Theory of excitons and excitonic quasimolecules formed from spatially separated electrons and holes in quasi-zero-dimensional nanosystems

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Abstract: The theory of an exciton formed from spatially separated electron and hole (the hole is in the quantum dot volume, and the electron is localized at the outer spherical quantum dot-dielectric matrix interface) is developed within the modified effective mass method. The effect of significantly increasing the exciton binding energy in quantum dots of zinc selenide, synthesized in a borosilicate glass matrix, relative to that in a zinc selenide single crystal is revealed. It was shown that the short-wavelength shift of the peak of the low-temperature luminescence spectrum of samples containing zinc-selenide quantum dots, observed under the experimental conditions, is caused by quantum confinement of the ground-state energy of the exciton with a spatially separated electron and hole. A review devoted to the theory of excitonic quasimolecules (biexcitons) (formed of spatially separated electrons and holes) in a nanosystem that consists of ZnSe quantum dots synthesized in a borosilicate glass matrix is developed within the context of the modified effective mass approximation. It is shown that biexciton (exciton quasimolecule) formation is of the threshold character and possible in nanosystem, in with the spacing between the quantum dots surfaces is larger than a certain critical spacing. On the basis of analogy spectroscopy of electronic states of superatoms (or artificial atoms) and individual alkali metal atoms theoretically predicted a new artificial atom, which is similar to the new alkali metal atom.

Keywords: Excitons, Modified Effective Mass Method, Exciton Binding Energy, Quantum Dots, Excitonic Quasimolecules, Biexcitons, Spatially Separated Electrons and Holes, Superatoms

1. Introduction

At present, quasi-zero-dimensional semiconductor nanosystems consisting of spherical semiconductor nanocrystals, i.e., quantum dots with radii of \( a = 1-10 \) nm, containing cadmium sulfide and selenide, gallium arsenide, germanium, silicon, and zinc selenide in their volume, synthesized in a borosilicate glass matrix, attract particular attention due to their unique photoluminescence properties, i.e., the ability to efficiently emit light in the visible or near infrared ranges at room temperature [1–10]. The optical and electro-optical properties of such quasi-zero dimensional nanosystems are controlled to a large extent by the energy spectrum of the spatially confined electron–hole pair (exciton) [4–16].

In most theoretical models for calculating the energy spectra of quasiparticles in quantum dots (QDs), the effective mass approximation is used, which was considered to be applicable to QDs by analogy with bulk single crystals [11–13]. However, the problem of the applicability of the effective mass approximation to the description of semiconductor QDs is still unsolved [4–18].

In [14], a new modified effective mass method was proposed to describe the exciton energy spectrum in semiconductor QDs with radii of \( a \approx a_{\text{ex}} \) (\( a_{\text{ex}} \) is the exciton Bohr radius in the semiconductor material contained in the QD volume). It was shown that, within a model in which the QD is represented as an infinitely deep potential well, the effective mass approximation can be applied to the description of an exciton in QDs with radii \( a \) comparable to the exciton Bohr radius \( a_{\text{ex}} \), assuming that the reduced effective exciton mass is a function of the radius \( a, \mu = \mu(a) \).
In the adiabatic approximation and within the modified effective mass method [14], an expression for the binding energy of an exciton whose electron and hole move in the semiconductor QD volume was derived in [15]. In [15], the effect of significantly increasing the exciton-binding energy in cadmium selenide and sulfide QDs with radii \( a \), comparable to the exciton Bohr radii \( a_{ex} \), relative to the exciton-binding energy in cadmium selenide and sulfide single crystals (by factors of 7.4 and 4.5, respectively) was also detected.

In the experimental study [7], it was found that excess electrons produced during interband excitation of the cadmium sulfide QD have a finite probability of overcoming the potential barrier and penetrating into the borosilicate glass matrix into which the QD is immersed. In experimental studies [10, 19] (as well as in [7]) of glass samples with cadmium-sulfide and zinc-selenide QDs, it was found that the electron can be localized in the polarization well near the outer QD surface, while the hole moves within the QD volume.

In [10, 19], the optical properties of borosilicate glass samples containing QD zinc selenide are experimentally studied. The average radii of such QDs are in the range \( a \approx 2.0–4.8 \) nm. In this case, the values of \( a \) are comparable to the exciton Bohr radius \( a_{ex} \approx 3.7 \) nm in a ZnSe single crystal. At low QD concentrations, when the optical properties of the samples are mainly controlled by those of individual QDs in the borosilicate glass matrix, a shift of the peak of the low temperature luminescence spectrum to shorter wavelengths was observed also for samples with a QD concentrations from \( x = 0.003 \) to \( 1\% \). It was noted [10, 19] 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 [23, 24] we develop the theory of a excitonic quasimolecules (biexcitons) formed from spatially separated electrons and holes in a nanosystem that consists of ZnSe QDs synthesized in a borosilicate glass matrix.

2. Exciton Ground - State Energy in the Nanosystem

Let us consider the simple model of a quasi-zero-dimensional system, i.e., a neutral spherical semiconductor QD of the radius \( a \), which contains semiconductor material with the permittivity \( \varepsilon_2 \) in its volume, surrounded by a dielectric matrix with the permittivity \( \varepsilon_1 \). A hole \( h \) with the effective mass \( m_h \) moves in the QD volume, while an electron \( e \) with the effective mass \( m_e^{(1)} \) lies in the matrix (\( r_e \) and \( r_h \) are the distances from the QD center to the electron and hole). Let us assume that the QD valence band is parabolic. Let us also assume that there is an infinitely high potential barrier at the spherical QD – dielectric matrix interface; therefore, the hole \( h \) cannot leave the QD volume and the electron \( e \) cannot penetrate into the QD volume in the model under study [20 – 22].

The characteristic dimensions of the problem are the quantities

\[
\begin{align*}
    a_h &= \varepsilon_2 \hbar^2 / m_h \varepsilon^2, \\
    a_{ex} &= \varepsilon_2 \hbar^2 / \mu \varepsilon^2, \\
    a_e &= \varepsilon_1 \hbar^2 / m_e^{(1)} \varepsilon^2,
\end{align*}
\]

where \( a_h \) and \( a_{ex} \) are the hole and exciton Bohr radii in the semiconductor with the permittivity \( \varepsilon_2 \), \( e \) is the elementary charge, \( \mu = m_e^{(2)} m_h / (m_e^{(2)} + m_h) \) is the reduced effective mass of the exciton, \( m_e^{(2)} \) is the effective mass of an electron in the semiconductor with the permittivity \( \varepsilon_2 \), and \( a_e \) is the electron Bohr radius in the dielectric matrix with the permittivity \( \varepsilon_1 \). The fact that all characteristic dimensions of the problem are significantly larger than the interatomic distances \( a_0 \):

\[
a_h, a_{ex} \gg a_0
\]
allows us to consider the electron and hole motion in the quasi-zero-dimensional nanosystem in the effective mass approximation [11–13].

We analyzed the conditions of carrier localization in the vicinity of a spherical dielectric particle of the radius \( a \) with the permittivity \( \varepsilon_2 \) in [25–27]. There the problem of the field induced by the carrier near a dielectric particle immersed in a dielectric medium with the permittivity \( \varepsilon_1 \) was solved in a final analytical form, and analytical expressions for the potential energy of the interaction of the carrier with the spherical interface of two media are presented.

Solving the Poisson equation with usual electrostatic boundary conditions

\[
\varphi(r', j | r, i) = \frac{\varepsilon}{\varepsilon_1} \left[ \varphi(r', j) \right]_{r'=\frac{r}{\varepsilon_1}} - \frac{e}{\varepsilon_1 |r'-r|} + \frac{e(r_2 | r)}{\varepsilon_2 |r'-r_2|} + \frac{1}{\varepsilon_2 \varepsilon_1 |r'-r_2|} \int \frac{dy r_2 (y, r)}{|r'-r_2|},
\]

the potential \( \varphi(r', j | r, i) \) at the observation point \( r' \) in a medium with the permittivity \( \varepsilon_2 \) induced by the charge \( e \) at the point \( r \) in a medium with the permittivity \( \varepsilon_1 \), can be presented as a sum of the potentials induced by the image point charge \( e(r_2 | r) \) at the point \( r_2 = (ar^2 r_0 + r (1 - \delta ij)) \) and the linear distribution with the density \( P_0(y, r) \) of the image charge along a straight line passing through the center of the dielectric particle with the radius \( a \) and the charge at the point \( r \) [25–27]:

\[
\varphi(r', j | r, i) = \frac{\varepsilon}{\varepsilon_1} \left[ \varphi(r', j) \right]_{r'=\frac{r}{\varepsilon_1}} - \frac{e}{\varepsilon_1 |r'-r|} + \frac{e(r_2 | r)}{\varepsilon_2 |r'-r_2|} + \frac{1}{\varepsilon_2 \varepsilon_1 |r'-r_2|} \int \frac{dy r_2 (y, r)}{|r'-r_2|},
\]

where

\[
r_{11} = \left( a^2 / r^2 \right) r \ , \ e'_{11} (r_{11} | r) = -\beta (a/r) e,
\]

\[
\rho_{11} (y, r) = \beta \alpha \left( a^2 / ry \right) (e/\alpha) \theta ((a^2/r) - y);
\]

\[
r_{11} = r \ , \ e'_{11} (r_{11} | r) = \beta e;
\]

\[
\rho_{12} (y, r) = \beta (1/\alpha) \left( r^2 / ry \right) (e/\alpha) \theta (y - (a^2/r));
\]

\[
r_{12} = r \ , \ e'_{12} (r_{12} | r) = -\beta e;
\]

\[
\rho_{21} (y, r) = \beta \alpha \left( r^2 / y \right) (e/\alpha) \theta (y - r);
\]

\[
r_{21} = r \ , \ e'_{21} (r_{21} | r) = \beta e;
\]

\[
\rho_{22} (y, r) = \beta (1/\alpha \alpha) \left( r^2 / r^2 \right) (e/\alpha) \theta (r - (a^2/r));
\]

\[
r_{22} = r \ , \ e'_{22} (r_{22} | r) = \beta e;
\]

where \( \theta (x) \) is the Heaviside unit-step function,

\[\beta = \frac{(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2 + \varepsilon_1} \alpha = \frac{\varepsilon_2}{\varepsilon_2 + \varepsilon_1} \] (4)

Using expressions (3)–(3d), the energy \( U(r, \varepsilon, a) \) of the polarization interaction of the electron and hole with the spherical QD–matrix interface at the relative permittivity \( \varepsilon = (\varepsilon_2/\varepsilon_1) \gg 1 \) can be presented as an algebraic sum of the energies of the interaction of the hole and electron with self- \( V_{bh}(r, a) \) and “foreign” \( V_{vb}(r, a) \) and “foreign” \( V_{vb}(r, a) \) images, respectively [15,16,26–28],

\[
U(r, \varepsilon, a) = \frac{e^2}{2 \varepsilon_0 a} \left( \frac{a^2}{a^2 - r_0^2} + e \right).
\]

where

\[
V_{bh}(r, \varepsilon, a) = \frac{e^2}{2 \varepsilon_0 a} \left( \frac{a^2}{r_0^2} (e^2 - a^2) \right),
\]

\[
V_{vb}(r, \varepsilon, a) = \frac{e^2}{2 \varepsilon_0 a} \left( \frac{a^2}{r_0^2} (e^2 - a^2)^2 \right),
\]

\[
V_{vb}(r, \varepsilon, a) = \frac{e^2}{2 \varepsilon_0 a} \left( \frac{a^2}{r_0^2} (e^2 - a^2)^3 \right),
\]

In the studied simple model of a quasi zero dimensional nanostructure within the above approximations and in the effective mass approximation using the triangular coordinate system [14–16], \( r = \left| r_1 \right|, r = \left| r_2 \right|, r = \left| r_3 - r_0 \right| \), with the origin at the center of the QD, the exciton Hamiltonian (with a spatially separated hole moving within the QD volume and an electron in the dielectric matrix) takes the form [20 – 22, 29–32]:

\[
H = \frac{\hbar^2}{2m_0} \left( \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) + \frac{\hbar^2}{2m_h} \left( \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} \right)
\]

\[
- \frac{\hbar^2}{2m_h} \left( \frac{\partial^2}{\partial r_3^2} + \frac{2}{r_3} \frac{\partial}{\partial r_3} \right) - \frac{\hbar^2}{2m_h} \left( \frac{\partial^2}{\partial r_4^2} + \frac{2}{r_4} \frac{\partial}{\partial r_4} \right)
\]

\[
+ V_{eh}(r) + U(r, \varepsilon, a) + V_{bh}(r) + V_{vb}(r) + E_g,
\]

where the first three terms are the operators of the electron, hole, and exciton kinetic energy, \( E_g \) is the band gap in the semiconductor with the permittivity \( \varepsilon_2 \). \( \mu_0 = m_0 (m_h / m_e) + m_h \) is the reduced effective mass of the exciton (with a spatially separated hole and electron). In the Hamiltonian (10), the polarization interaction energy \( U(r, \varepsilon, a, \varepsilon) \) (5) is defined by formulas (6)–(9), and the electron–hole Coulomb interaction energy \( V_{eh}(r) \) is described by the formula

\[
V_{eh}(r) = -\frac{1}{2} \left( \frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right)
\]

In the exciton Hamiltonian (10), the potentials

\[
V_{bh}(r_0) = \begin{cases} 0, & r_0 \leq a \\
\infty, & r_0 > a. \end{cases}
\]

\[
V_{Ve}(r_0) = \begin{cases} 0, & r_0 \leq a \\
\infty, & r_0 > a. \end{cases}
\]
describe the quasiparticle motion using the models of an infinitely deep potential well.

As the QD radius $a$ increases (so that $a \gg a_{ex}^0$), the spherical interface of the two media (QD–matrix) passes to the plane (semiconductor material with the permittivity $\varepsilon_2$)–matrix interface. In this case, the exciton with the spatially separated electron and hole (the hole moves within the semiconductor material and the electron lies in the borosilicate glass matrix) becomes two-dimensional [20 – 22].

The main contribution to the potential energy of the Hamiltonian (10) describing exciton motion in a nanosystem containing a large-radius QD, $a \gg a_{ex}^0$, is made by the electron–hole Coulomb interaction energy $V_{ch}(r)$ (11). The energy of the hole and electron interaction with self- $V_{hh}(r_h, a, \varepsilon)$ (6), $V_{eh}(r_h, a)$ (7) and “foreign” $V_{eh}(r, r_h, a)$ (9), $V_{eh}(r, r_h, a)$ (8) images makes a significantly smaller contribution to the potential energy of the Hamiltonian (10). In the first approximation, this contribution can be disregarded. In this case, only the electron–hole Coulomb interaction energy (11) remains in the potential energy of the Hamiltonian (10) [20 – 22]. The Schrodinger equation with such a Hamiltonian describes a two-dimensional exciton with a spatially separated electron and hole (the electron moves within the matrix, and the hole lies in the semiconductor material with the permittivity $\varepsilon_2$), whose energy spectrum takes the form [33, 34]:

$$E_n = -\frac{r_0^2}{(n+1/2)^2}$$

and

$$Ry_{ex}^0 = \frac{(\varepsilon_1 + \varepsilon_2)^2}{4\varepsilon_1^2 \varepsilon_2^2} \frac{\mu_0}{m_0} Ry_0$$

where $n = 0, 1, 2...$ is the principal quantum number of the exciton and $Ry_0 = 13.606$ eV is the Rydberg constant. The Bohr radius of such a two-dimensional exciton is described by the formula

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

and

$$E_0(a, \mu(a)) = \langle \psi_0(r_e, r_h, r, a) | H(r_e, r_h, r, a) | \psi_0(r_e, r_h, r, a) \rangle$$

where

$$\psi_0(r_e, r_h, r, a) = \int_a^{\infty} dr_e \int_0^{r_e} dr_h \int_0^{r_e+rr_h} dr \int_0^{r_e} \psi_0(r_e, r_h, r, a) H(r_e, r_h, r, a) \psi_0(r_e, r_h, r, a)$$

The dependence of the energy $E_0(a)$ of the exciton ground state ($n = 1, l = m_e = 0; n_h = 1, l_h = m_h = 0$), $m_e$, $l_e$, $m_h$, $l_h$ are the principal, orbital, and magnetic quantum numbers of the electron and hole, respectively) on the QD radius $a$ is calculated by minimizing the functional $E_0(a, \mu(a))$ (17),

$$\frac{\partial E_0(a, \mu(a))}{\partial \mu(a)} = F(\mu(a), a)$$

Without writing cumbersome expressions for the first derivative of the functional $F(\mu(a), a)$, we present the numerical solution to the equation $F(\mu(a), a) = 0$ (18) in tabulated form.

It follows from the table that the solution to this equation is the function $\mu(a)$ which monotonically weakly varies within the limits [20 – 22]:

$$0.304 \leq \mu(a)/m_0 \leq 0.359$$

as the QD radius $a$ varies within the range

$$2.0 \leq a \leq 29.8 \text{ nm}$$
\( m_0 \) is the electron mass in vacuum. In this case, the reduced exciton effective mass \( \mu(a) \) in the nanosystem slightly differs from the effective mass of an exciton (with a spatially separated hole and electron) \( \mu \approx 0.304m_0 \) by the value \( \mu(a) - \mu_0 \leq 0.18 \) when the QD radii vary within the range (20).

Substituting the values of the variational parameter \( \mu(a) \) (19) from the table simultaneously with the corresponding QD radii from the range (20) into the functional \( E_0(a, \mu(a)) \) (17), we obtain the exciton ground-state energy \( E_0(a, e) \) (17) as a function of the QD radius \( a \). [20 – 22].

The results of variational calculation of the energy of the ground state of an exciton \( E_0(a, e) \) (17) in the nanosystem under study containing zinc-selenide QDs of the radius \( a \) (20) are shown in the figure [20 – 22]. Here, the values of function \( \mu(a) \) (19) and the results of variational calculation of the exciton ground-state energy \( E_0(a, e) \) (17) are obtained for a nanosystem containing zinc-selenide QDs, synthesized in a borosilicate glass matrix, studied in the experimental works [10, 19].

In the experimental work [10], borosilicate glass samples doped with zinc selenide with concentrations from \( x = 0.003 \) to \( 1 \% \), obtained by the sol–gel method were studied. According to X-ray diffraction measurements, the average radii \( a \) of ZnSe QDs formed in the samples are within \( a \approx 2.0–4.8 \) nm. In this case, the values of \( a \) are comparable to the exciton Bohr radius \( a_\text{Bohr} \approx 3.7 \) nm in a zinc-selenide single crystal. At low QD concentrations (\( x = 0.003 \) and \( 0.06 \% \)), their interaction can be disregarded. The optical properties of such nanosystems are mainly controlled by the energy spectra of electrons and holes localized near the spherical surface of individual QDs synthesized in the borosilicate glass matrix.

In [10, 19], a peak in the low-temperature luminescence spectrum at an energy of \( E_1 \approx 2.66 \) eV was observed at the temperature \( T = 4.5 \) K in samples with \( x = 0.06 \% \); this energy is lower than the band gap of a zinc-selenide single crystal (\( E_g = 2.823 \) eV). The shift of the peak of the low-temperature luminescence spectrum with respect to the band gap of the ZnSe single crystal to the short-wavelength region is \( \Delta E_1 = (E_1 - E_g) \approx -165 \) meV. The authors of [10] assumed that the shift \( \Delta E_1 \) is caused by quantum confinement of the energy spectra of electrons and holes localized near the spherical surface of individual QDs and is associated with a decrease in the average radii \( a \) of zinc-selenide QDs at low concentrations (\( x = 0.06 \% \)). In this case, the problem of the quantum confinement of which electron and hole states (the hole moving within the QD volume and the electron localized at the outer spherical QD–dielectric matrix interface or the electron and hole localized in the QD volume) caused such a shift of the luminescence-spectrum peak remained open.

Comparing the exciton ground-state energy \( (E_0(a, e) - E_g) \) (17) with the energy of the shift in the luminescence-spectrum peak \( \Delta E_1 \approx -165 \) meV, we obtain the average zinc-selenide QD radius \( a_1 \approx 4.22 \) nm (see the figure) [20 – 22]. The QD radius \( a_1 \) may be slightly overestimated, since variational calculation of the exciton ground-state energy can give slightly overestimated energies [33, 34]. The determined average QD radius \( a_1 \) lies within the range of the average radii of zinc-selenide QDs (\( a \approx 2.0–4.8 \) nm), studied under the experimental conditions of [10, 19].

The exciton density of states (DOS) in the atomic limit can be written as

\[
\rho_{\text{exc}}(E) = \frac{1}{\pi} \frac{\text{df}}{\text{dE}} = \frac{1}{\pi} \frac{\partial E_{\text{g}}}{\partial a} \left( \frac{a}{a_0} \right)^2 \left( 1 - \frac{a}{a_0} \right)^2 \left( \frac{E}{E_{\text{g}}} \right)^2 \left( 1 - \frac{E}{E_{\text{g}}} \right),
\]

where \( \rho_{\text{exc}}(E) \) is the exciton DOS, \( E_{\text{g}} \) is the absorption edge, \( a_0 \) is the exciton Bohr radius at \( E_{\text{g}} \), and \( a \) is the QD radius.

It should be noted that the average Coulomb interaction energy \( V_{\text{eh}}(a, e) = \langle \psi_0(r_e, r_h, r, a) | V_{\text{eh}}(r_e) | \psi_0(r_e, r_h, r, a) \rangle \) between the electron and hole mainly contribute to the ground-state energy (17) of the exciton in the nanosystem containing zinc-selenide QDs with radii \( a_1 \) comparable to the exciton Bohr radius in a zinc-selenide single crystal (\( a_\text{Bohr} \approx 3.7 \) nm). In this case, the average energy of the interaction of the electron and hole with self- and “foreign” images,

\[
\left( \nabla_r(r_e, r_h, r, a) + \nabla_r(r_e, r_h, a) + \nabla_r(r, a) \right) = \langle \psi_0(r_e, r_h, r, a) \nabla_r(r_e, r_h, r, a) + \nabla_r(r, a) \rangle \psi_0(r_e, r_h, r, a)
\]

makes a significantly smaller contribution to the exciton ground-state energy (17), \( 0.04 \leq \langle | V_{\text{eh}}(r_e, r_h, r, a) | V_{\text{eh}}(r_e, r_h, r, a) | (r_e, r_h, r, a) \rangle \leq 0.12 \) [20 – 22].

Thus, the short-wavelength shift \( \Delta E_1 \) of the low temperature luminescence spectrum peak is caused by renormalization of the electron–hole Coulomb interaction energy \( V_{\text{eh}}(r) \) (11) and also renormalization of the energy \( U(r_e, r_h, r, a, e) \) (5) of the polarization interaction of the
electron and hole with the spherical QD–dielectric matrix interface, which is associated with spatial confinement of the quantization region by the QD volume. In this case, the hole moves within the QD volume, and the electron is localized at the outer spherical QD–dielectric matrix interface.

2.1. Binding Energy of the Exciton Ground State in the Nanosystem

The binding energy of the ground state of an exciton

\[ E_{ex}(a, \varepsilon) = E_{0}(a, \varepsilon) - \langle \psi_{0}(r_{e}, r_{h}, r, a) \rangle | V_{hh}(r_{e}, a, \varepsilon) + V_{eh}(r_{e}, r_{h}, \varepsilon) \rangle \psi_{0}(r_{e}, r_{h}, r, a) \]  
(21)

Where the term

\[ \langle \psi_{0}(r_{e}, r_{h}, r, a) \rangle | V_{hh}(r_{e}, a, \varepsilon) + V_{eh}(r_{e}, r_{h}, \varepsilon) \rangle \psi_{0}(r_{e}, r_{h}, r, a) \]

describes the average energy of hole and electron interaction with self-images.

Since the average energies of the interaction of the hole with its image make contributions with opposite signs to expression (21), they significantly compensate each other. Therefore, the binding energies of the exciton ground state \( E_{ex}(a, \varepsilon) \) (21) slightly differ from the corresponding total energies of the exciton ground state \( E_{0}(a, \varepsilon) \) (17). This difference

\[ \Delta = \left| E_{ex}(a, \varepsilon) - E_{0}(a, \varepsilon) \right| / E_{ex}(a, \varepsilon) \]

varies within \( \Delta \leq 4\% \) as QD radii \( a \) vary within the range 3.84 \( \leq a \leq 8.2 \) nm (see the figure) [20–22].

The figure shows the dependences of the total energy \( E_{0}(a, \varepsilon) \) (17) and the binding energy \( E_{ex}(a, \varepsilon) \) (21) of the exciton ground state with a spatially separated electron–hole pair on the QD size for a nanosystem containing zinc-selenide QDs of the radius \( a \). We can see that bound states of electron–hole pairs arise near the spherical surface of the QD starting from the QD critical radius \( a \geq a_{c}^{(1)} \approx 3.84 \) nm. In this case, the hole is localized near the QD inner surface, and the electron is localized at the outer spherical QD–dielectric matrix interface. Starting from the QD radius \( a \geq a_{c}^{(1)} \), the electron–hole pair states are in the region of negative energies (counted from the top of the band gap \( E_{g} \) for a zinc-selenide single crystal), which corresponds to the electron–hole bound state [20–22, 29–23].

In this case, the electron–hole Coulomb interaction energy \( V_{ch}(r) \) (11) and the energy \( U(r_{e}, r_{h}, r, a, \varepsilon) \) (5) of the polarization interaction of the electron and hole with the spherical QD–dielectric matrix interface dominate over the energy of quantum confinement of the electron and hole in the nanosystem under study.

The total energy \( E_{0}(a, \varepsilon) \) (17) and the binding energy \( E_{ex}(a, \varepsilon) \) (21) of the ground state of the exciton with a spatially separated electron and hole increase with QD radius \( a \). In the range of radii

\[ 4.0 \leq a \leq 29.8 \text{ nm} \]  
(22)

the binding energy \( E_{ex}(a, \varepsilon) \) (21) of the exciton ground state significantly (by a factor of 4.1–76.2) exceeds the exciton binding energy in a zinc-selenide single crystal, \( E_{ex}^{0} \approx -21.07 \text{ meV} \). Starting from the QD radius \( a \geq a_{c}^{(2)} \approx 29.8 \) nm, the total energies (17) and binding energies (21) of the exciton ground state asymptotically tend to the value \( E_{ex}^{0} = -1.5296 \text{ eV} \) which characterizes the binding energy of the ground state of a two-dimensional exciton with a spatially separated electron and hole (see the figure) [20–22, 29–32].

The obtained values of the total energy \( E_{0}(a, \varepsilon) \) (17) of the exciton ground state in the nanosystem satisfy the inequality

\[ E_{0}(a, \varepsilon) - E_{g} \leq \Delta V(a) \]  
(23)

where \( \Delta V(a) \) is the potential-well depth for the QD electron. For a large class of II–VI semiconductors in the region of QD sizes \( a \geq a_{c}^{(2)} \), \( \Delta V(a) = 2.3–2.5 \) eV [7]. Satisfaction of condition (23), probably, makes it possible to disregard the effect of the complex structure of the QD valence band on the total energy (17) and the binding energy (21) of the exciton ground state in the nanosystem under study when deriving these quantities.

The effect of a significant increase in the binding energy \( E_{ex}(a, \varepsilon) \) (21) of the exciton ground state in the nanosystem under study, according to formulas (5)–(9), (11), (13)–(15), (17), (21) is controlled by two factors [20–22, 29–32]: (i) a significant increase in the energy of the electron–hole Coulomb interaction \( V_{ch}(r) \) (11) and an increase in the energy of the interaction of the electron and hole with “foreign” images \( V_{ch}(r_{e}, r_{h}, r, a, \varepsilon) \) (9); (ii) spatial quantization of the quantization region by the QD volume; in this case, as the QD radius \( a \) increases, starting from \( a \geq a_{c}^{(2)} \approx 52 a_{e}^{0} \approx 29.8 \) nm, the exciton becomes two-dimensional with a ground-state energy \( E_{ex}^{0} \) (15) that exceeds the exciton binding energy \( E_{ex} \) in the zincselenium single crystal by almost two orders of magnitude \( \left| E_{ex}^{0} / E_{ex}^{0} \right| \approx 72.6 \).

The “dielectric enhancement” effect is caused by the following factor. When the matrix permittivity \( \varepsilon_{m} \) is significantly smaller than the QD permittivity \( \varepsilon_{Q} \), the most important role in the electron–hole interaction in the nanosystem under study is played by the field induced by these quasiparticles in the matrix. In this case, electron–hole interaction in the nanosystem appears to be significantly stronger than in an infinite semiconductor.
with the permittivity $\varepsilon_2$ [34].

In [16], in the nanosystem experimentally studied in [10], an exciton model in which the electron and hole move within the zinc-selenide QD volume is studied. Using the variational method, within the modified effective mass method, the dependence of the exciton ground-state energy $E_0(a, \varv)$ on the QD radius $a$ in the range (20) was obtained in [16] (see the figure). It was shown that, as the QD radius increases, starting from $a \geq a_c \approx 3.90 \, \text{A}_0 = 1.45 \, \text{nm}$, a bulk exciton appears in the QD; its binding energy

$$E_{\text{ex}}^0 = -\frac{k^2}{2\mu(\alpha_{\text{ex}}^2)}$$  \hspace{1cm} (24)

is $21.07 \, \text{meV} (\mu = 0.132m_0$ and $\alpha_{\text{ex}}^0 = 3.7 \, \text{nm}$ are the reduced effective mass and Bohr radius of the exciton in the zinc selenide forming the QD volume). The bulk exciton in the QD is understood as an exciton whose structure (reduced mass, Bohr radius, and binding energy) in the QD does not differ from the structure of an exciton in an infinite semiconductor material. As the QD radius $a$ increases ($a \geq a_c$), the exciton ground-state energy $E_0(a)$ asymptotically follows the binding energy of the bulk exciton (24) (see the figure) [20 – 22, 29 – 32].

Thus, using the exciton model in which an electron and hole move in the QD volume, it is impossible to interpret the mechanism of the appearance of the nanosystem luminescence - spectrum peak with the shift $\Delta E_1 \approx -165 \, \text{meV},$ obtained in [10, 19].

A comparison of the dependences of the exciton ground-state energy $E_0(a)$ in the nanosystem [10], obtained using two - exciton models (see the figure) (the electron and hole move within the zinc-selenide QD volume [16] (model I); the hole moves within the zinc-selenide QD volume, and the electron is localized in the boron silicate glass matrix near the QD spherical surface (model II) allows the following conclusion. In model I, as the QD radius $a$ increases, starting from $a \geq a_c \approx 14.5 \, \text{nm}$, the exciton ground-state energy $E_0(a)$ asymptotically follows the binding energy of the bulk exciton $E_{\text{ex}}^0 \approx -21.07 \, \text{meV}$ (24); in model II, as the QD radius increases, starting from $a \geq a_c^{(2)} \approx 29.8 \, \text{nm}$, the exciton ground-state energy (17) asymptotically follows $E_{\text{ex}}^0 = -1.5296 \, \text{eV}$ (15) (characterizing the binding energy of the ground state of a two-dimensional exciton with a spatially separated electron and hole), which is significantly lower than $E_{\text{ex}}^0 \approx -21.07 \, \text{meV}$ [20 – 22, 29 – 32].

3. Excitonic Quasimolecules Formed from Spatially Separated Electrons and Holes

We consider a model nanosystem [23, 24] that consists of two spherical semiconductor QDs, $A$ and $B$, synthesized in a borosilicate glass matrix with the permittivity $\varepsilon_1$. Let the QD radii be $a$, the spacing between the spherical QD surfaces be $D$. Each QD is formed from a semiconductor material with the permittivity $\varepsilon_2$. For simplicity, without loss of generality, we assume that the holes $h(A)$ and $h(B)$ 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. 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.

In the context of the adiabatic approximation and effective mass approximation, using the variational method, we obtain the total energy $E_{\text{ex}}(\bar{D}, \bar{a})$ and the binding energy $E_x(\bar{D}, \bar{a})$ of the biexciton singlet ground state (the spins of the electrons $e(1)$ and $e(2)$ are antiparallel) in such system as functions of the spacing between the QD surfaces be $D$ and the QD radius $a$ [23, 24]:

$$E_0(\bar{D}, \bar{a}) = 2E_{\text{ex}}(\bar{a}) + E_x(\bar{D}, \bar{a}),$$  \hspace{1cm} (25)

Here, the binding energy $E_{\text{ex}}(\bar{a})$ (17) 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 in [23, 24] (parameters $\bar{a} = (a/\bar{a}_0)$ ($\alpha_{\text{ex}} = 3.7 \, \text{nm}$ - the exciton Bohr radius in a single crystal ZnSe, $\bar{D} = (D/\bar{a}_0)$). For the nanosystem under study, the values of the binding energies $E_{\text{ex}}(\bar{a})$ are calculated in [23, 24] for the experimental conditions of [10, 19].

The results of variational calculation of the binding energy $E_x(\bar{D}, \bar{a})$ of the biexciton singlet ground state in the nanosystem of ZnSe QDs with average radii of $\bar{a}_1 = 3.88 \, \text{nm}$, synthesized in a borosilicate glass matrix are shown in [23, 24]. Such a nanosystem was experimentally studied in [10, 19]. In [10, 19], 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 $x = 0.06 \%$, one must take into account the interaction of charge carriers localized above the QD surfaces.

The binding energy $E_x(\bar{D}, \bar{a})$ of the biexciton singlet ground state in the nanosystem of ZnSe QDs with average radii of $\bar{a}_1 = 3.88 \, \text{nm}$ has a minimum of $E_x^{(1)}(D_1, \bar{a}_1) \approx -4.2 \, \text{meV}$ (at the spacing $D_1 \approx 3.2 \, \text{nm}$) [23, 24]. The value of $E_x^{(1)}$ corresponds to the temperature $T_c \approx 49 \, \text{K}$. In [23, 24], it follows that a biexciton (excitonic quasimolecule) is formed in the nanosystem, starting from a spacing between the QD surfaces of $D \geq D_1^{(1)} \approx 2.4 \, \text{nm}$. The formation of such an excitonic quasimolecule (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 $D_1^{(1)}$. Moreover, the excitonic quasimolecule (biexciton) can exist only at temperatures below a certain critical temperature: $T_c \approx 49 \, \text{K}$ [23, 24].

As follows from the results of variational calculation [23,
surfaces is increased, starting from 24].

As the spacing $D$ between the QD(A) and QD(B) surfaces is increased, starting from $D \geq D_c^{(2)} \equiv 16.4$ nm, the average Coulomb – interaction energy substantially decreases. In addition, because of the decrease in the overlapping of the electron wavefunction, the average exchange interaction energy substantially decreases as well. As a consequence, the average Coulomb – interaction energy and the average energy of the exchange interaction of the electrons $\epsilon(1)$ and $\epsilon(2)$ with the holes $h( A)$ and $h( B)$. The major contribution to the Coulomb – interaction energy is made by the energy of Coulomb interaction of the electron $\epsilon(1)$ with the holes $h( A)$ and $h( B)$, as well as of the electron $\epsilon(2)$ with the holes $h( A)$.

As the spacing $D$ between the QD(A) and QD(B) surfaces is increased, starting from $D \geq D_c^{(2)} \equiv 16.4$ nm, the average Coulomb – interaction energy substantially decreases. In addition, because of the decrease in the overlapping of the electron wavefunction, the average exchange interaction energy substantially decreases as well. As a consequence, the average Coulomb – interaction energy and the average energy of the exchange interaction of the electrons $\epsilon(1)$ and $\epsilon(2)$ with the holes $h( A)$ and $h( B)$ sharply decrease in comparison with the exciton binding energy $E_{ex}(\tilde{\alpha})$ (17) [23, 24], 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.

4. New Superatom in the Alkali - Metal Atoms

For the development of mesoscopic physics and chemistry was essential idea superatoms (or artificial atoms) [20-22,29,30]. Superatom are nanosized quasi-atomic nanostructure formed from spatially separated electrons and holes (the hole in the volume of the QD and the electron is localized on the outer spherical quantum dot matrix dielectric interface) [20-22,29,30]. This terminology may be correct, given the similarity of the spectra of discrete electronic states of atoms and superatomic and the similarity of their chemical activity [20-22,29,30].

In [20-22], in the framework of the modified effective mass method [14], developed the theory of artificial atoms formed from spatially separated electrons and holes (hole moving in the volume of a semiconductor (dielectric) QD and an electron localized on the outer spherical interface between the QD and a dielectric matrix) is developed.
includes within its scope semiconductor (dielectric) with a dielectric constant $\varepsilon_2$, surrounded by a dielectric matrix with a dielectric constant $\varepsilon_1$. A hole $h$ with the effective mass $m_h$ moves in the QD volume, while an electron $e$ with the effective mass $m_e$ lies in the dielectric matrix. In such a nanostructure, the lowest electronic level is situated in the matrix and the hole level is the volume QD. Large shift of the valence band (about 700 meV) is the localization of holes in the volume QD. Large shift of the conduction band (about 400 meV) is a potential barrier for electrons (electrons move in the matrix and do not penetrate into the volume QD). Coulomb interaction energy of an electron and a hole, and the energy of the electron polarization interaction with the surface section (QD - matrix) (since the permittivity $\varepsilon_2$ is far superior to QD permittivity $\varepsilon_1$ matrix) cause localization of the electron in the potential well above the surface of QD [20-22].

With increasing radius $a$ QD, so that $a \gg a_e^0$ (where $a_e^0$ (14) two-dimensional Bohr radius of the electron) spherical surface section (QD - matrix) transforms into a flat surface section. In this artificial atom, the electron localized on the surface (QD - matrix) becomes two-dimensional. In this case, the potential energy in the Hamiltonian describing the motion of an electron in superatom, the main contribution to the energy of the Coulomb interaction $V_{eh}(r)$ (11) between an electron and a hole [20-22]. Polarization interaction energy of the electron and hole with a spherical surface section (QD - matrix) gives a much smaller contribution to the potential energy of the Hamiltonian. Thus contribute to a first approximation can be neglected [20-22]. In this regard, the two-dimensional electron energy spectrum $E_n$ in the artificial atom takes the form (13).

Dependence of the binding energy $E_{eh}(a,e)$ of an electron in the ground state superatom (QD containing zinc selenide radius $a$ and surrounded by a matrix of borosilicate glass [10]), obtained in [20-22] by the variational method, it follows that the bound state of an electron occurs near spherical interface (QD-matrix), starting with the value of the critical radius QD $a \geq a_e^{(1)} = 3.84$ nm. When this hole moves in a volume QD, and the electron is localized on the surface of the spherical section (QD - matrix). In this case, the Coulomb interaction energy $V_{eh}(r)$ (11) between the electron and the hole, and the energy of the polarization interaction of electrons and holes with a spherical surface section (QD-matrix) prevail over the size quantization of the energy of electrons and holes in the artificial atom. Thus, in [20-22] found that the occurrence of superatom has a threshold, and is only possible since the radius of QD KT $a \geq a_e^{(1)} = 3.84$ nm.

With increasing radius of a QD scan, an increase in the binding energy of the electron in the ground state superatom. In the range of radii $4.0 \leq a \leq 29.8$ nm and the binding energy of the electron in the ground state superatom significantly exceeds (in (4.1-76.2) times) the value of the exciton binding energy $E_{ex}^{(0)} \approx 21.07$ meV in a single crystal of zinc selenide [20-22]. Beginning with a radius QD $a \geq a_e^{(2)} = 29.8$ nm, the energy of the ground state of an electron in superatom asymptotically follow the value $E_{ex}^{(0)} = -1.5296$ eV, which characterizes the energy of the ground state of two-dimensional electrons in an artificial atom (15) [20-22].

Effect of significantly increasing the energy of the ground state of an electron in superatom mainly determined by two factors [20-22]: 1) a significant increase in the Coulomb interaction energy $|V_{eh}(r)|$ (2) electron-hole (the "dielectric enhancement" [34]); 2) the spatial limitation on the quantization volume QD, while with increasing radius of a QD, since the radius of QD $a \geq a_e^{(1)} = 52a_e^{(2)} = 29.8$ nm superatomic becomes two-dimensional with a binding energy of the ground state $E_e^{(1)} (15)$, the value of which is almost two orders exceeds the exciton binding energy in a single crystal of zinc selenide. Effect of "dielectric enhancement" due to the fact that when the dielectric constant $\varepsilon_1$ of the matrix is much less than the dielectric constant of QD $\varepsilon_2$, an essential role in the interaction between the electron and the hole in the superatom playing field produced by these quasi-particles in a matrix. Thus, the interaction between the electron and the hole in the superatom is significantly larger than in a semiconductor permittivity $\varepsilon_2$ [34].

4.2. New Artificial Atom, Which is Similar to a new Single Alkali Metal Atom

Quantum discrete states of the individual atoms of alkali metals are determined by the movement of only one, the outermost valence electron around a symmetric atomic core (containing the nucleus and the remaining electrons) [35]. At large distances $r$ electron from the nucleus (so that $r \gg a_0$, where $a_0 = 0.053$ nm - the Bohr radius of the electron in a hydrogen atom), the field of the atomic core is described by the Coulomb field [35]:

$$V(r) = -\frac{Ze^2}{r},$$

(26)
determining the interaction of the valence electron with the atomic core ($Z$ - serial number of the atom in the periodic table Mendeleev). The energy spectrum of a single atom of an alkali metal hydrogen-described spectrum [35]:

$$E_n^* = -\frac{Ry^*}{(n^*)^2}, \quad \text{Ry}^* = Z^2 \text{Ry},$$

(27)
where $n^* = (n + y)$ - effective quantum number ($n = 1, 2, 3, \ldots$ - the principal quantum number), the amendment $y$ depends on the orbital quantum number $l$. Amendment $y$ in due to the fact that the valence electron moves in the Coulomb field of the atomic core, where the nuclear charge is screened by core electrons. Amendment $y$ correction is determined by comparing the spectrum of (6) with its experimental values. The value of $y < 0$, and numerically in the more closer to the atomic core suitable valence electron orbit. The number of possible orbits of the valence electron in a single alkali metal atom such as a hydrogen atom, and [35].

The similarity of the individual series of neutral alkali metal atoms with hydrogen Balmer series suggests that the energy spectra of neutral alkali metal atoms are called valence electron radiation in transitions from higher levels to the level of principal quantum number $n = 2$ [35].

In a single atom of an alkali metal valence electron
moving in the Coulomb field of the atomic core (26) having the same functional dependence on \( r \) as the Coulomb field (11), in which the valence electron in hydrogen-like model of artificial atom. This leads to the fact that the energy spectra of the valence electron in a single atom of an alkali metal (27) and in the artificial atom (13) describes the spectrum of hydrogen-type. At the same time, the number of possible quantum states of valence electron in hydrogen-like artificial atom model is the same as the number of quantum states of discrete valence electron in a single atom of an alkali metal [20-22,29,30].

The Table shows the position of the valence electron energy levels in individual atoms of alkali metals (K, Rb, Sc) [35] and the new artificial atom X, as well as the level shifts of the valence electron \( \Delta E_{\text{Rb}}, \Delta E_{\text{Sc}}, \Delta E_{\text{X}} \) relative to the adjacent level. Assume that the shift of the energy level \( E_{\text{X, artificial atom}} \) relative to the energy level \( E_{\text{Rb}} \) of the atom Rb (relative energy level \( E_{\text{X}} \) of the atom Sc) will be the same as the shift of the energy level \( E_{\text{X}} \) of the atom Rb (relative energy level \( E_{\text{X}} \) of the atom Sc), (i.e \( \Delta E_{\text{Rb, X}} = \Delta E_{\text{Sc, X}} \)). Then the level of the valence electron artificial atom will be \( E_x = -593 \) meV. Using the dependence of the binding energy \( E_{\text{X, ground state}} \) of the ground state of an electron in an artificial atom [20-22] (QD containing zinc selenide radius \( a \) and surrounded by a matrix of borosilicate glass [10]), we find the radius QD zinc selenide at \( a = 5.4 \) nm, which corresponds to the \( E_x = -593 \) meV. It should be noted that the energy levels of a valence electron in the individual atoms of alkali metals (K, Rb, Sc) [35] and the new artificial atom X are located in the infrared spectrum.

| alkali metal atoms selected | valence electron energy levels (meV) | level shifts of the valence electron (meV) |
|-----------------------------|-------------------------------------|------------------------------------------|
| K                           | -7.21                               | 0                                        |
| Rb                          | -7.112                              | 10                                       |
| Sc                          | -652                                | 59                                       |
| X                           | -5.93                               | 59                                       |

Thus, we proposed a new model of an artificial atom, which is a quasi-atomic heterostructure consisting of spherical QD (nucleus superatom) radius \( a \) and which contains in its scope, zinc selenide, surrounded by a matrix of borosilicate glass (in volume QD moves \( h \) hole effective mass \( m_h \), \( e \) and the electron effective mass \( m_e^{(1)} \) is located in the matrix), allowed to find a new artificial atom X (absent in the Mendeleev periodic system), which is similar to a new single alkali metal atom. This new artificial atom of valence electron can participate in various physical [20-22,29,30] and chemical (30,35) processes analogous atomic valence electrons in atomic systems (in particular, alkali metal atoms selected [35]) . Such processes are unique due to the new properties of artificial atoms: strong oxidizing properties, increasing the possibility of substantial intensity in photochemical reactions during catalysis and adsorption, as well as their ability to form a plurality of the novel compounds with unique properties (in particular, the quasi-molecule and the quasicrystals [23,24]).

Application of semiconductor nanoheterostructures as the active region nanolasers prevents small exciton binding energy in QD. Therefore, studies aimed at finding nanoheterostructures, which would be observed a significant increase in the binding energy of the local electronic states in QDs are relevant [20-22]. Effect of significantly increasing the energy of the electron in a hydrogen superatom [20-22,29,30] allows to detect experimentally the existence of such superatoms at room temperatures and will stimulate experimental studies nanoheterostructures containing superatoms that can be used as the active region nanolasers working on optical transitions.

5. Conclusions

The theory of an exciton with a spatially separated electron and hole is developed within the modified effective mass method [14] in which the reduced effective exciton mass is a function of the semiconductor QD radius \( a \). The average zinc- selenide QD radius was determined by comparing the dependence of the exciton ground-state energy (17) on the QD radius, obtained by the variational method within the modified effective mass method [14], with the experimental peak of the low-temperature luminescence spectrum [10, 19]. It was shown that the short-wavelength shift of the peak of the low-temperature luminescence spectrum of the samples containing zinc-selenide QDs, which was observed under the experimental conditions of [10, 19], is caused by renormalization of the electron–hole Coulomb interaction energy (11) and also the energy of the polarization interaction (5) of the electron and hole with the spherical QD–dielectric matrix interface, related to spatial confinement of the quantization region by the QD volume. In this case, the hole moves in the QD volume, and the electron is localized at the outer spherical QD–dielectric matrix interface [20-22, 29 – 32].

To apply semiconductor nanosystems containing zinc-selenide QDs as the active region of lasers, it is required that the exciton binding energy \( |E_{\text{X, ground state}}| \) (21) in the nanosystem be on the order of several \( kT_0 \) at room temperature \( T_0 \) (\( k \) is the Boltzmann constant) [13]. Nanosystems consisting of zinc- selenide QDs grown in a borosilicate glass matrix can be used as the active region of semiconductor QD lasers. In the range of zinc-selenide QD radii \( a \) (22), the parameter \( |E_{\text{X, ground state}}|/kT_0 \) take significant values in the range from 3.1 to 56 [20 – 22, 29 – 32].

The effect of significantly increasing the binding energy (21) of the exciton ground state in a nanosystem containing zinc-selenide QDs with radii \( a \) (22) was detected; in comparison with the exciton binding energy in a zinc-selenide single crystal, the increase factor is 4.1–72.6 [20 – 22, 29 – 32]. It was shown that the effect of significantly increasing the binding energy (21) of the exciton ground state in the nanosystem under study is controlled by two factors [20 – 22, 29 – 32]: (i) a substantial increase in the electron–hole Coulomb interaction energy (11) and an
increase in the energy of the interaction of the electron and hole with “foreign” images (8, 9) (the “dielectric enhancement” effect [34]); (ii) spatial confinement of the quantization region by the QD volume; in this case, as the QD radius \( a \) increases, starting from \( a \geq a_c^{(2)} \approx 29.8 \text{ nm} \), the exciton becomes two-dimensional with a ground-state energy (15) that exceeds the exciton binding energy in a zinc-selenide single crystal by almost two orders of magnitude.

A review devoted to the theory of excitonic quasimolecule (biexciton) (formed of spatially separated electrons and holes) in a nanosystem that consists of ZnSe QDs synthesized in a borosilicate glass matrix is developed within the context of the modified effective mass approximation. Using the variational method, we obtain the total energy and the binding energy of the biexciton singlet ground state in such a system as functions of the spacing between the QD surfaces and the QD radius. It is established that, in a nanosystem composed of ZnSe QDs with the average radii \( \overline{a}_1 \), the formation of a biexciton (exciton quasimolecule) is of the threshold character and possible in a nanosystem, in which the spacing \( D \) between the QD surfaces is defined by the condition \( D^{(1)} \leq D \leq D^{(2)} \) [23, 24]. Moreover, the exciton quasimolecule (biexciton) can exist only at temperatures below a certain critical temperature: \( T_c \approx 49 \text{ K} \) [23, 24]. It is established that the spectral shift of the low-temperature luminescence peak [10, 19] in such a nanosystem is due to quantum confinement of the energy of the biexciton singlet ground state.

Thus, we proposed a new model of an artificial atom, which is a quasi-atomic heterostructure consisting of spherical QD (nucleus superatom) radius \( a \) and which contains in its scope, zinc selenide, surrounded by a matrix of borosilicate glass (in volume QD moves \( h \) hole effective mass \( m_h \), \( e \) and the electron effective mass \( m_e^{(1)} \) is located in the matrix), allowed to find a new artificial atom \( X \) (absent in the Mendeleev periodic system), which is similar to a new single alkali metal atom. This new artificial atom of valence electron can participate in various physical \([20-22,29,30]\) and chemical \([30,35]\) processes analogous atomic valence electrons in atomic systems (in particular, alkali metal atoms selected \([35]\) ) . Such processes are unique due to the new properties of artificial atoms: strong oxidizing properties, increasing the possibility of substantial intensity in photochemical reactions during catalysis and adsorption, as well as their ability to form a plurality of the novel compounds with unique properties (in particular, the quasi-molecule and the quasicrystals \([23,24]\) ).

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