Excitonic quasi-molecule consisting of two semiconductor quantum dots: A theory

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Abstract. We have found the effect of significant (almost two orders of magnitude, when compared with the binding energy of biexcitons available in CdS single crystals) increase in the binding energy of the singlet ground state of the excitonic quasimolecule consisting of two CdS quantum dots.

Keywords: spatially separated electron and holes, quantum dots, binding energy, Coulomb and exchange interactions

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1. Introduction

The idea of superatom has proved to be fruitful for the development of nanophysics [1]. A superatom as a notion associated with quasiatomic nanoheterostructures consists of a spherical quantum dot (QD) with some radius *a*, of which volume contains a semiconducting (or dielectric) material. Here the QD is surrounded by a dielectric or semiconductor matrix [2, 3], a hole is localized inside the volume of the QD, and the electron is localized on a spherical interface (a QD-matrix). The lowest electronic level in this nanosystem corresponds to the matrix, and the lowest hole level to the volume of the QD. A large shift of the valence band (700 meV) induces localization of holes in the volume of the QD. A significant shift of the conduction band (about 400 meV) represents a potential barrier for electrons. Then the latter move inside the matrix and do not penetrate into the volume of the QD [2]. The energy of electron–hole Coulomb interaction and the energy of polarization interaction of the electron with the interface, i.e. the QD-matrix, form a potential well, in which the electron is localized on the surface of the QD. Some orbitals localized in the neighbourhood of the QD correspond to electrons in the superatom [3].

The optical properties of nanosystem consisting of CdS and ZnSe QDs formed in a dielectric matrix of a borosilicate glass have been studied in the experimental work [2]. The authors have found that the electron can become localized on the surface of the QD and, at the same time, the hole moves in the volume of the latter. In Ref. [3], an effect of significant increase, if compared with the exciton binding energy typical for the single crystals of CdS and ZnSe, in the binding energy of the ground state of electron in the superatom has been detected.

The convergence of two or more QDs up to a certain critical distance D_c between the surfaces of the QD leads to overlapping of electron orbitals of the superatoms and emergence of exchange interactions [4]. In this case the overlap integral of the electron wave functions acquires significant magnitudes. As a result, the conditions for the formation of quasimolecules from the QDs can appear [4]. One can also assume that the above conditions are provided by external physical fields. The assumption has been evidenced by the authors of studies [5, 6] who have observed experimentally the occurrence of efficient interactions between the QDs separated by considerable distances, under electromagnetic field. In Ref. [7] the energies of the ground state of 'vertically' (or 'horizontally') located pairs of interacting QDs (i.e., 'molecules' consisting of two QDs) have been determined as functions of the steepness of confining potential and the magnetic field strength. The quantum part of a nanocomputer, which has been implemented using a pair of QDs with charged states, is equal to n qubits [8]. Notice that the first smoothly working quantum computer has been built just on the QDs with two electron orbital states as qubits described by the pseudospin ½, with a couple of asymmetric pairs of the QDs with different sizes and significantly different own energies taken as a single cell. Here the electron injected into heterostructure from a channel occupies its lower level, i.e. it is located in the QD with a larger size.

The authors of Ref. [2] have studied the optical properties of the samples composed basing on a borosilicate glass and doped with CdS and ZnSe at the concentrations changed from $x \approx 0.003$ to 1%. The average radii $\bar{a}$ of CdS and ZnSe QDs have been in the range $\bar{a} \approx 2$–20 nm. For high enough CdS and ZnSe QDs concentrations (beginning from $x \approx 0.6\%$ and up to $x \approx 1\%$) [2], it has been assumed that the interaction of electrons and holes leads to binding of the QDs and formation of QD clusters. A peak has been detected in the low-temperature absorption spectra for those samples [2]. To explain the optical properties of the nanosystem containing ZnSe QDs, we have suggested a model of quasimolecule consisting of two QDs, which form the excitonic quasi-molecule due to interactions of electrons and holes [4]. Nonetheless, the appearance of the peak in the absorption spectra of the nanosystem that contains CdS QDs is still unknown (see Ref. [2]).

Using the variational method, in this work we obtain dependences of the total energy and the binding energy of the singlet ground state of the quasi-molecule consisting of the two CdS QDs as functions of the distance D between the surfaces of the QDs and the QD radius. In particular, we find a significant increase, almost two orders of magnitude, in the binding energy of the singlet ground state of the excitonic quasi-molecule, when compared with the binding energy of biexcitons available in CdS single crystals. Moreover, we demonstrate that the peak observed in Ref. [2] in the absorption spectra of the nanosystems under test originates from the formation of excitonic quasi-molecules.

2. Binding energy of the singlet ground state of excitonic quasi-molecule

Let us consider a model of nanosystems containing two superatoms. In this model, the superatoms consist of spherical semiconductor QDs, A and B, synthesized in the borosilicate glass matrix with the dielectric constant ε_1. Let the QD radii be equal to a and the spacing between the spherical QD surfaces be equal to D. Each QD is formed by some semiconductor material with the dielectric constant ε_2. With no loss of generality, one can assume for simplicity that the holes $h(A)$ and $h(B)$ with the effective masses m_h are localized in the centres of QD(A) and QD(B), and the electrons $e(1)$ and $e(2)$ with the effective masses $m_e^{(1)}$ are localized near the spherical surfaces of QD(A) and QD(B), respectively. The above assumption is reasonable since the ratio of the effective masses of electron and hole in our nanosystem is much smaller than unity ($m_e^{(1)} / m_h \ll 1$). Let us now suppose that there is an infinitely high potential barrier on the spherical QD-matrix interface. Then the holes in the nanosystem do not leave the volume of the QD, whereas the electrons do not penetrate into the QDs.

For this modelling nanosystem, we will study a possibility of formation of the excitonic quasi-molecule that consists of spatially separated electrons and holes. As stressed above, the holes are localized at the centres of QD(*A*) and QD(*B*), and the electrons on the spherical surfaces of QD(*A*) and QD(*B*). Using the adiabatic approximation and the effective mass approximation, one can represent the Hamiltonian of the quasi-molecule as follows:

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

Here $\hat{H}_{A(1)}$ and $\hat{H}_{B(2)}$ are Hamiltonians of the superatoms. The hole *h*(*A*) and the electron *e*(1) are localized respectively in the centre and on the surface of QD(*A*), while the hole *h*(*B*) and the electron *e*(2) in the centre and on the surface of QD(*B*).

As a first approximation, one can ignore the contribution of the energy of polarization interactions of the electrons and holes with the surface of the QD into the Hamiltonians $\hat{H}_{A(1)}$ and $\hat{H}_{B(2)}$ of the superatoms [3]. Therefore the superatom Hamiltonian $\hat{H}_{A(1)}$ takes the form

$$\hat{H}_{A(1)} = -\frac{\hbar^2}{2\mu}\Delta_{(1)} + V_{e(1)h(\mathrm{A})}(r_{A(1)}, r_{h(A)}) + E_g \ , \ V_{e(1)h(A)} = -\frac{1}{2}\left(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2}\right)\frac{e^2}{r_{A(1)}} , \tag{2}$$

where the first term is the operator of kinetic energy of the electrons and holes, $\mu = m_e^{(1)} m_h / (m_e^{(1)} + m_h)$ the reduced electron and hole mass, $V_{e(1)h(A)}$ the energy of the Coulomb interaction between the electron *e*(1) and the hole *h*(*A*), $r_{A(1)}$ the distance between the electron *e*(1) and the centre of QD(*A*), and E_g the bandgap for the CdS bulk. The form of the Hamiltonian $\hat{H}_{B(2)}$ is similar to that given by Eq. (2) for $\hat{H}_{A(1)}$. In the first approximation, we can neglect the contribution to the Hamiltonian $\hat{H}_{\text{int}}$ originated from the energy of interaction of the electrons *e*(1) and *e*(2) and the holes *h*(A) and *h*(B) with the fields of polarization induced by these carriers on the surfaces of QD(*A*) and QD(*B*). Therefore the Hamiltonian $\hat{H}_{\text{int}}$ includes only the energies of the Coulomb interactions for the pairs of the electron *e*(1) and the hole *h*(*B*), the electron *e*(2) and the hole *h*(A), the electrons *e*(1) and *e*(2), and the holes *h*(*A*) and *h*(*B*).

Assuming that the spins of the electrons *e*(1) and *e*(2) are antiparallel, we write the normalized wave function of the singlet-state excitonic quasi-molecule in the form of a symmetric linear combination of the wave functions $\Psi_1(r_{A(1)}, r_{B(2)})$ and $\Psi_2(r_{A(2)}, r_{B(1)})$ [4]:

$$\Psi_s\left(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)}\right) = \left[2\left(1 + S^2(D,a)\right)\right]^{-1/2}\left[\Psi_1(r_{A(1)}, r_{B(2)}) + \Psi_2(r_{A(2)}, r_{B(1)})\right] \tag{3}$$

Here *S*(*D*, *a*) is the overlap integral for the single-electron wave functions. Considering that the electrons *e*(1) and *e*(2) move independently of each other, we can represent the wave functions $\Psi_1(r_{A(1)}, r_{B(2)})$ and $\Psi_2(r_{A(2)}, r_{B(1)})$ appearing in Eq. (3) as derivatives of respectively single-electron variational wave functions $\varphi_{A(1)}(r_{A(1)})$ and $\varphi_{B(2)}(r_{B(2)})$, and the wave functions $\varphi_{A(2)}(r_{A(2)})$ and $\varphi_{B(1)}(r_{B(1)})$ [4]. If the spins of the electrons *e*(1) and *e*(2) were parallel, the excitonic quasi-molecule consisting of two QDs is not formed, quite similar to the case of theory of chemical bonds in the hydrogen molecule [9]. Hence, we do not consider this case further on.

Within the framework of the variational method, the total energy of the ground singlet state of the excitonic quasi-molecule is determined in the first approximation by the average value of the Hamiltonian $\hat{H}$ given by Eq. (1), which is peculiar for the states described by the zero-approximation wave functions associated with Eq. (3):

$$E_0(D,a)=2E_{ex}(a)+E_B(D,a), \tag{4}$$

where $E_B(D,a)$ denotes the binding energy of the singlet ground state of the excitonic quasi-molecule, and the binding energy $E_{ex}(a)$ of the ground state of electron in the superatom has been found in Ref. [3]. Table 1 and Table 2 show the results of variational estimations of the binding energy $E_B(D,a)$ of the ground singlet state for the excitonic quasi-molecule containing the two CdS QDs with the average radii $\bar{a}_1 = 4$ nm and $\bar{a}_2 = 4.4$ nm , respectively. Here $\varepsilon_2 = 9.3$ and the effective hole mass m_h / m_0 in the QD is equal to 5. The QDs are assumed to be grown in the borosilicate-glass matrix ($\varepsilon_1 = 2$ and the electron effective mass $m_e^{(1)} / m_0$ in the matrix is equal to 0.537). The above nanosystem represents a subject investigated in detail in the experimental work [2].

Table 1. Dependences of binding energy $E_B(D,\bar{a}_1)$ and total energy $E_0(D,\bar{a}_1)$ of the ground singlet state of the excitonic quasi-molecule consisting of two CdS QDs on the distance *D* between the surfaces of QDs. The average QD radii are equal to $\bar{a}_1 = 4\,\text{nm}$ and the binding energies of electron in the superatoms are $E_{ex}(\bar{a}_1) \cong -320\,\text{meV}$.

D, nm	$E_B(D,\bar{a}_1)$, meV	$E_0(D,\bar{a}_1)$, eV
1.8	0	–640.0
2.2	–27.0	–667.0
2.6	–28.1	–668.1
3.0	–27.8	–667.8
4.0	–23.2	–663.2
6.0	–9.5	–649.5
8.4	0	–640.0

Table 2. Dependences of binding energy $E_B(D,\bar{a}_2)$ and total energy $E_0(D,\bar{a}_2)$ of the ground singlet state of the excitonic quasi-molecule consisting of two CdS QDs on the distance *D* between the surfaces of QDs. The average QD radii are equal to $\bar{a}_2 = 4.4\,\text{nm}$ and the binding energies of electron in the superatoms are $E_{ex}(\bar{a}_2) \cong -344\,\text{meV}$.

D, nm	$E_B(D,\bar{a}_2)$, meV	$E_0(D,\bar{a}_2)$, meV
1.6	0	–688.0
2.2	–29.4	–717.4
2.48	–32.8	–720.8
2.6	–31.9	–719.9
3.0	–28.9	–716.9
4.0	–24.4	–712.4
6.0	–13.2	–701.2
8.0	–3.4	–691.4
9.8	0	–688.0

As already noticed, the work [2] has dealt with the optical properties of borosilicate glass samples doped with CdS at the concentrations ranging from $x \approx 0.003\%$ to 1%. The average radius $\bar{a}$ of the CdS QDs has been changed in the range $\bar{a} \approx 2$–20 nm. At the CdS QD concentrations $x \approx 0.6$–1.0%, the peak has been found in the absorption spectra at the temperature 4 K. It should amount to $(E - E_{\mathrm{g}}) \approx -712$ meV, where E_{g} implies the bandgap for the CdS QDs. It is worthwhile that the variational method used by us for estimating the binding energy $E_B(D,a)$ of the ground singlet state of the excitonic quasi-molecule remains valid if the binding energy $E_B(D,a)$ of the quasi-molecule is small enough, when compared with the binding energy $E_{ex}(a)$ of the ground state of the superatom [4]:

$$E_B(D,a)\,/\,E_{ex}(a) \ll 1\,. \tag{5}$$

The binding energy $E_B(D,a)$ of the ground singlet state of the excitonic quasi-molecule containing the two CdS QDs with the average radii $\bar{a}_1 = 4$ nm and $\bar{a}_2 = 4.4$ nm has the minimum $E_B^{(1)}(D_1,\bar{a}_1) \approx -28.1$ meV occurring at the distance $D_1 \cong 2.6$ nm and the minimum $E_B^{(2)}(D_2,\bar{a}_2) \approx -32.8$ meV at the distance $D_2 \cong 2.48$ nm (note that $E_B^{(1)}$ and $E_B^{(2)}$ correspond to the critical temperatures $T_{c(1)} \approx 326$ K and $T_{c(2)} \approx 380$ K – see Table 1 and Table 2). The appropriate binding energies of the ground state of electron in the superatoms are $E_{ex}(\bar{a}_1) \cong -320$ meV and $E_{ex}(\bar{a}_2) \cong -344$ meV [3]. As seen from Tables 1 and 2, the energies of the singlet ground state of the excitonic quasi-molecule (see Eq. (4)) are equal in this case to $E_0(D_1,\bar{a}_1) \approx -668.1\,\mathrm{meV}$ and $E_0(D_2,\bar{a}_2) \approx -720.8\,\mathrm{meV}$. Comparing the total energy $E_0(D,\bar{a}_2)$ of the quasi-molecule with the maximum $(E - E_g) \approx -712$ meV, we obtain the distance $D_3 \approx 4.0$ nm between the QDs. Then the criterion of applicability of our variational estimation of the binding energy $E_B(D,a)$ given by Eq. (5) is surely valid $(E_B^{(1)}(D_1,\bar{a}_1)\,/\,E_{ex}(\bar{a}_1))$ and $(E_{в}^{(2)}(D_2,\bar{a}_2)\,/\,E_{ex}(\bar{a}_2) \cong 0{,}09\,)$.

The binding energy $E_{ex}\ (a)$ of the ground state of electron in the superatom increases with increasing QD radius a [3]. Than we have an decreae the distance, at which the square of the overlap integral $S(D,\ a)$ of the single-electron wave functions takes on a maximum value. Moreover, it also decreases with increasing QD radius a, and so the distance D_2 between the surfaces of the QD is less than D_1. As a result, the maximum binding energy of the singlet ground state of the excitonic quasi-molecule $\left|E_B(D,a)\right|$ increases with increasing QD radius a (i.e., $\left|E_B^{(2)}\right|$ is larger than $\left|E_B^{(1)}\right|$). In this case the criterion given by Eq. (5) still remains valid. Thus, the model of the excitonic quasi-molecule suggested above can indeed explain the optical properties of the nanosystems, which consist of the CdS QDs grown in the borosilicate glass matrix [4]. In particular, in this way one can easily explain the appearance of the peak $(E - E_{\mathrm{g}}) \approx -712$ meV in the absorption spectra observed at 4 K.

It should be noted that the binding energy $E_{ex}\ (a)$ of the ground state of electron in the superatom remains applicable as long as the inequality $\left(\left(E_{ex}(a) - E_g\right) \ll \Delta V\right)$ is correct, with ΔV being the depth of the potential well for electron and hole in the QD. For example, we have

$\Delta V = 2.5$ eV for the CdS QDs with the radii $a \leq 20$ nm [2]. This condition makes it reasonable to consider the motion of electron and hole in the superatom, using the QD model as an infinitely deep potential well [3]. The Hamiltonian of quasi-molecule constituents given by Eq. (1) does not include the terms that cause QD fluctuations in this molecule. As seen from Table 1 and Table 2, the binding energies obtained for the quasi-molecule are significantly higher than the typical QD fluctuation energies.

It follows from Table 1 and Table 2 that the excitonic quasi-molecule consisting of two QDs can really exist starting from the distances $D \geq D_c^{(1)} \cong 1.8$ nm between the QD surfaces in case if the QDs have the radius $\overline{a}_1 = 4\,\text{nm}$. When the QD radii are equal to $\overline{a}_2 = 4.4\,\text{nm}$, we obtain the estimation $D \geq D_c^{(1)} \cong 1.6$ nm. In other words, the formation of such a quasi-molecule has a threshold character. It is possible only in the nanosystems that contain the QDs with the average radii ranging from $\overline{a}_1$ to $\overline{a}_2$, for which the distance D between the surfaces of the QDs exceeds some critical distance $D_c^{(1)}$. The existence of this critical distance $D_c^{(1)}$ is associated with the dimensional quantum effect: whenever the distance D between the QD surfaces decreases, decreasing interaction energies for electrons and holes in the Hamiltonian (1) of the quasi-molecule can no more compensate the increase in the kinetic energy of electrons.

The excitonic quasi-molecule splits into two superatoms with increasing distance D between the surfaces of the QDs, starting from the value $D \geq D_c^{(2)} \cong 8.4$ nm for the QDs with the radius $\overline{a}_1 = 4\,\text{nm}$ and the value $D_c^{(2)} \cong 9.8\,\text{nm}$ for $\overline{a}_2 = 4.4\,\text{nm}$. Thus, as seen from the data presented in Table 1 and Table 2, the excitonic quasi-molecule in our nanosystem can occur when the condition $D_c^{(1)} \leq D \leq D_c^{(2)}$ is satisfied. In addition, the quasi-molecule can exist only at the temperatures lower that a certain critical temperature ($T_{c(1)} \approx 326$ K or $T_{c(2)} \approx 380\,\text{K}$). It is known [2] that biexcitons in the CdS single crystals arise when the binding energy is equal to $E_B = 0.59$ meV. Hence, the binding energies $E_B^{(1)}$ and $E_B^{(2)}$ of the excitonic quasi-molecule turn out to be very large. They exceed the E_B value by almost two orders of magnitude.

Apparently, the latter fact opens some novel possibilities for observing the excitonic quasi-molecules at the room temperature. The energy of the exchange interaction between the electrons and holes contributes mainly to the binding energy of the excitonic quasi-molecule, which is significantly greater than the energy of the Coulomb interactions between the electrons and holes (the relevant ratio is less or equal to 0.11). Finally, we state that our calculations for the binding energy $\left|E_B(D,a)\right|$ of the singlet ground state of the quasi-molecule are variational in their nature and so can yield in underestimated values. The same is true of the parameter $\left|E_B^{(1)}\right|$.

3. Conclusion

In this work we have demonstrated that the binding energy of the singlet ground state of the excitonic quasi-molecule that consists of two QDs can have significantly large values, which exceed the binding energy of biexciton in the CdS single crystals almost by two orders of magnitude. This effect opens possibilities for using excitonic quasi-molecules as active media in nanolasers, developing radiation sources for the infrared spectral range, working with the excitonic transitions at the room temperature, and building quantum computers based on nanoelements [10].

Our results also demonstrate new fundamental possibilities for creating excitonic quasi-molecules with novel physical properties basing upon quasiatomic nanosystems, including analogues of the natural systems. On this basis, it would also be possible to construct new quantum nanosystems and quasicrystals managed by the symmetry and the lattice period. These systems are expected to allow for implementing a number of unique physical effects and ascertaining new principles in the materials science.

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Анотація. *Виявлено явище значного (майже на два порядки величини) зростання енергії зв'язку основного синглетного стану екситонної квазімолекули, яка складається з двох квантових точок CdS, порівняно з енергією зв'язку біекситона в монокристалах CdS.*