



Quasi – zero – dimensional nanostructures: Excitonic quasimolecules

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ABSTARCT

The 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.

Key words: excitonic quasimolecules, biexcitons, spatially separated electrons and holes, quantum dots. .

INTRODUCTION

At present, quasi-zero-dimensional semiconductor nanosystems consisting of spherical semiconductor nanocrystals, i.e., quantum dots (QDs) 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 [1–9]. 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) [1–9].

In [10], a new modified effective mass method was proposed to describe the exciton energy spectrum in semiconductor QDs with radii of $a \approx a_{ex}$ (a_{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_{ex} , assuming that the reduced effective exciton mass is a function of the radius a , $\mu = \mu(a)$.

In the experimental work [6], 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

$a \approx 2.0\text{--}4.8$ nm. In this case, the values of a are comparable to the exciton Bohr radius $a_{ex} \approx 3.7$ nm in a zinc-selenide single crystal. At low QD concentrations ($x = 0.003$ and 0.03%), 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.

At low QD concentrations ($x = 0.003$ and 0.03%), 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 the short wavelength region (with respect to the band gap E_g of the zinc selenide - single crystal) was observed. The authors of [6] assumed that this shift is caused by quantum confinement of the energy spectra of the electron and hole localized near the spherical surface of the QD.

Currently, the theory of exciton states in quasi-zero-dimensional semiconductor nanosystems has not been adequately studied, in particular, no theory exists for an exciton with a spatially separated electron and hole in quasi-zero-dimensional nanosystems [11,12]. Therefore, in [1, 2, 11,12], we developed the theory of an exciton (superatom) (formed from spatially separated electron and hole (the hole is in the semiconductor QD volume, and the electron is localized at the outer spherical surface of the QD–dielectric matrix interface)). It was shown that the short wavelength shift of the peak of the low temperature luminescence spectrum of samples containing zinc-selenide QDs, observed under the experimental conditions of [6], is caused by quantum confinement of the ground state energy of the exciton with a spatially separated electron and hole. The effect of significantly increasing the binding energy of an exciton (with a spatially separated electron and hole) in a nanosystem containing zinc-selenide QDs in comparison with the binding energy of an exciton in a zinc-selenide single crystal (by a factor of $4.1\text{--}72.6$) was detected [11,12].

In [6], a shift of the spectral peak of the low-temperature luminescence was observed also for samples with a QD concentrations from $x = 0.003$ to 1% . It was noted [6] 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 [4, 5,13] 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. The paper is organized as follows. The theory of an excitonic quasimolecules (biexcitons) formed from spatially separated electrons and holes (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 in Section 2.

MATERIALS AND METHODS

Excitonic quasimolecules formed from spatially separated electrons and holes

We consider a model nanosystem [13] that consists of two spherical semiconductor QDs, A and B , synthesized in a borosilicate glass matrix with the permittivity ϵ_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 ϵ_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: $\left(\left(m_e^{(1)}/m_h\right) \ll 1\right)$. 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 $E_0(\vec{D}, \vec{a})$ and the binding energy $E_b(\vec{D}, \vec{a})$ 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 [13]:

$$E_0(\vec{D}, \vec{a}) = 2E_{ex}(\vec{a}) + E_b(\vec{D}, \vec{a}), \quad (1)$$

Here, the binding energy $E_{ex}(\vec{a})$ of the ground state of the exciton (formed from an electron and a hole spatially separated from the electron) localized above the QD(A) (or QD(B)) surface is determined by in [13] (parameters $\vec{a} = (a/a_{ex}^0)$ ($a_{ex}^0 = 3,7 \text{ nm}$ - the exciton Bohr radius in a single crystal ZnSe, $\vec{D} = (D/a_{ex}^0)$). For the nanosystem under study, the values of the binding energies $E_{ex}(\vec{a})$ are calculated in [13] for the experimental conditions of [6].

The results of variational calculation of the binding energy $E_b(\vec{D}, \vec{a})$ 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 [13]. Such a nanosystem was experimentally studied in [6]. In [6], 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 $E_b(\vec{D}, \vec{a})$ 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 $E_b^{(1)}(D_1, \bar{a}_1) \approx -4,2 \text{ meV}$ (at the spacing $D_1 \cong 3,2 \text{ nm}$). The value of $E_b^{(1)}$ corresponds to the temperature $T_c \approx 49 \text{ K}$ [6]. In [13], it follows that a biexciton (exciton quasimolecule) is formed in the nanosystem, starting from a spacing between the QD surfaces of $D \geq D_c^{(1)} \cong 2,4 \text{ nm}$. The formation of such a exciton 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 $D_c^{(1)}$. Moreover, the exciton quasimolecule (biexciton) can exist only at temperatures below a certain critical temperature: $T_c \approx 49 \text{ K}$.

As follows from the results of variational calculation [13], the binding energy of an exciton (formed from an electron and a hole spatially separated from the electron) localized above the surface of the QD(A) (or a QD(B)) with an average radius of $\bar{a}_1 = 3,88 \text{ nm}$ is $E_{ex}(\bar{a}_1) \cong -54 \text{ meV}$. In this case the energy of the biexciton singlet ground state $E_0(\vec{D}, \vec{a})$ (1) takes the value $E_0(\vec{D}, \vec{a}) = -112 \text{ meV}$.

From the results of variational calculation [13], of the biexciton (exciton quasimolecule) binding energy $E_b(\vec{D}, \vec{a})$ (1), it follows that the major contribution to the binding energy (1) is made by the average energy of the exchange interaction of the electrons $e(1)$ and $e(2)$ with the holes $h(A)$ and $h(B)$. At the same time, the energy of Coulomb interaction makes a much smaller contribution of the biexciton binding energy $E_b(\vec{D}, \vec{a})$ (1).

The major contribution to the exchange – interaction energy is made by the energy of the exchange interaction of the electron $e(1)$ with the holes $h(B)$, as well as of the electron $e(2)$ with the holes $h(B)$, as well as of the electron $e(2)$ with the holes $h(A)$. The major contribution to the

Coulomb – interaction energy is made by the energy of Coulomb interaction of the electron $e(1)$ with the holes $h(B)$, as well as of the electron $e(2)$ with the holes $h(A)$.

As the spacing D between the QD(A) and QD(B) surfaces is increased, starting from $D \geq D_e^{(2)} \cong 16,4 \text{ nm}$, 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 $e(1)$ and $e(2)$ with the holes $h(A)$ and $h(B)$ sharply decrease in comparison with the exciton binding energy $E_{ex}(\bar{a})$ [11,12], 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.

CONCLUSION

The review devoted to the theory of excitonic quasimolecules (biexcitons) (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 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 \bar{a}_1 , the formation of a biexciton (exciton quasimolecule) is of the threshold character and possible in a nanosystem, in with the spacing D between the QD surfaces is defined by the condition $D_e^{(1)} \leq D \leq D_e^{(2)}$. Moreover, the exciton quasimolecule (biexciton) can exist only at temperatures below a certain critical temperature: $T_c \approx 49 \text{ K}$ [13]. It is established that the spectral shift of the low- temperature luminescence peak [6] in such a nanosystem is due to quantum confinement of the energy of the biexciton singlet ground state.

REFERENCE

- [1]. S I Pokutnyi; J. Appl. Chem., **2013**, 1, 5.
- [2]. S I Pokutnyi; Phys. Express, **2012**, 2, 20.
- [3]. S I Pokutnyi; Phys. Express, **2011**, 1, 158.
- [4]. S I Pokutnyi; P P Gorbyk; Progr. Phys. Metal., **2013**, 14, 144.
- [5]. S I Pokutnyi; P P Gorbyk; J. Appl. Chem., **2013**, 1, 44.
- [6]. N V Bondar; M S Brodyn; Physics E, **2010**, 42, 1549.
- [7]. S I Pokutnyi; P P Gorbyk; Optics., **2013**, 2, 47.
- [8]. S I Pokutnyi; J. Nanostruct. Chem., **2013**, 3, 39.
- [9]. S I Pokutnyi; J. Nanoscience Lett., **2011**, 1, 191.
- [10]. S I Pokutnyi; Semiconductors, **2007**, 41, 1323.
- [11]. S I Pokutnyi; Technic. Phys. Lett., **2013**, 39, 233.
- [12]. S I Pokutnyi; Semiconductors, **2013**, 47, 780.
- [13]. S I Pokutnyi; Semiconductors, **2013**, 47, 1653.