Exciton Binding Energy in Semiconductor Quantum Dots

S. I. Pokutnii

G.V. Kurdjumov Institute for Metal Physics, National Academy of Sciences of Ukraine, Kiev, 03680 Ukraine

E-mail: Pokutnyi_Sergey@inbox.ru

Submitted June 10, 2009; accepted for publication September 10, 2009

Abstract—In the adiabatic approximation in the context of the modified effective mass approach, in which the reduced exciton effective mass \( \mu = \mu(a) \) is a function of the radius \( a \) of the semiconductor quantum dot, an expression for the exciton binding energy \( E_{ex}(a) \) in the quantum dot is derived. It is found that, in the CdSe and CdS quantum dots with the radii \( a \) comparable to the Bohr exciton radii \( a_{ex} \), the exciton binding energy \( E_{ex}(a) \) is substantially (respectively, 7.4 and 4.5 times) higher than the exciton binding energy in the CdSe and CdS single crystals.

DOI: 10.1134/S1063782610040147

1. INTRODUCTION

At the present time, special attention is focused on studies of spherically shaped semiconductor nanocrystals, so-called quantum dots (QDs) synthesized with the radii \( a = 1–10 \) nm on the basis of cadmium sulfide and selenide, gallium arsenide, germanium, and silicon in a borosilicate glassy matrix [1–4]. Studies of such QDs are motivated by their unique photoluminescence properties, specifically, the capability of efficiently emitting light in the visible or near-infrared regions at room temperature [1–6].

In most theoretical models used for calculations of the energy spectra of quasiparticles in QDs, authors used the effective mass approximation that was thought as being valid for QDs, as for bulk single crystals [6–9]. The problem of applicability of the effective mass approximation to the description of quasiparticles in semiconductor QDs remains unsolved [6, 9, 10].

Recently [10], a newly modified effective mass approximation was suggested to describe the exciton energy spectrum of semiconductor QDs of radii \( a \) comparable to the exciton Bohr radius \( a_{ex} \). (Here, \( a_{ex} \) is the exciton Bohr radius in the bulk semiconductor material that forms the QDs.) It was shown that, for QDs simulated by infinitely deep potential wells, the effective mass approximation could be applied to the description of excitons in QDs of radii \( a \approx a_{ex} \), if the exciton reduced effective mass \( \mu \) was considered to be a function of the QD radius \( a \), \( \mu = \mu(a) \).

The use of semiconductor nanosystems for the active region of injection nanolasers is hindered by the low exciton binding energy \( E_{ex}(a) \) in QDs and by the breakdown of excitons at room temperature in most semiconductor QDs [1, 2, 6, 7]. Therefore, studies aimed at searching for nanostructures, in which the exciton binding energy \( E_{ex}(a) \) in QDs is high, are rather pressing.

In this study, in the adiabatic approximation in the context of the modified effective mass approximation, we show that the exciton binding energy \( E_{ex}(a) \) in the CdSe and CdS QDs of radii \( a \approx a_{ex} \) is substantially (respectively, 7.4 and 4.5 times) higher than the exciton binding energy in the CdSe and CdS single crystals. In addition, we discuss the possibilities of using the nanosystems of CdSe and CdS QDs synthesized in the borosilicate glassy matrix for the active region of semiconductor nanolasers.

2. THE EXCITON BINDING ENERGY IN QDS IN THE ADIABATIC APPROXIMATION

We consider a simple model of a quasi-zero-dimensional system, specifically, a neutral spherical semiconductor QD of radius \( a \). Let the QD be formed of a material with the permittivity \( \varepsilon_1 \) and surrounded by a matrix with the permittivity \( \varepsilon_2 \). Let the permittivity of the QD \( \varepsilon_2 \) be substantially higher than the permittivity of the matrix \( \varepsilon_1 \); i.e., we assume that the relative permittivity is much larger than unity: \( \varepsilon = \varepsilon_2/\varepsilon_1 \gg 1 \). Let an electron \( e \) and a hole \( h \) with the corresponding effective masses \( m_e \) and \( m_h \) be in motion in such a QD (\( r_e \) and \( r_h \) are the distances of the electron and hole from the QD center, as shown in Fig.1) [7–10]. We also assume that the bands of electrons and holes are parabolic. The characteristic lengths in the problem are the quantities \( a_e, a_h, a_{ex} \), where

\[
a_e = \frac{\varepsilon_2 \hbar^2}{m_e e^2}, \quad a_h = \frac{\varepsilon_2 \hbar^2}{m_h e^2}, \quad a_{ex} = \frac{\varepsilon_2 \hbar^2}{\mu e^2}
\]

are the Bohr radii of the electron, hole, and exciton in a semiconductor with the permittivity \( \varepsilon_2 \), respectively; \( e \) is the elementary charge; and \( \mu_0 = m_e m_h/(m_e + m_h) \) is the reduced exciton effective mass in a semiconductor with the permittivity \( \varepsilon_2 \). The fact that all characteristic...
lengths  in the problem are substantially larger than the interatomic spacing  allows us to treat the electron and hole in motion in the QD in the effective mass approximation.

At the relative permittivity  the energy of polarization interaction  of the electron and hole with the spherical QD—(insulator matrix) interface can be represented as an algebraic sum of the energies of interaction of the hole and electron with their “own” images,  and the self-interaction energy and with the “wrong” images,  and  respectively [7, 9]

\[
U(\mathbf{r}_e, \mathbf{r}_h, a) = V_{hh}(\mathbf{r}_h, a) + V_{ee}(\mathbf{r}_e, a) + V_{eh}(\mathbf{r}_e, \mathbf{r}_h, a). 
\]

Here,

\[
V_{hh}(\mathbf{r}_h, a) = \frac{\varepsilon^2}{2\varepsilon^2 a} \left( \frac{a^2}{a^2 - r_h^2} + \varepsilon \right), 
\]

\[
V_{ee}(\mathbf{r}_e, a) = \frac{\varepsilon^2}{2\varepsilon^2 a} \left( \frac{a^2}{a^2 - r_e^2} + \varepsilon \right), 
\]

\[
V_{eh}(\mathbf{r}_e, \mathbf{r}_h, a) = V_{he}(\mathbf{r}_e, \mathbf{r}_h, a) = \frac{-\varepsilon^2}{2\varepsilon^2 a} \left( \frac{a^2}{(r_e r_h/a)^2 - 2r_e r_h \cos \theta + a^2} \right)^{1/2}. 
\]

In formula (5), the parameters are

\[
\beta = \frac{(\varepsilon - 1)}{(\varepsilon + 1)} 
\]

and the angle  from the center of the QD.

In the model of the quasi-zero-dimensional structure treated here (Fig. 1), in the above-described approximations and the effective mass approach, the Hamiltonian of an exciton in motion in the QD is [7–9]

\[
H(\mathbf{r}_e, \mathbf{r}_h, a) = -\frac{\hbar^2}{2m_e} \Delta_e - \frac{\hbar^2}{2m_h} \Delta_h + E_g + U(\mathbf{r}_e, \mathbf{r}_h, a) + V_{eh}(\mathbf{r}_e, \mathbf{r}_h) + V_e(\mathbf{r}_e, a) + V_h(\mathbf{r}_h, a). 
\]

Here, the first two terms are the kinetic energy operators of the electron and hole,  is the band gap in an infinite-sized semiconductor with the permittivity , and  is the electron–hole Coulomb interaction energy described by the formula

\[
V_{eh}(\mathbf{r}_e, \mathbf{r}_h) = -\frac{\varepsilon^2}{\varepsilon^2 |\mathbf{r}_e - \mathbf{r}_h|}. 
\]

In the Hamiltonian of exciton (7), the potentials

\[
V_e(\mathbf{r}_e, a), V_h(\mathbf{r}_h, a) = \begin{cases} 0, & r_e, r_h \leq a \\ \infty, & r_e, r_h > a \end{cases} 
\]

describe the quasiparticles in motion within the QD in the model of an infinitely deep potential well.

If the condition

\[
a_h \ll a \ll a_e \approx a_{ex} 
\]

is satisfied, we can use the adiabatic approximation (in which the hole effective mass  is much larger than the electron effective mass ), considering the electron kinetic energy in the QD,

\[
T_{n_e, l_e} = 0(S) = \frac{\pi^2 \hbar^2 n_e^2}{S^2} \left( \frac{\mu_e}{m_e} \right) \text{ Ry}, 
\]

as the largest quantity in the problem (here,  is the dimensionless QD radius) [7–9]. In the first-order perturbation theory, we obtain the exciton binding energy  in the ground state  and  of the principal and orbital quantum numbers of the electron and hole) in the QD of radius  (10):

\[
E_{ex}^{1, 0, 1, 0}(a, \varepsilon) = V_{eh}^{1, 0, 1, 0}(a) + [V_{eh}^{1, 0, 1, 0}(a, \varepsilon)]'. 
\]

The average electron–hole Coulomb interaction energy  and the average energies of interaction of the electron and hole with the “wrong” images,  obtained by averaging energies (8) and (5) with the electron wave functions

Fig. 1. Schematic representation of an exciton in a spherical QD. The radius vectors  define the distance of the electron  and the hole  from the center of the QD of radius . The image charges  and  are located at the distances  and  from the center of the QD and represent the point image charges of the electron and hole, respectively.