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EXCITON QUASIMOLECULES IN NANOSYSTEMS WITH SEMICONDUCTOR AND DIELECTRIC COLLOIDAL QUANTUM DOTS: A REVIEW

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In review, deals with the theory of exciton quasimolecules (formed of spatially separated electrons and holes) in a nanosystems that consists of semiconductor and dielectric colloidal quantum dots (QDs) synthesized in a dielectric and semiconductor matrixs. It has been shown that the exciton quasimolecule formation is of the threshold character and possible in a nanosystem, where the distance D between the surfaces of QD is given by the condition $D_c^{(1)} \le D \le D_c^{(2)}$ *(where* $D_c^{(1)}$ *and* $D_c^{(2)}$ *are some critical distance).*

We have shown that in such a nanoheterostructures acting as "exciton molecules" are the QDs with excitons localizing over their surfaces. The position of the quasimolecule state energy band depends both on the mean radius of the QDs, and the distance between their surfaces, which enables one to purposefully control it by varying these parameters of the nanostructure.

It was found that the binding energy of singlet ground state of exciton quasimolecules, consisting of two semiconductor and dielectric QDs is a significant large values, larger than the binding energy of the biexciton in a semiconductor and dielectric single crystals almost two orders of magnitude. It is shown that the major contribution to tue binding energy of singlet ground state of exciton quasimolecule 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 the Coulomb interaction between the electrons and holes. It is established that the position of the exciton quasimolecule energy band depends both on the mean radius of the QDs and the distance between their surfaces.

It is shown that with increase in temperature above the threshold ($T \ge T_c$)*, a transition can occur from the exciton quasimolecule to exciton state. It has been found that at a constant concentration of excitons (i.e. constant concentration of QD) and temperatures T below* T_c*, one can expect a new luminescence band shifted from the exciton band by the value of the exciton quasimolecule binding energy. This new band disappears at higher temperatures* ($T \ge T_c$)*. At a constant temperature below* T_c*, an increase in exciton concentration (i.e. in QD concentration) brings about weakening of the exciton luminescence band and strengthening of the exciton quasimolecule.*

These exciton quasimolecules are of fundamental interest as new quasi-atomic colloidal nanostructures; they may also have practical value as new nanomaterials for nanooptoelectronics. The fact that the energy of the ground state singlet exciton quasimolecule is in the infrared range of the spectrum, presumably, allow the use of a quasimolecule to create new infrared sensors in biomedical research.

Keywords: *exciton quasimolequle, electrons, holes, quantum dots, binding energy, exchange interaction, Coulomb interaction*

Introduction

The studies of quasi – zero dimensional (0-D) nanosystems made up of spherical colloidal quantum dots (QDs) with the mean radius *a* in the range of 1 to 10 nm consisting of semiconductor (germanium, cadmium sulfide and selenide, gallium arsenide, zinc selenide) and dielectric (aluminum oxide) materials synthesized in dielectric (semiconductor) matrices attract considerable interest due to their unique photoluminescence properties, ability to effectively emit light in the visible and near infrared spectral range at room temperatures [1–11]. Optical and electro-optical properties of such quasi 0-D nanosystems are to a large extent governed by the energy spectrum of the spatially confined electron-hole pair (exciton) [1, 2, 5– 21].

In Ge/Si heterostructures, structures that have self-assembled Ge/Si nanoislands are promising in the implementation of effective sources of infrared radiation, since the photoluminescence signal of such nanostructures, in the spectral range (0.25 to 1.14 eV) is observable all the way to room temperature [1,2,6]. To create new Ge/Si - based heterostructures with new effective opto-electronic devices, the mechanism of light absorption in such nanoheterostructures must be studied [1–6]. Ge/Si hetero structures with germanium QDs are classified as heterostructures of the second type. Such nanoheterostructures are characterized by the presence of significant gaps in the valence and conduction bands. The ground electron state therein is located in the silicon matrix, and the ground hole level is in the volume of the germanium QD. The significant gap in the valence band (in the order of 610 meV) causes hole localization in the QD volume. A significant gap in the conduction band (in the order of 340 meV) is the potential barrier for electrons (electrons move throughout the matrix and do not penetrate into the QD volume) (see Fig. 1) [1–6].

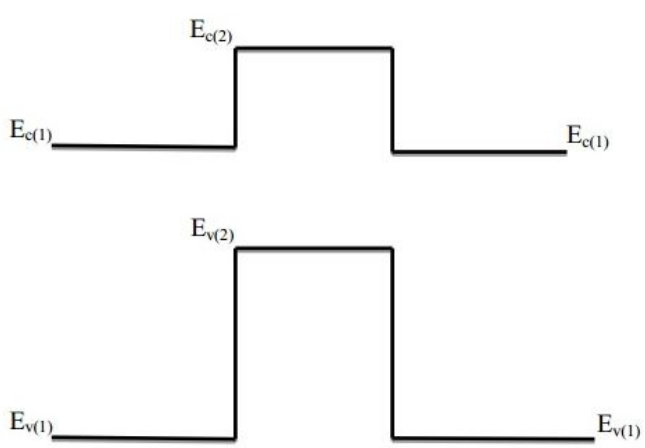

Fig. 1. Band diagram of the QD–matrix nanoheterostructure. In the nanoheterostructure, the QD is a potential well for a hole and a barrier for an electron. The energies $E_{c(1)}$, $E_{v(1)}$, and $E_{c(2)}$, $E_{v(2)}$ correspond to the positions of the bottom of the conduction band and the top of the valence band of the matrix and QD, respectively

The idea of a superatom (or artificial atom) was fruitful for the development of nanophysics [22, 23]. A superatom (quasiatomic nanoheterostructures) consists of a spherical QD with radius *a*, the volume of which contains a semiconductor (or dielectric) material. The QD is surrounded by a dielectric (semiconductor) matrix. In this nanosystem, the lowest

electronic levelis in the matrix, and the lowest hole level is within the volume of the QD. A electron can be localized in a potential well above the QD surface and, at the same time, the hole moves in the volume of the QD. The electrons move in the matrix and do not penetrate the volume of the QD. The energy of the Coulomb interaction of electrons with holes and the energy of the polarization interaction of electrons with the interface (QD-matrix) form a potential well in which the electron is localized over the surface of the QD. Certain orbitals, localized to the surrounding QD correspond to the electrons in a superatom [15–21]. A substantial increase in the binding energy of the ground state of an electron in a superatom in comparison with the binding energy of an exciton in zinc selenide, cadmium sulfide and selenide, germanium, aluminum oxide and single crystals was detected in Refs. [15–21].

The convergence of two (or more) QDs up to a certain critical value D_c between surfaces of the QD leads to the overlapping of electron orbitals of superatoms and the emergence of exchange interactions. In this case, the overlap integral of the electron wave functions takes a significant value. As a result, the conditions for the formation of quasimolecules from QDs can be created [24–28]. One can also assume that the above conditions for the formation of quasimolecules can be provided by external physical fields [29,30]. This assumption is evidenced by the results of Refs. 29 and 30, in in which the occurrence of the effective interaction between QDs at considerable distances under conditions of an electro magnetic field was experimentally observed. In Refs. 31, energies of the ground state of "vertical" and "horizontal" located pairs of interacting QDs ("molecules"from two QDs) were determined as a function of the steepness of the confining potential and the magnetic field strength. The quantum part of a nanocomputer which was implemented on a pair of QDs ("molecules"from two QDs) with charge states is *n* qubits [32].

Ref. 33, theoretically analyzed the exciton transitions in the double vertically conjugated QD of germanium, separated by a silicon layer of *d* thickness. The QD of germanium was in the form of pyramids, in which the ratio of the height *h* to the lateral dimension l = (10, 15, and 20) nm was (≈ 0.1). The spatial structure of excitons and the oscillator was theoretically studied [33]. The ground state of the exciton in a single germanium QD corresponded to the configuration in which the hole was in the ground state in germanium QD, and an electron moving in the silicon matrix was localized near the apex of the pyramidal QD. It is shown that for small distances (d < 3 nm) among QDs, the electron configuration is analogous to the case of single QDs. It is found that with the increase of the distance *d* to the values (d = (3,0 to 3.5) nm) for l = (10, 15) nm, the oscillator strength for the interband transition with the formation of the ground state of the exciton can be much larger (up to a factor of 5) than the analogous value in a single QD.

In [4] using the method of electron-beam lithography obtained heterostructures which are linear chains of QDs germanium on Si substrates. The average sizes of the QD Ge is less than 60 nm. It was noted [27] that, at such a QD content in the samples, one must take into account the interaction between charge carriers localized above the QD surfaces.

In Ref. 33, in contrast to work [27], when studying the occurrence of exciton states between the QD surfaces, the exchange interaction between electrons was not taken into account. Such exchange interactions, as was shown in [27], made the main contribution to the binding energy of the biexciton.

In Refs. 19 and 20, the theory of the exciton formed by spatially separated electron and hole is developed (the hole moves in the bulk of a germanium QD and the electron is localized above the spherical interface between the QD and the silicon matrix). It was found that the binding energy of an exciton in such a nanosystem is much higher (almost an order of magnitude) than the binding energy of an exciton in the silicon single crystal. In Refs. 19 and 20, in the framework of classical electrodynamics, an expression was obtained that describes the Coulomb interaction between an electron and hole. In Refs. 19 and 20, the exciton appeared as a result of the Coulomb interaction between the electron and hole, which, in contrast to Refs. 1, 2

and 33, was dependent on the permittivities of the QD and the matrix. The energy spectrum of the exciton, as a function of the radius of the germanium QD, was obtained in Ref. 19 and 20, for QDs with radii exceeding 3 nm. This is due to the fact that the study of exciton states in the nanosystem containing germanium QDs with radii a less than 3 nm in the framework of the approach in which the expression describing the Coulomb interaction between the electron and hole was obtained by the methods of classical electrodynamics is incorrect.

When there were large concentrations of cadmium sulfide, zinc selenide, germanium QDs in the samples (from $x \approx 0.6\%$ to $x \approx 1\%$) a maximum, interpreted on the basis of the appearance of bonded QD states, was detected in the low-temperature absorption spectra. In order to explain the optical characteristics of such nanosystems, we proposed a model of a quasimolecule representing two cadmium sulfide, zinc selenide and germanium QDs that form an exciton quasimolecule as a result of the interaction of electrons and holes [24–28].

It was noted [24–28] that at such levels of QD content in the samples (from $x \approx 0.6\%$ to $x \approx 1\%$), one must take into account the interaction between charge carriers localized above the QD surfaces. Therefore, in Refs. [24–28], we developed the theory of an exciton quasimolecule (or biexciton) (formed from spatially separated electrons and holes) in a nanosystem that consists of zinc selenide, cadmium sulfide and selenide, germanium, aluminum oxide QDs synthesized in a dielectric and semiconductor matrixs. Using the variational method, we obtained the total energy and the binding energy of the exciton quasimolecule (or biexciton) singlet ground state in such a systems as functions of the spacing D between the QD surfaces and of the QD radius a. We showed that the exciton quasimolecule formation is of a threshold character and is possible in a nanosystem, in which the spacing between the QD surfaces exceeds a certain critical spacing.

It was found that the binding energies E_b of the exciton quasimolecule consisting of two zinc selenide, cadmium sulfide and selenide, germanium, aluminum oxide colloidal QDs acquired an anomalously high value that exceeds the binding energy of the biexciton in zinc selenide, cadmium sulfide and selenide, germanium, aluminum oxide by almost two orders of magnitude. This effect consisted in a significant increase in the binding energy of the ground singlet state exciton quasimolecule due to the fact that because of their presence in nanoscale interfaces (QD-matrix), the energy of the exchange interaction of the electrons with the holes (renormalized Coulomb interaction between electrons and holes) in the exciton quasimolecule was much greater than the energy exchange interaction between electrons and holes in a single crystal [24–36]. It is established that the spectral shift of the low-temperature luminescence peak [8] in such a nanosystems is due to quantum confinement of the energy of the exciton quasimolecule ground state.

In review, deals with the theory of exciton quasimolecules (formed from spatially separated electrons and holes) in nanosystems consisting of semiconductor and dielectric colloidal QDs is insufficiently studied. Therefore, in this review, deals with the theory of exciton quasimolecules (formed of spatially separated electrons and holes) in a nanosystems that consists of semiconductor and dielectric QDs synthesized in a dielectric and semiconductor matrixs. It is shown that exciton quasimolecules formation is of the threshold character and possible in nanosystems, in with the spacing between the QDs surfaces is larger than a certain critical spacing. It was found that the binding energy of singlet ground state of exciton quasimolecules, consisting of two semiconductor and dielectric QDs is a significant large values, larger than the binding energy of the biexciton in a semiconductor and dielectric single crystals almost two orders of magnitude. It is shown that the major contribution to tue binding energy of singlet ground state of exciton quasimolecule 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 the Coulomb interaction between the electrons and holes. It is established that the position of the biexciton state energy band depends both on the mean radius of the QDs and the

distance between their surfaces. This circumstance allows one to purposefully control the position of the biexciton state energy band by varying these parameters of the nanostructure.

Energy of the exciton quasimolecule ground singlet state

Consider a model of a nanosystem that consists of two spherical semiconductor (or dielectric) QDs [24–28]: QD(A) and QD(B) with radius a, grown in a matrix of semiconductor (or dielectric) with a dielectric constant ε_1. Let the spacing between the spherical QD surfaces be D, and the spacing between the spherical QD centers be L. Each QD is formed from a semiconductor (or dielectric) material with dielectric constant ε_2. For simplicity and without loss of generality, we assume that holes $h(A)$ and $h(B)$ with effective masses m_h are localized in centers of QD(A) and QD(B) and electrons $e(1)$ nd $e(2)$ with effective masses $m_e^{(1)}$ are localized near the spherical surfaces of QD(A) and QD(B), respectively ($r_{A(1)}$ is the distance of the electron $e(1)$ from the QD(A) center; $r_{B(2)}$ is the distance of the electron $e(2)$ from the QD(B) center; $r_{A(2)}$ is the distance of the electron $e(2)$ from the QD(A) center; $r_{B(1)}$ is the distance of the electron $e(1)$ from the QD(B) center; r_{12} is the distance between the electron $e(1)$ and $e(2)$ (see Fig. 2). The above assumption is reasonable, since the ratio between the effective masses of electron and hole in the nanosystem is much smaller than unity $\left(\left(m_e^{(1)} / m_h\right) \ll 1\right)$. Let us assume that there is an infinitely high potential barrier on a spherical interface (QD – matrix). In the nanosystem the holes do not therefore escape from the volume of the QD while the electrons do not enter the QD.

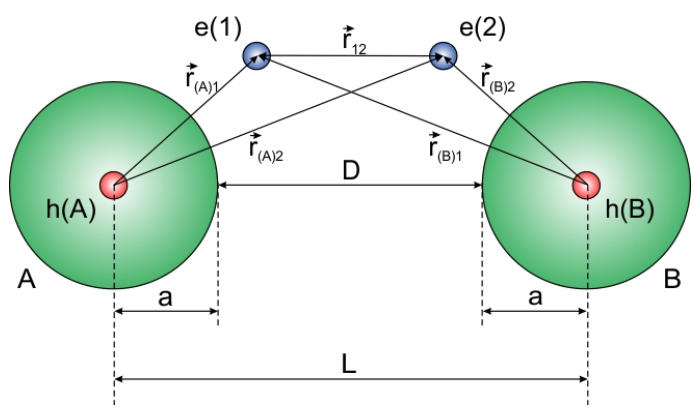

Fig. 2. Schematic representation of a nanosystem consisting of two spherical semiconductor (or dielectric) QDs: QD(A) and QD(B) of radii a. The holes $h(A)$ and $h(B)$ are located in the QD(A) and QD(B) centers, and the electrons $e(1)$ and $e(2)$ are localized near the QD(A) and QD(B) surfaces. $r_{A(1)}$ is the distance of the electron $e(1)$ from the QD(A) center; $r_{B(2)}$ is the distance of the electron $e(2)$ from the QD(B) center; $r_{A(2)}$ is the distance of the electron $e(2)$ from the QD(A) center; $r_{B(1)}$ is the distance of the electron $e(1)$ from the QD(B) center, and r_{12} is the distance between the electrons $e(1)$ and $e(2)$, L is the spacing between the QD centers, and D is the spacing between the QD surfaces.

Let us now use this model to consider the possibility of the formation of an exciton quasimolecule from spatially separated electrons and holes (the holes are located at the centers of QD(A) and QD(B) and electrons are localized near their spherical surfaces). Using adiabatic approximation and the effective mass approximation, the Hamiltonian of the exciton quasimolecule (of spatially separated electrons and holes) can be written in the form [24–28]:

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

where $\widehat{H}_{A(1)}$ and $\widehat{H}_{B(2)}$ are the Hamiltonians of the excitons of spatially separated hole *h(A)* and electron *e*(1) and hole *h(B)* and electron *e*(2), respectively. The contribution of the energy of polarization interaction with the surface of QD to the Hamiltonians of the excitons $\widehat{H}_{A(1)}$ and $\widehat{H}_{B(2)}$ can be, as a first approximation neglected [24–28]. Thus the exciton Hamiltonian $\widehat{H}_{A(1)}$ takes the form The contribution of the energy of polarization interaction with the surface of QD to the Hamiltonians of the excitons $\widehat{H}_{A(1)}$ and $\widehat{H}_{B(2)}$ can be, as a first approximation neglected [24–28]:

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

In (2), the first term is the kinetic energy operator of the exciton; the energy of Coulomb interaction $V_{e(1)h(A)}$ between the electron *e*(1) and the hole *h*(A) is described by the formula [15]:

$$V_{e(1)h(a)} = -\frac{e^2}{\tilde{\varepsilon}\left|r_{e(1)} - r_{h(A)}\right|} \tag{3}$$

where $\mu = -m_e^{(1)} m_h / \left(m_e^{(1)} + m_h\right)$ is the reduced mass of the 2D exciton (of spatially separated electron and hole) [6,7], $\tilde{\varepsilon} = 2\varepsilon_1\varepsilon_2 / (\varepsilon_1 + \varepsilon_2)$ is the dielectric constant of nanosystem.The potentials

$$V_{h(A)}(r_{h(A)}) = \begin{cases} 0, \; r_{h(A)} \le a \\ \infty, \; r_{h(A)} > a \end{cases} \tag{4}$$

$$V_{e(1)}(r_{A(1)}) = \infty, \; r_{e(1)} \le a \tag{5}$$

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 (or dielectric) material with dielectric constant ε_2.

The Hamiltonian $\widehat{H}_{B(2)}$ is of the same form as $\widehat{H}_{A(1)}$ (2). In the first approximation we can neglect the contributions to the Hamiltonian $\widehat{H}_{int}$ of the interaction energies of the electrons *e*(1) and *e*(2) and the holes $h(A)$ and $h(B)$ with polarization fields induced by these charge carriers on the surfaces of QD (A) and QD (B) [5]. Thus the Hamiltonian $\widehat{H}_{int}$ incorporates only the energies of Coulomb interaction of electron *e*(1) with hole *h(B),* and electron *e*(2) with hole *h(A)*, as well as that between electrons *e*(1) and *e*(2), and holes *h(A)* and *h(B).*

Under the assumption that the spins of the electrons *e*(1) and *e*(2) are antiparallel let us write down the normalized wave function of the ground singlet state of the exciton quasimolecule as a symmetric linear combination of wave functions $\Psi_1\left(r_{A(1)}, r_{B(2)}\right)$ and $\Psi_2\left(r_{A(2)}, r_{B(1)}\right)$ [24–28],

$$\Psi_S(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)}) = \left[2\left((1 + S^2(D,a)\right)\right]^{-\frac{1}{2}}\left[\Psi_1\left(r_{A(1)}, r_{B(2)}\right) + \Psi_2\left(r_{A(2)}, r_{B(1)}\right)\right], \tag{6}$$

where $S(D, a)$ is the overlap integral of single-electron wave functions. Assuming that the electrons $e(1)$ and $e(2)$ move independently from each other, let us represent the wave functions $\Psi_1\left(r_{A(1)}, r_{B(2)}\right)$ and $\Psi_2\left(r_{A(2)}, r_{B(1)}\right)$ (6) as a product of single-electron wave functions $\varphi_{A(2)}(r_{A(1)})$ and $\varphi_{B(2)}(r_{B(1)})$, as well as $\varphi_{A(2)}(r_{A(2)})$ and $\varphi_{B(2)}(r_{B(1)})$, respectively. Let us also represent the single-electron wave functions as variational functions of Coulomb type [15–21]:

$$\begin{aligned}
\varphi_{A(1)}(r_{A(1)}) &= \tilde{A}\exp\left(-\mu(a)(r_{A(1)} / a_{ex}^{2D})\right), \\
\varphi_{B(2)}(r_{B(1)}) &= \tilde{A}\exp\left(-\mu(a)(r_{B(2)} / a_{ex}^{2D})\right),, \\
\varphi_{A(2)}(r_{A(2)}) &= \tilde{A}\exp\left(-\mu(a)(r_{A(2)} / a_{ex}^{2D})\right), \\
\varphi_{B(1)}(r_{B(1)}) &= \tilde{A}\exp\left(-\mu(a)(r_{(B1)} / a_{ex}^{2D})\right),
\end{aligned} \tag{7}$$

where $\mu(a)$ is a variational parameter, $a_{ex}^{2D} = (\hbar^2 \cdot \tilde{\varepsilon} / \mu e^2)$ is the Bohr radius of two – dimensional (2D) exciton localized over the flat interface between the zinc selenide (or aluminum oxide) and the matrix of dielectric.

In the framework of the variational method, the energy of the exciton quasimolecule ground singlet state, as a first approximation, is given by the mean value of the Hamiltonian $\hat{H}$ (1) over the states described by the wave functions of the zeroth approximation

$$E\left(D, \bar{\mu}\left(a, D\right), a\right) = \left\langle \Psi_S\left(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)}\right| \hat{H} \left|\Psi_S(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)}\right)\right\rangle, \tag{8}$$

where $\bar{\mu}(a, D)$ is a variational parameter.

With the explicit form of the wave functions (5), (6), the energy functional of the exciton quasimolecule singlet ground state takes the form [24–28]

$$E_0(D,\ \bar{\mu}(a, D), a = 2E_{ex}(a, \mu(a)) + \frac{j(D, \bar{\mu}(a, D + K(D, \bar{\mu}(a, D), a)}{1 + S^2(D, \bar{\mu}(a, D), a)}, \tag{9}$$

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

$$E_{ex}(a, \bar{\mu}(a) = \left\langle \varphi_{A(1)}(r_{A(1)}) \middle| \hat{H}_{A(1)} \middle| \varphi_{A(1)}(r_{A(1)}) \right\rangle \tag{10}$$

The second term in (9)

$$E_b(a, \bar{\mu}(a, D), a) = \frac{j(D, \bar{\mu}(a, D + K(D, \bar{\mu}(a, D), a)}{1 + S^2(D, \bar{\mu}(a, D), a)} \tag{11}$$

is a functional of the binding energy of singlet ground state of excitonic quasimolecule. In the functional determined by formula (9), $j(D, \bar{\mu}(a, D), a)$ is determined by the expression.

$$j(D, \bar{\mu}(a, D), a) = \left\langle \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)}) \middle| \hat{H}_{\text{int}} \middle| \varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)}) \right\rangle \tag{12}$$

The functional $j(D,\bar{\mu}(a,D),a)$ (12) can be represented as the algebraic sum of the functionals of the average energies of Coulomb interaction. In the functional described by (9), $K(D,\bar{\mu}(a,D),a)$ is determined by the formula

$$K(D,\bar{\mu}(a,D),a)=\left\langle \varphi_{B(1)}(r_{B(1)})\varphi_{A(2)}(r_{A(2)})\left|\widehat{H}_{\text{int}}\right|\varphi_{A(1)}(r_{A(1)})\varphi_{B(2)}(r_{B(2)})\right\rangle \tag{13}$$

The functional $K(D,\bar{\mu}(a,D),a)$ (13) can be represented as the algebraic sum of the functionals of the average energies of the exchange interaction.

Within the framework of the variational method at the first approximation the total energy of ground singlet state of excitonic quasimolecule is determined by average value of the Hamiltonian $\hat{H}$ (1) for states, which are described by wave functions of the zero approximation $\Psi_S(r_{A(1)},r_{A(2)},r_{B(1)},r_{B(2)})$ [24–28]

$$E_0(D,a)=2E_{ex}(a)+E_b(D,a) \tag{14}$$

where $E_0(D,a)$ is the binding energy of the ground singlet state of the excitonic quasimolecule and $E_{ex}(a)$ is the binding energy of the ground state of the exciton (consisting of spatially separated electron and hole) localized over the surface of QD, which was worked out in [15 - 21]. In (14) energy is measured in units

$$E_{ex}^0=4(\mu/m_0)Ry_0/(\tilde{\varepsilon})^2 \tag{15}$$

where $Ry_0=13.606$ eV is the Rydberg constant.

In [24, 25] presents the results of the variational calculations of the binding energy $E_b(D,a)$ of the exciton quasimolecule ground state in a nanosystem with a QD of zinc selenide with the mean radius $\bar{a}=3.9$ nm, (permittivity $\varepsilon_2=9.25$, effective mass of the hole in QD $(m_h/m_0)=0.7$, the reduced exciton mass (with a spatially separated electron and hole) $(\mu/m_0)=0.30$, the dielectric constant of nanosystem $\tilde{\varepsilon}=3.29$, synthesized in a dielectric matrix of the borosilicate glass (permittivity $\varepsilon_1=2$, the effective mass of the electron in the matrix $(m_b^{(1)}/m_0)$ was deduced in Ref. 34 and amounts to 0.537), as well as in the nanosystem with a QD of aluminum oxide with the mean radius $\bar{a}_1=3.2$ nm, (permittivity $\varepsilon_2=10$, effective mass of the hole in QD (m_h/m_0) = 6.2, the reduced exciton mass (with a spatially separated electron and hole) $(\mu/m_0)=0.49$, the dielectric constant of nanosystem $\tilde{\varepsilon}=3.28$, synthesized in a dielectric matrix of the vacuum oli VM - 4 (permittivity $\varepsilon_1=1.96$, the effective mass of the electron in the matrix $(m_b^{(1)}/m_0)=0,537$. The variational method that we used for the calculation of the exciton quasimolecule ground state binding energy $\varepsilon_b=(D,a)$ is applicable provided that it is much smaller than the binding energy of the exciton ground state $\varepsilon_{ex}=(a)$, i.e. the following condition must be fulfilled [24–28]

$$(E_b(D,a)/E_{ex}(a))\ll 1. \tag{16}$$

The binding energy $E_b=(D,a)$ of the exciton quasimolecule ground state in the nanosystem containing QDs of zinc selenide with average radii $\bar{a}_1=3.9$ nm, has a minimum of

$E_b^{(1)}(D_1,\bar{a}_1 \approx -4.2$ meV (at the distance $D_1 \cong 3.2$ nm) (The value of $E_b^{(1)}$ corresponds to the temperature $T_c \approx 49\ K$) [24]. As it follows form [24], the exciton quasimolecule appears in the nanosystem at distances $D_1 \geq D_c^{(1)} \cong 2.4$ nm between the surfaces of QD. The formation of such a exciton quasimolecule is of threshold character and can occur in a nanosystem with QDs of the mean radius $\bar{a}_1$, where the distance D between the surfaces of QD exceeds a certain critical value $D_c^{(1)}$. The existence of such distance $D_c^{(1)}$ arises from quantum size effects in which the decrease in the energies of interaction of the electrons and holes entering into the Hamiltonian (Eq. (1)) of the exciton quasimolecule with decrease of the distance D between the surfaces of the QD cannot compensate for the increase in the kinetic energy of the electrons and holes [24]. The binding energy of the exciton $\varepsilon_{ex} = (a)$ amounts to $\varepsilon_{ex} = (\bar{a}_1) \cong -54$ meV [15], with the energy of the exciton quasimolequle ground state (8) taking the value $\varepsilon_0 = (D_1,\bar{a}_1) \approx -112.2$ meV. It should be emphasized that the criterion (16) of the applicability of the variational method for the calculation of the exciton quasimolecule binding energy $\varepsilon_b = (D,a)$ is fulfilled $\left(E_b^{(1)}(D_1,\bar{a}_1 / E_{ex}(\bar{a}_1)\right) \cong 0.08$. At larger distances D between the surfaces of QD: $D \geq D_c^{(2)} \cong 16.4$ nm, the exciton quasimolecule breaks down into two excitons (consisting of spatially separated electrons and holes), localized over QD surfaces. Thus a exciton quasimolecule can be formed in a nanosystem where $D_c^{(1)} \leq D \leq D_c^{(2)}$ [24]. Furthermore, a exciton quasimolecule can exist only at temperatures lower than the critical temperature T_c = 49 K. In the zinc selenide single crystal, the biexciton is formed with the binding energy $E_b = 0,45$ meV corresponding to the temperature 5.2 K. At the same time, the exciton quasimolecule binding energy $E_b^{(1)}$ in the nanosystem is about an order of magnitude higner than E_b

The binding energy $E_b(D,a)$ of the exciton quasimolecule ground state in the nanosystem containing QDs of aluminum oxide with average radii $\bar{a}_1 = 3.2$ nm has a minimum of $E_b^{(1)}(D_1,\bar{a}_1) \approx -7.03$ meV (at the distance $D_1 \cong 2.9$ nm) (Fig. 3) (The value of $E_b^{(1)}$ corresponds to the temperature $T_c \approx 82\,K$). In such a nanosystem, an exciton quasimolecule can be formed where $D_c^{(1)} \leq D \leq D_c^{(2)}$ (where $D_c^{(1)} = 2.1$ nm and $D_c^{(2)} = 4.4$ nm) [25] (see Fig. 3). The binding energy of the exciton $\varepsilon_{ex} = (a)$ amounts to $\varepsilon_{ex} = (\bar{a}_1) \cong -100.8$ meV [18], with the energy of the exciton quasimolequle ground state (8) taking the value $\varepsilon_0 = (D_1\bar{a}_1) \approx -208.63$ meV. It should be emphasized that the criterion (16) of the applicability of the variational method for the calculation of the exciton quasimolecule binding energy $E_b = (D,a)$ is fulfilled $\left(E_b^{(1)}(D_1,\bar{a}_1) / E_{ex}(\bar{a}_1)\right) \cong 0.07$ [25]. Furthermore, a exciton quasimolecule can exist only at temperatures lower than the critical temperature T_c = 82 K. In the aluminum oxide monocrystal, the biexciton is formed with the binding energy E_b = 0.61 meV corresponding to the temperature 7.04 K. The exciton quasimolecule binding energy $E_b^{(1)}$ in the nanosystem is more than an order of magnitude higner than E_b.

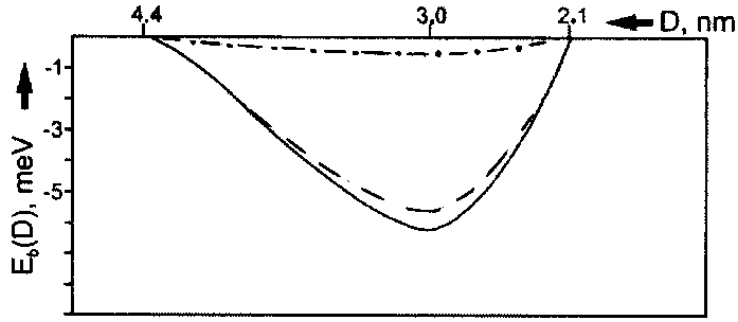

Fig. 3. The dependence of the binding energy of the ground singlet state $E_b(D,\bar{a}_1)$ of the excitonic quasimolecule (continuous line) in a nanosystem made up of two spherical aluminum oxide quantum dots QD(A) and QD(B) with the mean radius $\bar{a}_1 = 3.2\,\text{nm}$, on the distance *D* between the surfaces of QD(A) and QD(B). Dependence of the exchange interaction energy of the electrons and holes (dashed line) and the energy of the Coulomb interaction between electrons and holes (dot dashed line) on the distance *D* between the surfaces of the quantum dots

The values of the binding energy $E_b(D,a)$ of the exciton quasimolecule, as well as the total energy $E_0(D,\bar{a}_1)$ (14) of the excitonic quasimolecule in the nanosystem consisting of QD of of aluminum oxide significantly exceed the corresponding values of $E_b(D,a)$ and $E_0(D,\bar{a}_1)$ (14) in the nanosystem containing QD of zinc selenide. This is due to the fact that, according to formulas (14) and (15), the values of the binding energy $E_b(D,a)$ of an excitonic quasimolecule and the total energy $E_0(D,\bar{a}_1)$ (14) of an excitonic quasimolecule with increasing value (μ/m_0) the reduced exciton mass (with a spatially separated electron and hole) increase (~ (μ/m_0). The values of $E_b(D,a)$ and $E_0(D,\bar{a}_1)$ (14) also increase $(\sim(\tilde{\varepsilon})^{-2}$ with a decrease in the dielectric constant ε of the nanosystem.

As follows from the results of the variational calculations, the major contribution to the exciton quasimolecule binding energy is from the energy of exchange interaction of electrons and holes, which by far surpasses that from their Coulomb interaction (i.e., the ratio ≤ 0.08) [24 - 28]. Upon an increase in the distance *D* between the surfaces of the QDs, the overlap integral *S (D,a)* of single-electron wave functions (7) decreases. This leads to the fact that starting from the values of $D \geq D_c^{(2)}$, the exciton quasimolecule breaks down into two excitons (consisting of spatially separated electrons and holes), localized over QD surfaces (see Fig. 2 and Fig. 3). Since the calculations of the biexciton ground state binding energy $E_b(D,a)$ in the nanosystem are variational, the values of $E_b(D,a)$ and E_b^1 can be somewhat underestimated [24–28].

Correlation of the theory with experiments

In [8] observed a low-tempeature luminescence peak at $\bar{E}_1 \approx 2.716$ eV (at a temperature of $T = 4.5$ K) in samples with a zinc selenide QD content of $x \approx 0.6\%$; this peak was below the band gap ($E_g \cong 2{,}823$ eV) of the zinc selenide single crystal. The shift of the $\bar{E}_1$ – low-temperature luminescence peak with respect to the band gap of the zinc selenide single crystal was $\Delta\bar{E}_1 = \bar{E}_1 - E_g \cong -103$ eV.

Comparing the energy $E_0(D,a)$ (14) of the biexciton ground state with the shift $\bar{E}_1 \cong -103$ eV of the luminescence spectral peak, we obtain the average spacing $\bar{D}_1 \approx 4.5$ nm between the QD(A) and QD(B) surfaces (at an average QD radius of $\bar{a}_1 = 3.9\,nm$ [24]. In this case, the biexciton binding energy is $E_b^2 \cong -3\ meV$ (corresponding to a temperature of $T_2 \approx 35\,K$), and the value of a_1 = 3.9 nm is in the range of the average zinc selenide QD radii ($\bar{a}^0 = 2.0 - 4.8$ nm) studied in the experimental conditions of [8].

Thus, the experimentally observed shift $\Delta\bar{E}_1$ of the low-temperature peak of the luminescence spectrum in the samples containing zinc selenide QDs with a content of $x \approx 0.6\%$ [8] is due to the dependence of the energy $E_0(D,a)$ (14) 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 [24].

Thus, the proposed model of the biexciton gives the explanation of the optical properties of the nanosystem consisting of zinc selenide QDs grown in a dielectric matrix [24], in particular the occurrence of a maximum of $\Delta\bar{E}_1$ in the low-temperature luminescence spectra of the samples [8]. Since the values of the binding energies $\Delta\bar{E}_1$ $E_b(D,a)$ of the biexciton singlet ground state are negative, this means that additional energy is required to excite the second electron–hole pair in the nanosystem. The latter circumstance leads to a shift of the absorption edge of the nanosystem at high excitation intensities, as observed in experiments [8]

Conclusions

Thus it has been shown that the exciton quasimolecule formation is of the threshold character and possible in a nanosystem, where the distance D between the surfaces of colloidal QD is given by the condition $D_c^{(1)} \le D \le D_c^{(2)}$ (where $D_c^{(1)}$ and $D_c^{(2)}$ are some critical distance). A significant increase in the binding energy of the singlet ground state of exciton quasi-molequle (of spatially separated electrons and holes) in a nanosystem that consist of zinc selenide QDs and aluminum oxide QDs and grown in a dielectric matrixs has been predicted; the effect is almost two orders of magnitude larger than the binding energy of biexciton in a zinc selenide and aluminum oxide monocrystals. It is shown that the major contribution to the exciton quasi-molequle 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 [24–28].

It is shown that the major contribution to tue binding energy of singlet ground state of exciton quasimolecule 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 the Coulomb interaction between the electrons and holes. It is established that the position of the exciton quasimolecule energy band depends both on the mean radius of the QDs and the distance between their surfaces [24–28].

It is shown that with increase in temperature above the threshold (T), a transition can occur from the exciton quasimolecule to exciton state. It has been found that at a constant concentration of excitons (i.e. constant concentration of QD) and temperatures T below $9T_c$, one can expect a new luminescence band shifted from the exciton band by the value of the exciton quasimolecule binding energy E_b. This new band disappears at higher temperatures ($(T \ge T_c)$. At a constant temperature below T_c, an increase in exciton concentration (i.e. in QD concentration) brings about weakening of the exciton luminescence band and strengthening of the exciton quasimolecule one [25–28].

These exciton quasimolecules are of fundamental interest as new quasi-atomic nanostructures; they may also have practical value as new nanomaterials for nanooptoelectronics. The fact that the energy of the ground state singlet exciton quasimolecule is in the infrared range of the spectrum, presumably, allow the use of a quasimolecule to create new infrared sensors in biomedical research.

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ЕКСИТОННІ КВАЗІМОЛЕКУЛИ В НАНОСИСТЕМАХ З НАПІВПРОВІДНИКОВИМИ ТА ДІЕЛЕКТРИЧНИМИ КОЛОЇДНИМИ КВАНТОВИМИ ТОЧКАМИ: ОГЛЯД

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У огляді розглядається теорія екситонних квазимолекул (утворених із просторово розділених електронів і дірок) у наносистемі, що складається з напівпровідникових та діелектричних колоїдних квантових точок (КТ), синтезованих у діелектричній та напівпровідниковій матрицях. Показано, що утворення екситонної квазимолекули має пороговий характер і можливе в наносистемі, в якої відстані D між поверхнями КТ визначаються умовою $D_c^{(1)} \leq D \leq D_c^{(2)}$ *(де* $D_c^{(1)}$ *та* $D_c^{(2)}$ *деякі критичні відстані).*

Показано, що в такій наногетероструктурі «екситонні квазімолекули» являють собою дві КТ, на поверхні яких локалізуються екситони. Положення смуги енергії такого стану екситонної квазімолекули залежить як від середнього радіусу КТ, так і від відстані між їх поверхнями. Така залежність дозволяє цілеспрямовано керувати величиною енергії екситонної квазімолекули, змінюючи ці параметри наноструктури.

Встановлено, що енергії зв'язку основного синглетного стану екситонних квазімолекул приймають суттєві значення, значно більші (майже на два порядки) за енергію зв'язку біекситону в напівпровідникових і діелектричних монокристалах. Показано, що основний внесок в енергію зв'язку основного синглетного стану екситонної квазімолекули вносить енергія обмінної взаємодії електронів з дірками, і цей внесок є значно більшим, ніж внесок енергії кулоновської взаємодії між електронами і дірками.

Встановлено, що з підвищенням температури вище порога (T $\geq T_c$*), може відбуватися перехід зі стану екситонної квазімолекули в екситонний стан. Показано, що при постійній концентрації екситонів (тобто постійній концентрації КТ) і температурах T нижче* T_c *можна очікувати нову смугу люмінесценції, зміщену від екситонної смуги на величину енергії зв'язку екситонної квазимолекули. Ця нова смуга зникає при більш високих температурах (T ≥* T_c*). При постійній температурі нижче* T_c *збільшення концентрації екситонів призводить до ослаблення смуги екситонної люмінесценції та посилення смуги екситонної квазімолекули.*

Такі екситонні квазімолекули становлять фундаментальний інтерес як нові квазіатомні наноструктури; вони також можуть мати практичну цінність як нові наноматеріали для нанооптоелектроніки. Оскільки енергія основного синглетного стану квазімолекули знаходиться в інфрачервоному діапазоні спектра, то це дозволяє використовувати такі квазімолекули для створення нових інфрачервоних датчиків у біомедичних дослідженнях.

Ключові слова: *екситонна квазімолекула, електрони, дірки, квантові точки, енергія зв'язку, обмінна взаємодія, Кулонівська взаємодія*