x \approx 0.6\%$ [6, 7] is due to the dependences of the energy of the ground singlet state of biexcitons (formed from spatially separated electrons and holes) on the spacing D between the QD surfaces and on the QD radius a.

REFERENCES

1. Al. L. Efros and A. L. Efros, Sov. Phys. Semicond. **16**, 772 (1982).
2. A. Ekimov, F. Hache, and M. C. Schanne-Klein, J. Opt. Soc. Am. B **20**, 100 (2003).
3. Zh. I. Alferov, Usp. Fiz. Nauk **172**, 1068 (2002).
4. G. C. La Rocca, F. Bassani, and V. M. Agranovich, J. Opt. Soc. Am. B **15**, 652 (1998).
5. V. M. Agranovich, G. C. La Rocca, and F. Bassani, J. Luminesc. **76/77**, 161 (1998).
6. N. V. Bondar and M. S. Brodyn, Semiconductors **44**, 884 (2010).
7. N. V. Bondar and M. S. Brodyn, Phys. E **42**, 1549 (2010).
8. V. Ya. Grabovskis, Ya. Ya. Dzenis, and A. I. Ekimov, Sov. Phys. Solid State **31**, 149 (1989).
9. S. I. Pokutnyi, Semiconductors **41**, 1323 (2007).
10. S. I. Pokutnyi, Semiconductors **44**, 488 (2010).
11. S. I. Pokutnyi, Semiconductors **46**, 165 (2012).
12. S. I. Pokutnyi, Semiconductors **47**, 791 (2013); S. I. Pokutnyi, Phys. Express **2** (20), 1 (2012).
13. S. Davydov, *Quantum Mechanics* (Nauka, Moscow, 1973; Pergamon, Oxford, 1976).
14. A. V. Klyuchnik and Yu. E. Lozovik, Sov. Phys. Solid State **20**, 364 (1978).
15. L. N. Ivanov, Yu. E. Lozovik, and D. R. Musin, J. Phys. C **11**, 2527 (1978).
16. S. A. Moskalenko, P. I. Khadzhi, and A. I. Bobrysheva, Sov. Phys. Solid State **5**, 2377 (1963).

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