

## Trions and biexcitons in ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS core/shell nanowires

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### ABSTRACT

A study of the trion and biexciton in a nanowire (NW) in the framework of the effective-mass model is presented. We consider the formation of trions and biexcitons under the action of both the lateral confinement and the localization potential. The analytical expressions for the binding energy and eigenfunctions of the trion and biexciton are obtained and expressed by means of matrix elements of the effective one-dimensional cusp-type Coulomb potentials whose parameters are determined self-consistently by employing eigenfunctions of the confined electron and hole states. Our calculations for the ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS core/shell cylindrical shaped NWs show that the trion and biexciton binding energy in NWs are size-dependent and for the same input parameters the biexciton binding energy in NWs is always larger than the binding energy of the trion. The trion and biexciton remain stable in CdSe/ZnS NW with the increase of the dielectric shell, while in ZnO/ZnMgO NW they become unstable when the surrounding dielectric shell exceeds 2.5 nm and 2 nm for each, respectively. The associative ionization of biexciton antibonding states into trion bonding states that leads to the formation of trions is studied. Based on the results for size dependence of biexciton binding energy and probability associative ionization an optimal radius for optoelectronic application NW is suggested.

### 1. Introduction

The optical properties of quantum nanostructures have been increasingly investigated over the past decades. This is connected to the fact that the system characteristics that govern optical response, such as electronic level structure, oscillator strength, Coulomb interaction between charge carriers and electron-phonon interaction dramatically changes with size variation at nanometer scale [1,2]. Consequently, the issue of tuning of optical response by means of size and shape control has become important. Excitons and excitonic complexes in quantum nanostructures have been one of the hot topics since the early days of quantum nanostructures [3]. The reason for this is that on the one hand excitons are main intrinsic emitters in short wavelength region and therefore, optimization of excitonic emission is very important for emitting device fabrication. On the other hand, the investigation of excitons and their complexes can provide deep insight into the peculiarities of inter particle interaction at low dimensions. Multi-particle states, like single particle ones, are strongly affected by space and dielectric confinement [4]. Therefore, the new possibilities of controlling their characteristics appear in quantum nanostructures.

In the late 1950s Lampert [5] predicted the existence of charged and neutral exciton complexes formed when an electron in a conduction band or a hole in a valence band is bound to a neutral exciton or two single excitons are correlated. This idea gave rise to many publications

in the 60s and the 70s in bulk materials (see, for example, the works [6–8] and citations therein). The binding energies of the exciton complexes are very small in bulk at room temperature, but they are substantially enhanced in structures of reduced dimensionality. Theoretical calculations performed at the end of the 1980s [9] predicted a considerable (up to tenfold) increase of the trion binding energy in quantum well heterostructures compared with bulk. Trions were first observed in quantum wells (QW) [10] in 1993 and shortly thereafter in GaAs-AlGaAs quantum wells [11–13].

In the last two decades these complexes have been the subject of an extensive theoretical and experimental studies in QW [14–21], quantum dots (QD) [22–28], nanotubes [29–42] and quantum wires [43–55]. We cited these articles, but the recent literature on the subject is not limited by them. The reduced dimensionality considerably increases the binding energy of trions and biexcitons and, thus facilitates the formation of these exciton complexes in semiconductor quantum wells, quantum wires with different confinement geometry, nanotubes and quantum dots.

Whilst in bulk materials excitonic characteristics are defined by dielectric constant and effective masses of electrons and holes, in quantum nanostructures, new controlling parameters, such as size, shape and material distribution profile become crucial. According to numerous investigations the main trend that has been revealed is that with size reduction binding energy of excitons and excitonic complexes,

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as well as their decay probability are strongly enhanced [56–58], which seems very promising, and is crucial for applications in optoelectronics [59], such as light-emitting diodes [60], photovoltaics [61], and phototransistors [62], to cite just a few.

However, the situation is not always so straightforward; e.g. in Ref. [64] it was reported that with decreasing size biexciton binding energy was dropped to zero in InAs/AlAs quantum dots. Much more challenging is the fact, that, with size reduction, some nonradiative processes also become more intensive. In nanocrystal quantum dots/rods, non-radiative carrier losses are dominated by surface trapping and multi-particle Auger relaxation [65]. Nonradiative processes connected to surface traps increase with the size reduction due to the increase in surface-to-volume ratio. However, these processes can be suppressed by using core/shell structures for passivating surface traps. Auger recombination is a nonradiative process in which the electron–hole recombination energy is transferred to a third particle [66]. Auger recombination has a relatively low efficiency in bulk semiconductors. However, Auger decay is greatly enhanced in quantum-confined systems, which is mainly connected to the increase of particle wave functions overlap and breakdown of translational symmetry [63]. Auger recombination is effective at high excitation regime when number of excited carrier pairs exceeds one per quantum dot [67] and when multi-exciton effects are intensive as well. This is why trions and biexcitons still are subjects of extensive investigations [68–72].

Recent studies of one-dimensional (1D) nanostructures such as nanotubes [35,40–42] and nanowires [46,51–53,55,73] show that the trion and biexciton binding energy depend on the electron to hole mass ratio and the geometric characteristics of a nanostructure. Although the exciton complexes like trions in solid state physics are very similar to the few-body bound systems in atomic and nuclear physics there is a major difference related to band effects, which make the effective masses of the electrons and holes smaller than the bare electron mass, and screening effects, resulting from the host lattice, which make the Coulomb force much weaker than in atomic systems.

The majority of recent research is conducted with core/shell NWs in which the emitting core is overcoated with a thin layer of a semiconductor material that has much higher band gap which enhances carrier localization and suppresses Auger recombination. In group II–IV materials ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS are prime examples of such core/shell NWs which are the subject of the present study.

In this paper, we present a theoretical approach to study a trion and a biexciton in a NW in the framework of the effective-mass model. We consider the formation of trions and biexciton under the action of both the lateral confinement and the localization potential. Our approach allows us to obtain analytical expressions for the binding energy and eigenfunctions of the trion and biexciton. The corresponding energies are expressed by means of matrix elements of effective one-dimensional cusp-type Coulomb potentials whose parameters are determined self-consistently by employing the same eigenfunctions of the confined electron and hole states. We calculated the exciton, trion and biexciton binding energies in ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS core/shell NWs of cylindrical shape and their dependence on NW radius. Because of high exciton binding energy ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS are a very good candidates for achieving efficient excitonic laser action at room temperature and Auger recombination is expected to be reduced for this class of materials [74] as well as for elongated core/shell structures [75]. Having chosen the system where Auger recombination is expected to be low, we aimed to find size dependence of trion and biexciton binding energies in order to define size/composition optimal for effective lasing. We also investigated the process of autoionization during which the biexciton transforms to a trion. We propose that as numbers of photo generated electrons and holes are the same, this

process should be the main source of generation of trions, which in its turn are suspected to be the main reason of photoluminescence intermediacy and efficiency drop [76].

The paper is organized in the following way. In Sec. 2, we provide the theoretical model for a trion and biexciton in a core/shell NW and obtain single-particle wavefunctions for confined electrons and holes, which allows us to find the effective electron-hole, hole-hole and electron-electron interactions in 1D. Using these interactions in the framework of the effective-mass model we solve the one-dimensional Schrödinger equations within the fixed center approximation for an exciton, trion and biexciton and obtain the analytical expressions for the binding energies and wavefunctions for these exciton complexes in Subsections 2.3, 2.4, and 2.5, respectively. In Sec. 3 the results of calculations and discussion are presented. Conclusions follow in Sec. 4.

## 2. Theoretical formalism

### 2.1. Setting the model

We consider a formation of trions and biexcitons in a core/shell nanowire. The system represents a cylindrical core of radius  $a$ , surrounded by a cylindrical shell of thickness  $b$ . The trion and biexciton are a three- and four-body system and the corresponding Schrödinger equations cannot be solved analytically, while a solution of the Faddeev equations for a few-body system widely used in nuclear and atomic physics is a challenging task, which involves complex numerical computations. To overcome this difficulty, for the core/shell NW we consider the theoretical model that is based on two assumptions:

- Coulomb interaction is assumed to be decisive only along the NW axis and in radial direction motion of carriers is governed by the strong lateral confinement perpendicular to the NW.
- Heavy holes on the average, move appreciably more slowly than the electrons, which allows one to use the Born-Oppenheimer approximation and solve Schrödinger equation for fixed interhole distances.

To solve the problem of a positive trion (two holes and one electron) and biexciton (two holes and two electrons) laterally confined in a quantum NW we adopt the Born-Oppenheimer approximation, very well known in physics of molecules [77]. The Born-Oppenheimer approximation [78] accounts for a difference in masses of light and heavy particles and assumes that the light particles can respond almost instantly to heavy particles' displacement [79]. The best example for a such system is a hydrogen molecular ion  $H_2^+$  and a hydrogen molecule  $H_2$ , which as a positively charged trion and biexciton consist from two heavy and one light and two heavy and two light particles, respectively [77,80]. Therefore, instead of solving the three-body Schrödinger equation for all particle simultaneously one can treat heavy particles as motionless and solve the Schrödinger equation for a definite position of heavy particles, taking the interparticle separation as a parameter  $R$ . After that calculations are carried out for different  $R$ .

The application of the Born-Oppenheimer approximation naturally separates the calculation into the following steps: due to the strong lateral confinement perpendicular to the NW one first calculates the two-dimensional (2D) energies and wave functions of the electron and hole, while neglecting the Coulomb interaction between them. Therefore, the fast transverse motions of charge carriers remain independent of each other. Next, using these wave functions of transverse electron and hole motion, one can average the three-dimensional (3D) Coulomb potential to a 1D Coulomb interaction between the charge carriers along the NW. Finally, after an appropriate modeling of these

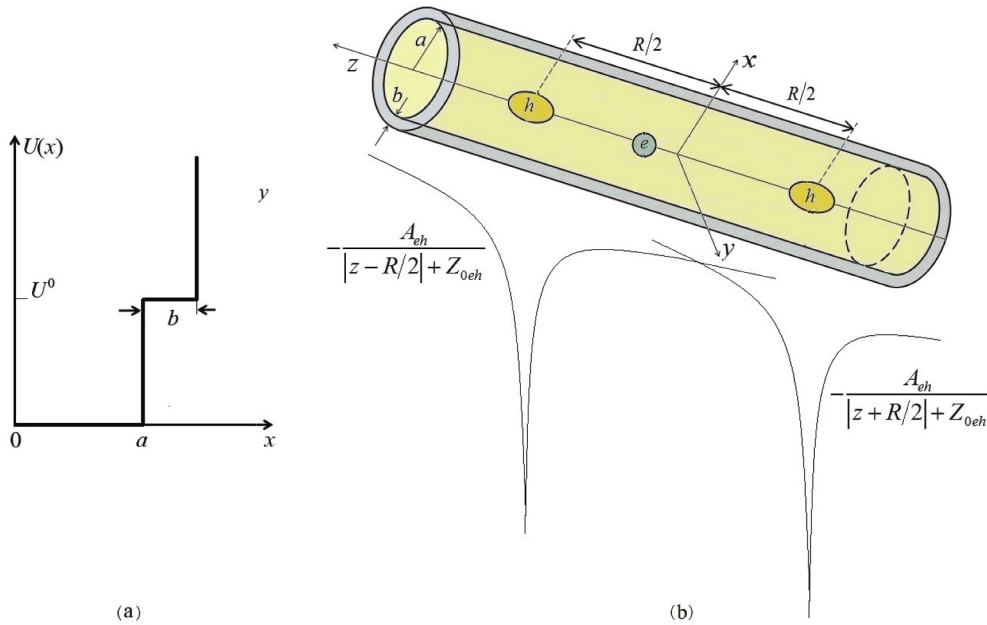


Fig. 1. (a) A lateral confinement potential. (b) Schematic of the two 1D excitons sharing the same electron in a nanowire to form a positive trion. Schematically the electron in the field of two one-dimensional cusp-type Coulomb potentials of the holes is shown in Fig. 1b.

potentials by functions which depend on the distance between the charge carriers, one should find energies and wavefunctions for a trion or a biexciton for each fixed position of the holes by solving the corresponding reduced 1D Schrödinger equations.

Let us assume that the conduction and highest valence bands are decoupled, which is a reasonable approximation for the below considered type of a NW because of the large direct band gap of the ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS materials. The full Hamiltonian for a three- or four-particle excitonic complexes in a confinement within the single-band effective-mass approximation can be written as

$$H = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \nabla_i^2 + V + \sum_{i=1}^N U(\mathbf{r}_i), \quad (1)$$

where  $r_i$  and  $m_i$  are the position and effective mass of the  $i$ -th particle, correspondingly,  $N$  is a number of particle that is equal to 3 and 4 for the trion and biexciton, respectively, and  $U(\mathbf{r}_i)$  are confinement potentials for each of particles. For example, one can consider a lateral confinement potential shown in Fig. 1a for a core/shell NW. In the Hamiltonian (1)  $V = \sum_{i<j}^N V(\mathbf{r}_i, \mathbf{r}_j)$  describes the Coulomb interactions between particles with the electric charge  $e$  in a medium with a dielectric constant  $\epsilon$  and is

$$V = \frac{e^2}{\epsilon |\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e^2}{\epsilon |\mathbf{r}_1 - \mathbf{r}_3|} - \frac{e^2}{\epsilon |\mathbf{r}_2 - \mathbf{r}_3|} \quad (2)$$

in case of the trions and

$$V = \frac{e^2}{\epsilon |\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{\epsilon |\mathbf{r}_3 - \mathbf{r}_4|} - \frac{e^2}{\epsilon |\mathbf{r}_1 - \mathbf{r}_3|} - \frac{e^2}{\epsilon |\mathbf{r}_2 - \mathbf{r}_3|} - \frac{e^2}{\epsilon |\mathbf{r}_2 - \mathbf{r}_4|} - \frac{e^2}{\epsilon |\mathbf{r}_1 - \mathbf{r}_4|} \quad (3)$$

in case of the biexciton.

Below we consider the formation of trions and biexcitons in a core/shell NW. The system represents a cylindrical core of radius  $a$ , surrounded by a shell of thickness  $b$ , as schematically shown in Fig. 1b. To find the binding energies, calculate the energy spectra of trions and biexcitons and find eigenfunctions needed for calculation their optical

properties, we must solve the Schrödinger equation with Hamiltonian (1). We assume that the lateral confinement is strong, so that only the lowest subband for the electron and hole is occupied. This assumption allows a reduction of the Schrödinger equation to an effective one-dimensional form. Assuming strong lateral confinement, we are allowed to separate the  $z$  motion from the lateral motion in the  $xy$  plane. In other words, we assume that the Coulomb interaction does not affect the  $xy$  motion of the particles, so that we can separate the electron and hole motion confined in the lateral direction from the electron-hole relative motion. Therefore, the envelope function for a trion or biexciton can be approximated as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Phi(z_1, z_2, \dots, z_N) \prod_i \psi_i(\rho_i, \varphi_i), \quad (4)$$

where  $\Phi(z_1, z_2, \dots, z_N)$  is the envelope function describing the electron-hole relative motion in the trion ( $N = 3$ ) or biexciton ( $N = 4$ ) in the  $z$  axis along the NW and  $\psi_e(\rho_e, \varphi_e)$  ( $\psi_h(\rho_h, \varphi_h)$ ) is the radial single-particle wave functions for an electron (hole) for the lateral motion in the  $xy$  plane, which due to the axial symmetry of the system depend on cylindrical coordinates for each of particles. Here and below the Cartesian coordinates, wavefunctions and masses of the electron (hole) are denoted with the subscript  $e$  and  $h$ , respectively.

By averaging the Schrödinger equation with Hamiltonian (1) by using function (4) after the separation of variables we obtain

$$-\frac{\hbar^2}{2m_{e(h)}} \left[ \frac{1}{\varphi} \frac{\partial}{\partial \varphi} \left( \varphi \frac{\partial}{\partial \varphi} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \rho^2} \right] \psi_{e(h)}(\rho, \varphi) + U_{e(h)}(\varphi) \psi_{e(h)}(\rho, \varphi) = E_{e(h)} \psi_{e(h)}(\rho, \varphi), \quad (5)$$

which is the Schrödinger equation of single-particle states for electrons and holes confined in a NW and the following Hamiltonian

$$H_{X^+} = -\frac{\hbar^2}{2m_h} \left[ \frac{\partial^2}{\partial z_{1h}^2} + \frac{\partial^2}{\partial z_{2h}^2} \right] - \frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z_{3e}^2} + V_{eh}^{eff}(z_{1h} - z_{3e}) + V_{eh}^{eff}(z_{2h} - z_{3e}) + V_{hh}^{eff}(z_{1h} - z_{2h}), \quad (6)$$

in the case of positively charged trion, while in the case of biexciton the

corresponding Hamiltonian reads

$$H_{XX} = -\frac{\hbar^2}{2m_h} \left[ \frac{\partial^2}{\partial z_{1h}^2} + \frac{\partial^2}{\partial z_{2h}^2} \right] - \frac{\hbar^2}{2m_e} \left[ \frac{\partial^2}{\partial z_{3e}^2} + \frac{\partial^2}{\partial z_{4e}^2} \right] + V_{eh}^{\text{eff}}(z_{1h} - z_{3e}) + V_{eh}^{\text{eff}}(z_{1h} - z_{4e}) + V_{eh}^{\text{eff}}(z_{2h} - z_{3e}) + V_{eh}^{\text{eff}}(z_{2h} - z_{4e}) + V_{ee}^{\text{eff}}(z_{3e} - z_{4e}) + V_{hh}^{\text{eff}}(z_{1h} - z_{2h}). \quad (7)$$

In Hamiltonians (6) and (7)  $V_{eh}^{\text{eff}}$ ,  $V_{hh}^{\text{eff}}$  and  $V_{ee}^{\text{eff}}$  are effective electron-hole, hole-hole and electron-electron interactions that are defined in Appendix A. Conceptually a positively charged 1D trion can be considered as two ground-state 1D excitons sharing the same electron to form a positive trion state and 1D biexciton as two 1D excitons that are sharing the same two interacting electrons to form a biexciton bound state. A schematic of this concept for the trion is depicted in Fig. 1b.

Thus, finding the eigenfunctions and eigenenergies for the trion and biexciton for the Hamiltonian (1) is reduced to the solution of the Schrödinger equation for single-particle states of the electrons and the hole confined in a NW (5) and a solution of the Schrödinger equation with the Hamiltonian (6) for the trion and Hamiltonian (7) for the biexciton with the effective potentials (A.1) - (A.3). The effective potentials (A.1) - (A.3) between charged particles are free from the singularity of the bare Coulomb potential at the origin as a result of averaging with the lateral subband wave functions. However, these effective potentials can be given only numerically. Following Ogawa and Takagahara [22] the effective potentials (A.1) - (A.3) for 1D semiconductors usually are modeled by effective one-dimensional cusp-type Coulomb potentials approximated by the first order rational function  $\frac{A}{(z+Z_0)}$ , where  $z$  is interparticle distance in  $z$ -direction and  $A$  and  $Z_0$  are fitting parameters. These parameters are defined by wave functions  $\psi_{e(h)}(\rho, \varphi)$  that are the solutions of (5), which in its turn, depend on a NW geometry, particles' effective masses, and band offsets  $U_{e(h)}$ . Consequently, they vary with the NW radius and are different for the electron-hole, hole-hole and electron-electron interactions (see Appendix A).

## 2.2. Single-particle states for confined electrons and holes

Let us solve the Schrödinger equation (5) for single-particle states of the electron and the hole confined in a core-shell NW. We assume that confinement potentials for the electron and hole depicted in Fig. 1a have a stepped well shape, are different and have an axial symmetry

$$U(\rho) = \begin{cases} 0, & \text{when } \rho < a, \\ U_{e(h)}^0, & \text{when } a \leq \rho \leq a + b, \\ \infty, & \text{when } \rho > a + b, \end{cases} \quad (8)$$

where  $U_{e(h)}^0$  is the conduction (valence) band offset between core and shell materials and, obviously, it is different for electrons and holes due to the different bands that leads to their different masses. Proceeding from the cylindrical symmetry the solution of Eq. (5) should have the form

$$\psi_{e(h)}(\rho, \varphi) = \phi_{e(h)}(\rho) e^{in\varphi}, \quad n = 0, \pm 1, \pm 2, \dots \quad (9)$$

By substituting (9) into (5) we obtain

$$-\frac{\hbar^2}{2m_{e(h)}} \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + \frac{m^2}{\rho^2} \right] \phi_{e(h)}(\rho) + U(\varphi) \phi_{e(h)}(\rho) = E_{e(h)} \phi_{e(h)}(\rho). \quad (10)$$

The solutions of this equation are Bessel functions: within the core we have the Bessel function of first kind  $J_n$ , which is finite at  $\rho = 0$ , while within the shell the solution is a linear combination of the Bessel functions of second type  $K_n$  and  $I_n$

$$\phi_{e(h)}(\rho) = \begin{cases} C J_n(k\rho), & \text{when } \rho < a, \\ C_1 K_n(\chi\rho) + C_2 I_n(\chi\rho), & \text{when } a \leq \rho \leq a + b, \end{cases} \quad (11)$$

where

$$k^2 = \frac{2m_{e(h)} E_{e(h)}}{\hbar^2}, \quad \chi^2 = \frac{2m_{e(h)} U_{e(h)}^0}{\hbar^2} - k^2. \quad (12)$$

The  $C$ ,  $C_1$  and  $C_2$  coefficients in (11) are defined from the condition of continuity and smoothness of the wavefunction at the boundary, and from the condition of its normality:  $C J_n(ka) = C_1 K_n(\chi a) + C_2 I_n(\chi a)$ ,  $C \left[ \frac{dJ_n(k\rho)}{d\rho} \right]_{\rho=a} = C_1 \left[ \frac{dK_n(\chi\rho)}{d\rho} \right]_{\rho=a} + C_2 \left[ \frac{dI_n(\chi\rho)}{d\rho} \right]_{\rho=a}$ , and  $\int_0^{a+b} J_0^{2\pi} |\phi_{e(h)}(\rho, \varphi)|^2 \rho d\rho d\varphi = 1$ . Consequently, the energy of radial motion of electrons (holes) are defined by means of the boundary condition at  $\rho = a + b$ :  $C_1 K_n(\chi(a + b)) + C_2 I_n(\chi(a + b)) = 0$ . Having found  $k$ , we can define the  $E_{e(h)}$  energy and the wave functions of a confined non-interacting electron and hole, respectively. The solutions  $\psi_{e(h)}(\rho, \varphi)$  of a single-particle radial Schrödinger equation (5) are used to average three-dimensional potentials in (A.1) - (A.3). As a result, one-dimensional effective potentials are obtained for the electron-hole, hole-hole and electron-electron interactions that then are parameterized in the form  $\frac{A}{(z+Z_0)}$  as shown in Appendix A.

## 2.3. Exciton in a nanowire

In the ideal limit the 1D electron-hole system with a perfect confinement, can be treated as a “one-dimensional hydrogen-atom” problem in the framework of the effective-mass approximation. As a first step let us consider the interacting electron and hole in a 1D NW and model an exciton by using an effective one-dimensional cusp-type Coulomb potential. Following [22] one can write the equation that describes relative motion of the electron and hole bound with the cusp-type Coulomb interaction in one-dimensional radially confined NW in the form

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \Phi_X(z)}{dz^2} - \frac{A_{eh}}{|z| + Z_{0eh}} \Phi_X(z) = E_X \Phi_X(z). \quad (13)$$

Here  $\mu$  is the reduced effective mass of electron-hole pair,  $A_{eh}$ ,  $Z_{0eh}$  are the fitting parameters for the effective electron-hole one-dimensional cusp-type Coulomb potentials obtained through the parametrization of Eqs. (A.1),  $z = z_e - z_h$  is the relative electron-hole motion coordinate,  $E_X$  is the binding energy of the electron and hole that form the exciton and  $\Phi_X(z)$  is the corresponding wavefunction. Eq. (13) has the same form as the equation for one-dimensional hydrogen atom studied by Loudon [81]. One can introduce the following notations

$$\xi^2 = -\frac{\hbar^2 \eta_0^2}{2\mu E_X}, \quad \eta_0 = \frac{A_{eh} \mu}{\hbar^2}, \quad x = \frac{2\eta_0 (|z| + Z_{eh})}{\xi} \quad (14)$$

and reduce (13) to the Whittaker's equation

$$\frac{d^2 \zeta(x)}{dx^2} + \left( -\frac{1}{4} + \frac{\xi}{x} \right) \zeta(x) = 0. \quad (15)$$

The solution of (15) is the Whittaker function  $W_{\xi, \pm 1/2}(x)$ ,  $\zeta(x) = W_{\xi, \pm 1/2}(x)$ , as shown in Refs. [81,82]. The value of  $\xi$  which defines  $E_X$  and  $\Phi_X(z)$ , is determined by the boundary condition stating that for even states the derivative of wave function at  $z = 0$  must turn to zero

$$\frac{d}{dz} \left[ W_{\xi, \pm 1/2} \left( \frac{2\eta_0 (|z| + Z_{eh})}{\xi} \right) \right]_{z=0} = 0. \quad (16)$$

#### 2.4. Positive trion in a nanowire

Following [77] for positively charged trions bound by the effective one-dimensional cusp-type Coulomb potentials the Hamiltonian (6) in the Born-Oppenheimer approximation can be written as

$$H_{X^+} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dz^2} - \frac{A_{eh}}{|z - R/2| + Z_{0eh}} - \frac{A_{eh}}{|z + R/2| + Z_{0eh}} + \frac{A_{hh}}{R + Z_{0hh}}, \quad (17)$$

where  $\mu$  is electron-hole reduced mass,  $R$  is distance between two holes, which are assumed to be motionless at  $z = \pm R/2$ , and  $A_{eh}$ ,  $Z_{0eh}$  and  $A_{hh}$ ,  $Z_{0hh}$  are the fitting parameters for the effective electron-hole and hole-hole one-dimensional cusp-type Coulomb potentials obtained through the parametrization of Eqs. (A.1) and (A.2), correspondingly. Schematically the electron in the field of two 1D cusp-type Coulomb potentials is shown in Fig. 1b.

For solution of the Schrödinger equation for the trion with Hamiltonian (17) we use the method of linear combination of atomic orbitals (LCAO) [77]. In the framework of the LCAO method the eigenfunction of trion is presented as a linear combination of single exciton wave functions centred at  $z = \pm R/2$

$$\Phi = c_1 \Phi_{X_1} + c_2 \Phi_{X_2}, \quad (18)$$

where  $\Phi_{X_1}$  and  $\Phi_{X_2}$  are the solutions of the Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \Phi_{X_i(X_2)}(z)}{dz^2} - \frac{A_{eh}}{|z \pm R/2| + Z_{0eh}} \Phi_{X_i(X_2)} = E_{X_i(X_2)} \Phi_{X_i(X_2)}. \quad (19)$$

In Eq. (19)  $E_{X_1}$  and  $E_{X_2}$  are the energy of the exciton when the hole is localized at  $R/2$  and  $-R/2$ , respectively. Close to the hole located at  $R/2$  the wavefunction  $\Phi_{X_1}$  will resemble a single electron orbital, while the wavefunction  $\Phi_{X_2}$  will represent the electron orbital near the hole located at  $-R/2$ . Thus, the linear combination (18) represents both cases. The states  $\Phi_{X_1}$  and  $\Phi_{X_2}$  are degenerate due to symmetry. Following the well-known perturbation theory for the degenerate states [83], one can obtain the normalized wavefunctions for the first two states

$$\Phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (\Phi_{X_1} \pm \Phi_{X_2}), \quad (20)$$

where  $S = \langle \Phi_{X_1} | \Phi_{X_2} \rangle$  is an overlap integral. The wavefunction  $\Phi_+$  corresponds to the localization of the electron density between holes (bonding orbital) and the accumulation of electron density in the interhole region is simulated due to the constructive interference that takes place between the two electron waves centred on neighboring holes, while the wavefunction  $\Phi_-$  has a node between the holes (antibonding orbital). Trion energies corresponding to these states are:

$$E_{X^+}^+(R) = E_X + \frac{J+K}{1+S} + E_{hh}(R), \quad (21)$$

$$E_{X^+}^-(R) = E_X + \frac{J-K}{1-S} + E_{hh}(R), \quad (22)$$

where the expressions for  $J$  and  $K$ , which parametrically depend on  $R$ , are given in Appendix B. The last term in (21) and (22) is the energy of interaction between two holes

$$E_{hh}(R) = \frac{A_{hh}}{R + Z_{0hh}}. \quad (23)$$

Thus, to find the dependence of the trion energy on interhole separation  $R$  one needs to evaluate the relevant matrix elements  $J$  and  $K$  and calculate the interaction energy between two holes (23). The maximum of the positive value of  $E_{X^+} + E_{hh}(R) - E_{X^+}^{\pm}(R)$  correspond to binding energy of the positively charged trion. However, this approach is not applicable for consideration of a negatively charged trion.

#### 2.5. Biexciton in a nanowire

Now let us consider a 1D biexciton for which the model of the hydrogen molecule  $H_2$  is used. Following [80] for the biexciton, where two electrons and two holes are bound via the effective one-dimensional cusp-type Coulomb potentials, the Hamiltonian (7) in the Born-Oppenheimer approximation can be written as

$$H_{XX} = -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dz_1^2} + \frac{d^2}{dz_2^2} \right) - \frac{A_{eh}}{|z_1 - R/2| + Z_{0eh}} - \frac{A_{eh}}{|z_2 - R/2| + Z_{0eh}} - \frac{A_{eh}}{|z_1 + R/2| + Z_{0eh}} - \frac{A_{eh}}{|z_2 + R/2| + Z_{0eh}} + \frac{A_{hh}}{R + Z_{0hh}} + \frac{A_{ee}}{z_{12} + Z_{0ee}}, \quad (24)$$

where  $z_{12} = |z_1 - z_2|$  and  $A_{ee}$  and  $Z_{0ee}$  are the fitting parameters for the effective one-dimensional cusp-type Coulomb potentials in the Hamiltonian (7) for the electron-electron interaction obtained from (A.3), while the other fitting parameters are already defined in Subsec. 2.4. The wave function of the biexciton can be constructed by means of single exciton wave functions again. If the electron-electron and hole-hole interactions are ignored one can use  $\Phi_{X_1}(z_1)\Phi_{X_2}(z_2)$  as an approximation for the biexciton wavefunction. However, the symmetry of the wavefunction has to be taken into account. Following [80] we construct symmetric and antisymmetric wave functions coinciding to antiparallel (singlet state) and parallel orientation (triplet state) of spins of electrons as:

$$\Phi_{\pm}(z_1, z_2) = \frac{1}{\sqrt{2(1 \pm S)}} [(\Phi_{X_1}(z_1)\Phi_{X_2}(z_2) \pm \Phi_{X_1}(z_2)\Phi_{X_2}(z_1))]. \quad (25)$$

The energies of bonding symmetric and antibonding antisymmetric states in the first order perturbation theory are found as mean values of (24). The corresponding energies for these states are:

$$E_{XX}^+(R) = 2E_X + \frac{Q+P}{1+S^2}, \quad (26)$$

$$E_{XX}^-(R) = 2E_X + \frac{Q-P}{1-S^2}, \quad (27)$$

where  $Q$  and  $P$  parametrically depend on  $R$  and are given in Appendix C.

The binding energy of biexciton is the maximum value of  $2E_X - E_{XX}(R)$ .

### 3. Results of calculations and discussion

Our calculations are based on the assumption that the Coulomb interaction strength in the radial direction is much weaker than the lateral confinement effect and the Coulomb interaction is significant only along the  $z$ -axis and is presented by the 1D cusp-type Coulomb potentials for the electron-hole, hole-hole and electron-electron interactions. The Born-Oppenheimer approximation successfully used in the physics of molecules assumes that the ratio of mass of the atomic nuclei and electrons is large enough. In the case of positively charged trions

**Table 1**

Input parameters for ZnO/ZnMgO and CdSe/ZnS NWs.  $m_e$  and  $m_h$  are the mass of the electron and hole, respectively,  $U_c^0$  and  $U_h^0$  are the lateral confinement potentials for a conduction and valence band offset between core and shell materials, respectively, and  $\epsilon$  is dielectric constant.  $m_0$  is the mass of free electron.

	$m_e/m_0$	$m_h/m_0$	$U_c^0$ , eV	$U_h^0$ , eV	$\epsilon$
ZnO/ZnMgO	0.24 [85]	0.86 [85]	0.37 [86]	0.31 [86]	8.13
CdSe/ZnS	0.13 [84]	0.45 [84]	1.2 [88]	0.7 [88]	10.2
CdSe/CdS	0.13	0.45	0.30 [88]	0.44 [88]	10.2



and biexcitons the ratio of hole-electron mass is much less than the proton-electron mass ratio, which makes questionable not only the validity of the Born-Oppenheimer approximation, but also the existence of bound states. In Ref. [84] it is stated that exciton bound to neutral/ionized donor for which models of  $H_2^+$  and  $H_2$  are also used, the binding energy sharply increases when the hole-electron mass ratio varies from 1 to 3. For II–VI semiconductors, where the mass ratio  $m_h/m_e$  varies between 3 and 5, for calculation of trion and biexciton states the Born-Oppenheimer approximation is often used [94]. Even in the case when  $m_h = m_e$  satisfactory values are obtained for the binding energy of the two- and three-dimensional biexcitons [95].

We calculate the trion and biexciton binding energies in ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS core/shell quantum structures of a cylindrical shape. The calculations are performed for the set of parameters listed in Table 1. Here the effect of the differences in the effective masses in core and shell material is not taken into account. For ZnO/ZnMgO and CdSe/CdS structures this difference is not significant. In CdSe/ZnS structure the barrier height is very high, penetration of carriers into the barrier is not substantial. Because of high exciton binding energy ZnO/ZnMgO is a very good candidate for achieving efficient excitonic laser action at room temperature. ZnO is a wide bandgap (3.4 eV) material [87], has sufficient hole-electron mass ratio. The most important part of the ZnO/ZnMgO band structure, which is the bottom of the conduction band and the top of the valence bands in the vicinity of the  $\Gamma$ –point, can be well described within the effective-mass approximation [96].

CdSe/ZnS and CdSe/CdS are also promising direct-bandgap II–VI semiconductors active in the visible range, with potential applications in electronics and optoelectronics [89]. Nanostructures based on CdSe are one of the most extensively investigated low dimensional semiconductor structures with potential applications towards field-effect transistors, photodetectors, and light-emitting diodes [90]. The bandgap of CdSe is lower than that of ZnO - 1.74 eV [91]. Exciton binding energy in bulk CdSe also is significantly lower than that in bulk ZnO - 0.13 eV [92]. However, investigations show possibility of effective control/enhancement of stability of excitonic complexes in nanostructures [92,93]. Let us mention that when the quantum confined physical system, such as a quantum wire, approaches the nanometric range, a reduction of the static dielectric constant becomes important for small radii of the wire. A reduced static dielectric constant increases Coulomb interaction energy between electrons and holes. A polarization of the Coulomb interaction arising from the dielectric mismatch, can be found by numerically integrating the Poisson equation [97]. A momentum dependent dielectric function  $\epsilon(q)$  is especially suitable for situations that involve dielectric discontinuity, which requires solving a full electrostatic boundary value problem. Calculations become more simple if one instead  $\epsilon(q)$  uses a constant, but a wire radius-dependent effective dielectric constant  $\epsilon(a)$  [98]. Thus, the effective dielectric constants are expected to change as a function of radius because of the reduced screening. In our calculations we neglect this effect and use the bulk dielectric constants when calculating the Coulomb interaction in Eqs. (2) and (3). In Ref. [99] was studied the effect of the polarization discontinuity between interfaces such as ZnO/ZnMgO. Our model does not include this effect. However, role of this effect for trions/biexcitons binding energy requires detailed consideration which is out of the scope of this article.

As a first step we calculate the effective interactions (A.1)–(A.3) by averaging over the electron  $\psi_e(\rho_e, \varphi_e)$  and hole  $\psi_h(\rho_h, \varphi_h)$  wavefunctions, which reduce the 3D Coulomb potential to a one-dimensional potential that depends only on the coordinate of two particle relative motion. The corresponding computational modeling allows one to find the numerical values of the fitting parameters  $A$  and  $Z_0$  for the 1D cusp-type

Coulomb potentials. Once these constants are known one can use them as the input parameters and evaluate  $J$  and  $K$  given in (B.4) and (B.5), and using Eqs. (21) and (21) find the trion energy for given interhole separation  $R$ . In the case of biexciton using the same matrix elements  $J$  and  $K$  given in (B.4) and (B.5), and the matrix elements  $\mathfrak{J}$  and  $\mathfrak{K}$  given in (C.6) and (C.7), one can find  $Q$  and  $P$  defined in (C.8) and determine the biexciton energy by means of Eqs. (26) and (27).

We study the dependence of the trion and biexciton binding energy on the interhole distance, the NW radius and the thickness of the surrounding dielectric shell using Eqs. (21) and (22), and (26) and (27), respectively. When the trion or biexciton energies in ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS as a function of interhole distance exhibit minimums at the particular interhole distances and for the particular NW radius it can be a signature of possible existence of the bound state of the trion or biexciton. If the minimum lies below the energy of a separated exciton and hole, this indicates the formation of the trion, while if the minimum energy is below the energy of two separated excitons, it is an indication of the biexciton formation.

The results of calculations for the trion energies in ZnO/ZnMgO and CdSe/ZnS NWs as a function of interhole distance  $R$  are presented in Fig. 2. The calculation is performed for different radii of a NW. The energy curves vary with the interhole distance. The upper branches of curves correspond to the antibonding orbital for the antisymmetric state, while the lower branches of curves correspond to the bonding orbital for the symmetric state. The steep rise dependence in energy at  $R < 1.5$  nm for both ZnO/ZnMgO and CdSe/ZnS NWs is largely due to the increase in the hole-hole potential energy as the two holes are brought close together. When a curve exhibits minimum and its energy is below the energy of a separated exciton and a hole one can confirm the existence of a bound trion. For all values of a NW radius the typical behavior of a symmetric bonding state for ZnO/ZnMgO NW is observed with minimum at some particular hole-hole distance, while one can see the minimum of the energy for the antisymmetric state only for the NW with the smallest radius  $a = 1.0$  nm. The minimums are not sharp, nevertheless bound states of trions exist. In the case of CdSe/ZnS the curves for the trion energies as a function of interhole distance exhibit minimum for the symmetric bonding states as well as for the antibonding antisymmetric states. The minimums are pronounced for antisymmetric states for the radius of NW  $a = 1.0$  nm and  $a = 1.5$  nm, however, there is no minimum in the antibonding state for the other considered values of NW radii.

Let us now present results of calculations for the biexciton in ZnO/ZnMgO and CdSe/ZnS NWs. Using Eqs. (26) and (27) the dependence of biexciton energies on interhole distance for different NW radii are calculated and presented in Fig. 3. The lower branches of curves correspond to the bonding symmetric state, while the upper branches of curves correspond to the antibonding antisymmetric state. In the antisymmetric state when the holes approach one another the energy increases monotonically for all considered radii of the NW. It follows from Fig. 3 for the symmetric state when the holes approach one another the energies are lowered down to a particular distance  $R$  after which the energies rise steeply for when the distance is further decreased. The minimums of energy for the symmetric state are sharply pronounced and lie below the energy of two separated excitons for all considered NW radii. The minimums are much deeper for ZnO/ZnMgO NW and occur when  $R > 2$  nm, while in the case of CdSe/ZnS the minimums appear at about  $1.5 < R < 2.5$  nm. The confinement potentials for the electrons and holes in ZnO/ZnMgO and CdSe/ZnS NWs are significantly different. The comparison of Figs. 2a, b and 3a, b illustrates the effect of the confinement on the energy dependence on interhole distance for trions and biexciton, respectively. The dependences of trion and biexciton energies on interhole distance for CdSe/CdS are different

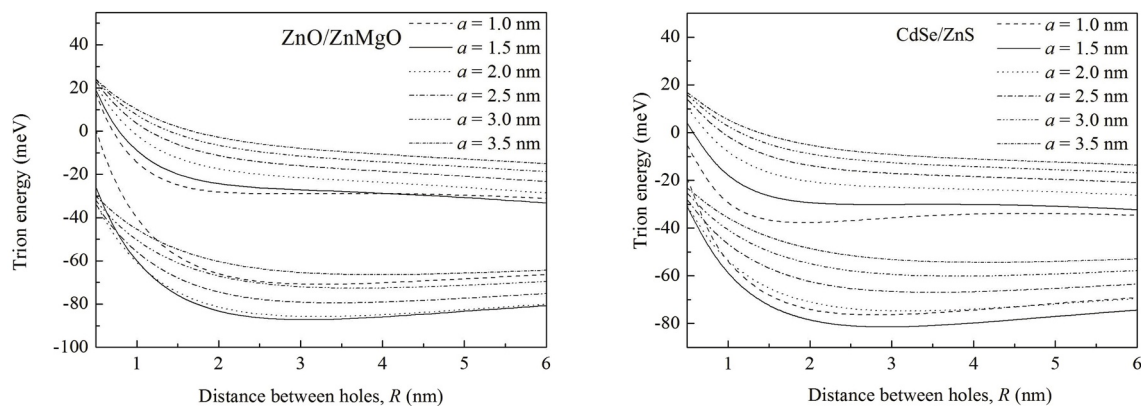


Fig. 2. The dependence of trion energy in ZnO/ZnMgO and CdSe/ZnS NWs on interhole distance for different radii of a NW. The thickness of the surrounding dielectric shell is  $b = 2$  nm.

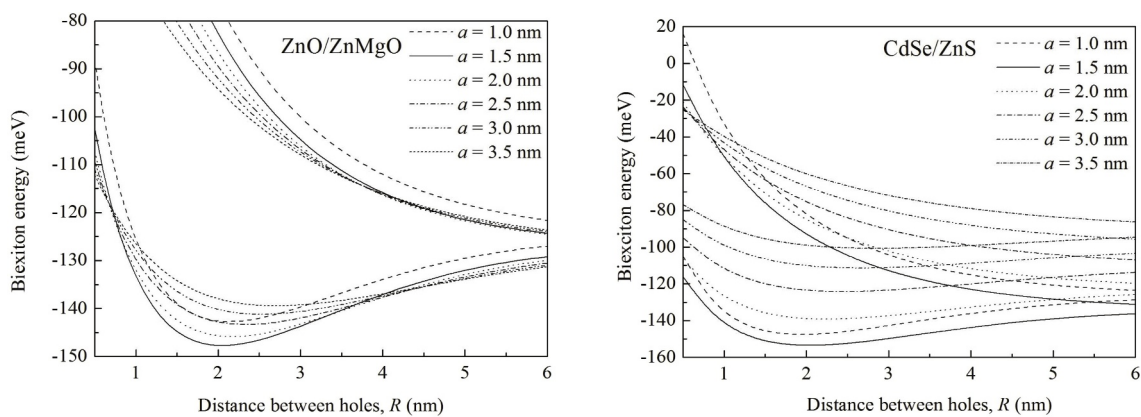


Fig. 3. The dependence of biexciton energy in ZnO/ZnMgO and CdSe/ZnS NWs on interhole distance for different radii of a NW. The thickness of the surrounding dielectric shell is  $b = 2$  nm.

compared to CdSe/ZnS due to the smaller confinement potentials and have similarity to that for ZnO/ZnMgO NW.

The results of our calculations demonstrate an appreciable dependence of the exciton, trion and biexciton binding energy on the radius of NW. In Fig. 4 are presented dependence of the binding energies of the exciton, trion and biexciton in ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS on the radius of NW. We perform calculations for the lateral

confinement potentials  $U_c^0$  and  $U_h^0$  for a conduction and valence band offset between core and shell materials presented in Table 1. The comparison of the binding energies for the exciton, trion and biexciton shows that for the same hole to electron mass ratio the binding energy of biexciton is larger than for the trion and smaller than for the exciton in all NWs. Moreover, for the same input parameters the exciton and biexciton have the maximum binding energy in ZnO/ZnMgO for the

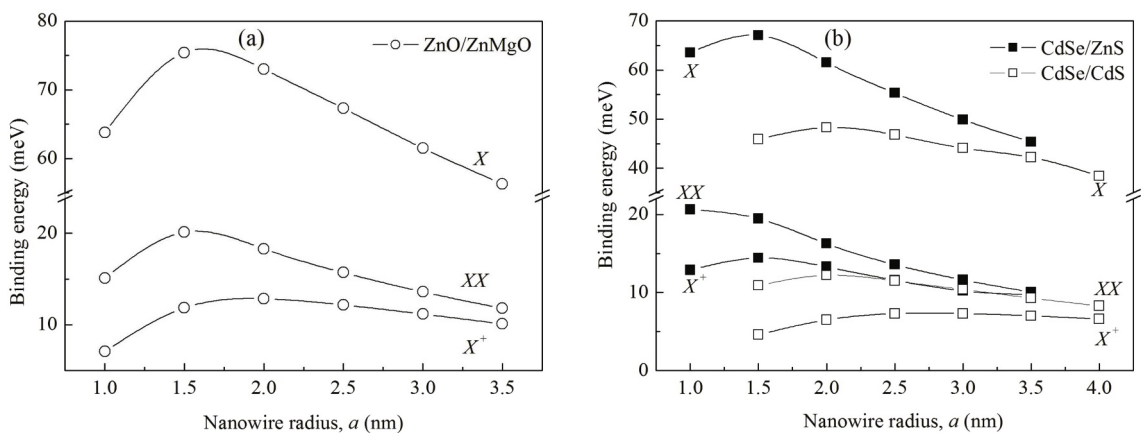


Fig. 4. Dependence of the binding energies of excitonic complexes on the radius of a nanowire in ZnO/ZnMgO (°) (a), CdSe/ZnS (■) and CdSe/CdS (□) (b) NWs, respectively, The thickness of the surrounding dielectric shell is  $b = 2$  nm.

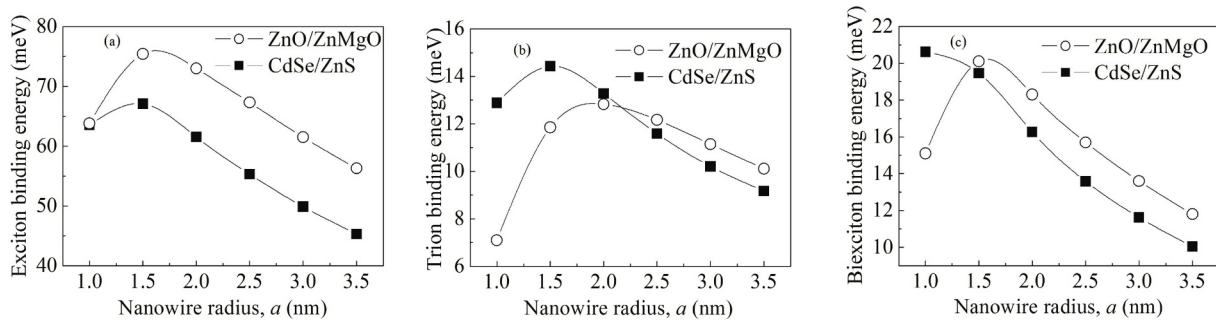


Fig. 5. Comparison of the dependence of the binding energies of the exciton (a), trion (b) and biexciton (c) in ZnO/ZnMgO (°) and CdSe/ZnS (■) NWs on radius of a NW. The thickness of the surrounding dielectric shell is  $b = 2$  nm.

same radius  $a = 1.5$  nm, while the maximum for the binding energy of the trion is shifted and occurs for the radius of the NW  $a = 2$  nm. In CdSe/CdS for the set of the lateral confinement potentials  $U_e^0 = 0.30$  meV and  $U_h^0 = 0.44$  meV the maximum of the binding energies for these excitonic complexes are pronounced at  $a = 2.0$  nm for the exciton and biexciton, while the trion has the maximum binding energy for about 80% larger radius. The increase of the confinement potentials in CdSe/ZnS qualitatively and quantitatively changes the binding energy of the excitonic complexes: i) the binding energies of excitonic complexes are increased; ii) they are bound for a smaller NW radius,  $a = 1.0$  nm; iii) while the biexciton binding energy is monotonically decreases, the maximum of binding energy for the exciton and trion occurs at the radii of NW  $a = 1.5$  nm. Our calculations show that the biexciton binding energy exceeds that for the trion rather significantly at a small NWs radius ( $a = 1.5$  nm in ZnO/ZnMgO and CdSe/CdS, and  $a = 1.0$  nm in CdSe/ZnS) and with the increase of the radius the difference between binding energies decreases. Moreover, in both CdSe/ZnS and CdSe/CdS NWs the biexciton-to-trion binding energy ratio is greater than unity, decreasing with the NW radius increase. The same tendency one can observe for in ZnO/ZnMgO NW when the radius  $a \geq 1.5$  nm.

Now let us present, discuss and compare the results for the binding energies of the exciton, trion and biexciton. In Fig. 5a the single exciton binding energies in ZnO/ZnMgO and CdSe/ZnS calculated by means of Eqs. (16) and (14) are presented. The binding energy varies between 56.3 and 75.3 meV when the NW radius varies between 1.0 and 3.5 nm, and has maximum at about 1.5 nm NW radius and at  $a = 3.5$  nm the exciton binding energy drops to that of bulk materials. The same behavior of exciton binding energy is observed for ZnO/ZnMgO quantum wells [100], with maximum at about 2 nm QW width. The dependence

of trion binding energy on the NW radius is depicted in Fig. 5b. The maximum of the binding energy 12.8 meV is obtained for the NW radius  $a = 2.0$  nm. With the further decrease of wire radius the binding energy sharply drops. With increasing of the wire radius from 2.0 nm to 3.5 nm the binding energy decreases again. Let us mention that the maximum of a binding energy for biexcitons occurs for the smaller radius of NWs than for trions for all considered materials.

The dependences of the binding energy of biexciton in ZnO/ZnMgO and CdSe/ZnS on the NW radius is plotted in Fig. 5c. The biexciton has the maximum binding energy about 21 meV for the wire radius  $a = 1.5$  nm. Interestingly, in Ref. [56] biexcitons were investigated in the ZnO/ZnMgO multiple quantum wells. Experimentally determined binding energies for biexcitons vary between 17.5 and 30.9 meV depending on the width of quantum well and the maximum value was obtained for 2 nm width and binding energy drops to that of bulk materials. Interestingly enough, our results are in qualitative agreement with the earlier predictions in Ref. [41] that the trion and biexciton binding energies decrease as the diameter quasi-1D systems increases beyond the 1 nm range. However, for a core/shell wire when the radius of the core becomes smaller, the penetration range of the electron-hole wave function into the barrier (shell region) increases, and due to delocalization their bonding becomes weaker. As stated above, the effective mass of the electron is considerably lower than that for the hole, which is why the electronic component of the wave function significantly leaks into the shell region, while the heavy hole mainly stays within the core. The latter results in the decrease of the binding energy of excitonic complexes in core/shell nanowires, which is illustrated by our calculations presented in Figs. 4 and 5.

We also study the influence of the thickness of dielectric shell on the

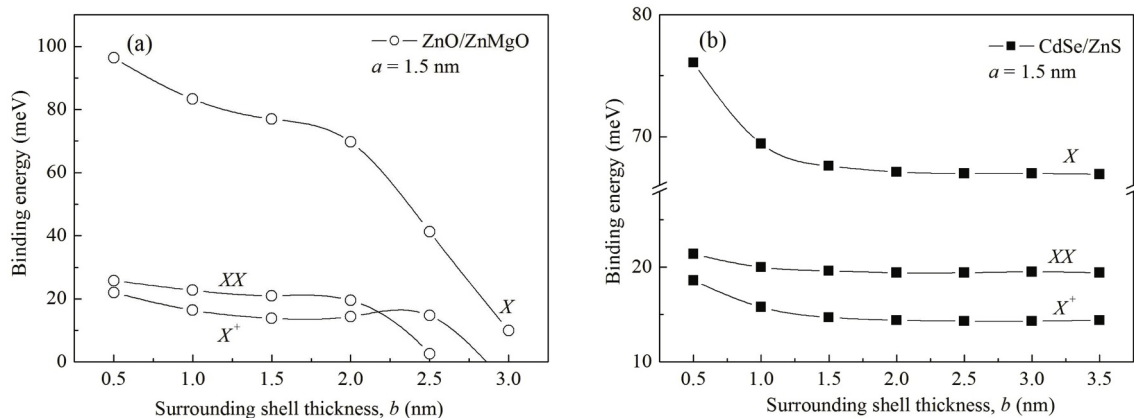


Fig. 6. Dependence of the exciton, trion and biexciton binding energy in ZnO/ZnMgO (a) and CdSe/ZnS (b) on the thickness of the surrounding dielectric shell.



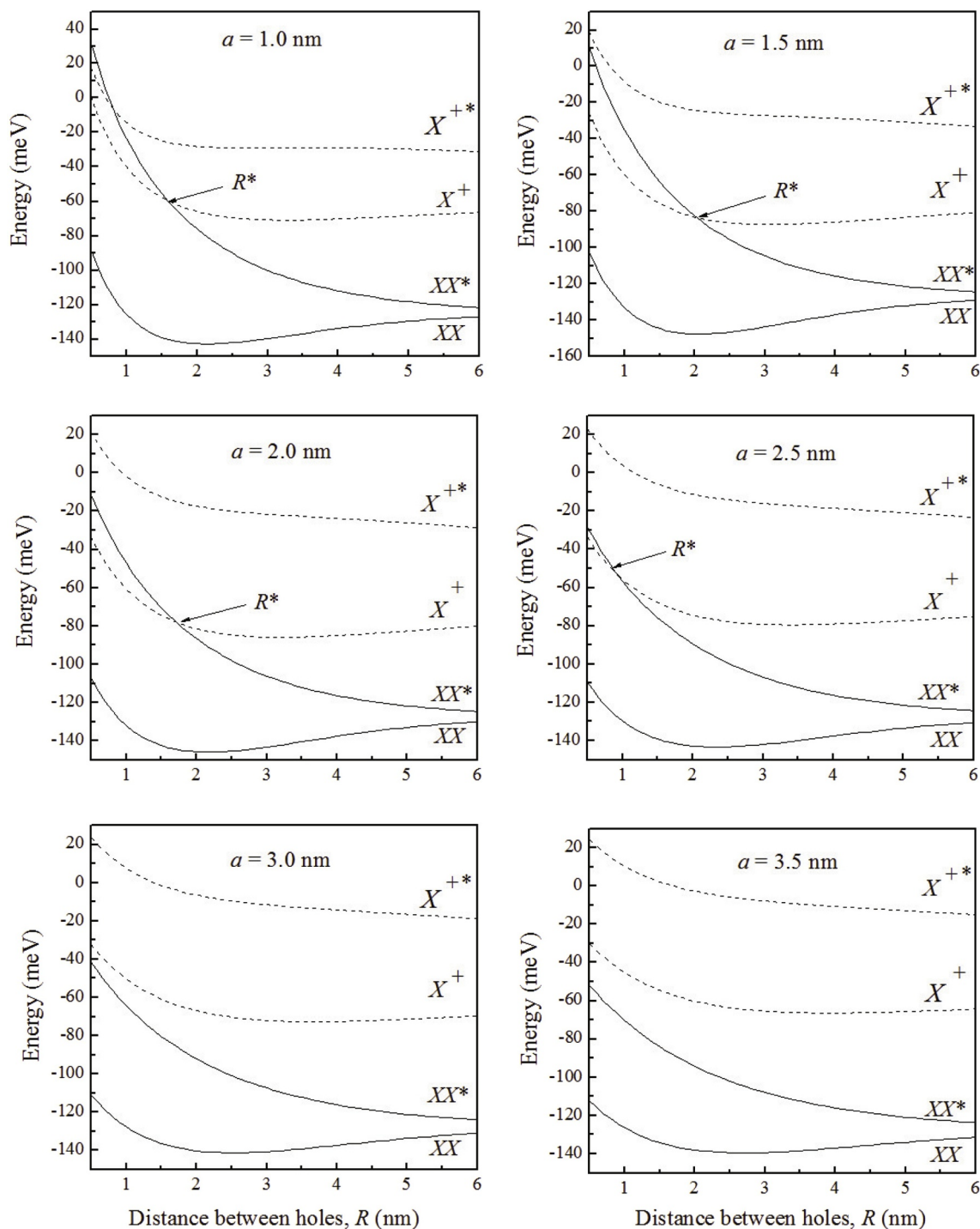
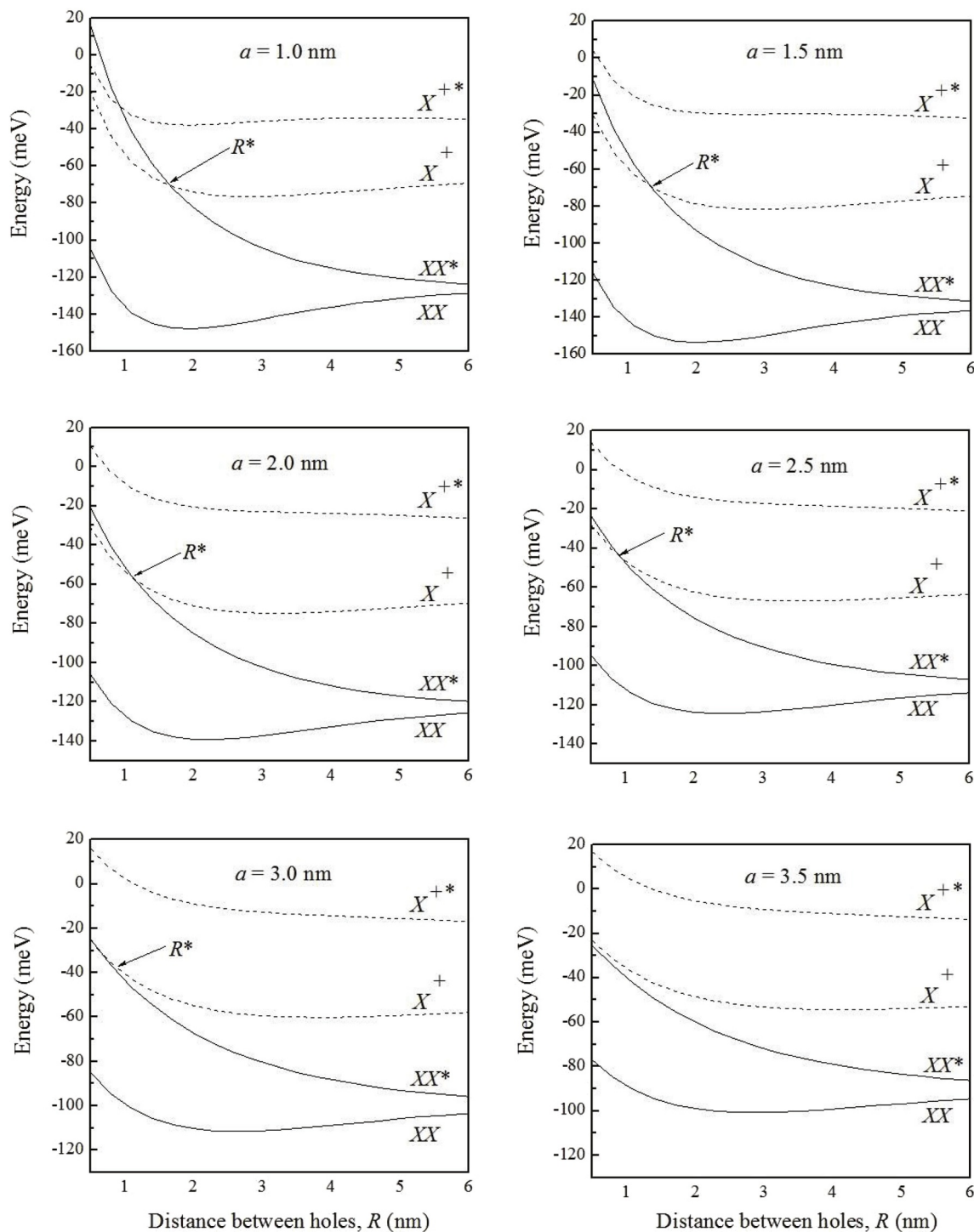


Fig. 7. The dependence of the trion and biexciton energies on the interhole separation for NWs of 1.0–3.5 nm radius. The notations  $X^+$  and  $XX$  indicate bounding states energy for the trion and biexciton, respectively, while  $X^{+*}$  and  $XX^*$  represents trions and biexciton antibonding states.  $R^*$  indicates the interhole distance of the crossing of the biexciton antibonding state energy curve with the trion bonding state energy curve. Results for ZnO/ZnMgO NW.

binding energy of excitonic complexes. In Fig. 6 are presented the dependence of the binding energy of the exciton, trion and biexciton binding energy on the thickness of the surrounding dielectric shell in ZnO/ZnMgO and CdSe/ZnS. We have calculated the binding energy as a function of barrier width  $b$  for the exciton, trion and biexciton in ZnO/ZnMgO and CdSe/ZnS NWs. One can conclude that in the case of CdSe/

ZnS NW all excitonic complexes remain stable with the increase of dielectric shell thickness, while in ZnO/ZnMgO NW biexcitons become unstable when the surrounding dielectric shell exceeds 2 nm. The trion remains stable for the thickness of the dielectric shell  $b < 2.5$  nm. The stability of excitonic complexes in CdSe/ZnS NW can be explained by the high lateral confinement potentials for the electron and hole. The



**Fig. 8.** The dependence of the trion and biexciton energies on the interhole separation for NWs of 1.0–3.5 nm radius. The notations  $X^+$  and  $XX$  indicate bounding states energy for the trion and biexciton, respectively, while  $X^{+*}$  and  $XX^*$  represents trions and biexciton antibonding states.  $R^*$  indicates the interhole distance of the crossing of the biexciton antibonding state energy curve with the trion bonding state energy curve. Results for CdSe/ZnS NW.

relatively low potential barriers for the lateral confinement of electrons and holes in ZnO/ZnMgO NW allow the penetration of the corresponding electronic wave functions in the surrounding dielectric shell area which leads to the strong decrease of the binding energies of the exciton and biexciton when  $b > 2$  nm. Our calculations demonstrate

that the size of the core of the NW has stronger influence on the binding energy of trions and biexcitons compared to the thickness of interfacial alloying. Let us mention that observation for CdSe/CdS [57] suggested that the size of the surrounding shell has equal or less influence on Auger suppression compared to the radius of the core of NW.

Our calculations show a radius dependence of characteristics of excitons, trions and biexcitons and enhancement of their binding with size reduction as expected in nanostructures. Our calculations show that the binding energy of trions are smaller than the binding energy of biexcitons. One can consider the mechanism of formation of a trion as a dissociation of a biexciton into a trion bonding state and an electron. To verify this hypothesis let us to rearrange the data for bonding and antibonding states given in Figs. 2 and 3 as presented in Figs. 7 and 8, where are indicated crossings of bonding and antibonding states energy curves. In Fig. 7 biexciton and trion energies for the same radius of wire are depicted in the same figure to investigate associative ionization (AI) [101], the process in which two excitons interact to produce a free electron and a bound trion. With the radius reduction quantitative change of energy level alignment is observed as one can see in Fig. 7. Indeed, a biexciton in the antibonding state can dissociate into a trion bonding state and an electron. When two excitons approach one another along Born-Oppenheimer potential energy curve  $E(R)$  the ionization occurs only after this reactant pair enters a region of the  $(E, R)$  plane in which the bound initial electronic state becomes embedded in the continuum associated with the final state, trion-electron. One can see that for the radii  $a = 1.0$  nm,  $a = 1.5$  nm,  $a = 2.0$  nm and  $a = 2.5$  nm of wire the energy of the antibonding biexciton state sharply increases and the energy curve crosses the trion bonding state energy curve at the interhole distance  $R^*$ . At distances  $R < R^*$  the biexciton energy in the antibonding state becomes larger compared to the trion energy. Therefore, it is possible to transition from the biexciton antibonding state to the trion bonding state with release of an electron - *e.a.*, the associative ionization. During photoexcitation the antibonding states of biexciton are created at different interhole distances  $R$ . Such states will survive if holes go away from each other on the distance larger than  $R^*$  before AI, and then stabilize (dissociate). Quantitatively the probability of surviving can be estimated by means of  $R^*$ . The larger  $R^*$ , the smaller the probability would be. Fig. 7 shows that the probability should drop with the NW size reduction. In Fig. 8 are presented the crossings of energy curves for the biexciton in the antibonding states and trion in the bonding states energies for the same radii for CdSe/ZnS NW. These results also demonstrate a possible transition from the biexciton antibonding state to the trion bonding state with release of an electron at some particular interhole distances  $R^*$ .

Taking into account the behavior of the biexciton binding energy with the NW size variation, we can propose that there exists an optimal radius of elongated ZnO/ZnMgO quantum wire, for which biexciton binding energy is still larger than the bulk value, whilst associative ionization into trion state (which in its turn has strong tendency to the Auger decay) is weakened. This radius ranges between 1.5 and 2.0 nm. At the same time for the elongated CdSe/ZnS quantum wire this range

is 2.0–2.5 nm due to the stronger lateral confinement.

#### 4. Conclusions

In summary, we presented the theoretical description of the trion and biexciton in a NW in the framework of the effective-mass model using Born-Oppenheimer approximation and considered both the lateral confinement and the localization potential. The analytical expressions for the binding energy and wavefunctions are obtained and expressed by means of matrix elements of the effective one-dimensional cusp-type Coulomb potentials which parameters are determined self-consistently by employing the same eigenfunctions of the confined electron and hole states. We investigated biexcitons and trions in ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS quantum NWs of a cylindrical shape and study the dependence of their binding energies on the radius of the NW. It is found that for the same input parameters the biexciton binding energy in NWs is always larger than binding energy of the trion. For the same input parameters the exciton, trion and biexciton have the maximum binding energy for the same radius of ZnO/ZnMgO NW, (while the trion has the maximum binding energy for about 70% larger radius of a NW.) We found an appreciable dependence of the trion binding energy on the radius of the quantum wire. In CdSe/CdS and ZnO/ZnMgO quantum NWs trions appear to have maximum binding energy for 1.5 nm and 2.0 nm, respectively. It was revealed that a radius reduction down to 1.5 nm enhances binding energy of the exciton, trion and biexciton in ZnO/ZnMgO NW, while for the biexciton in CdSe/CdS quantum NW the maximum binding energy is obtained for the thinner NW with 1 nm radius. For very thin NWs binding energies of excitonic complexes decrease. The excitonic complexes remain stable in CdSe/ZnS NW with the increase of the dielectric shell, while in ZnO/ZnMgO NW the trion and biexciton become unstable when the surrounding dielectric shell exceeds 2.5 nm and 2 nm, respectively. We suggest the mechanism of formation of the trion via associative ionization of a biexciton. As for probability of the associative ionization of biexciton into vulnerable to Auger decay trion states, it continually decreases with increasing the radius of NW. This leads us to the conclusion that 1–2 nm radius of NW should be optimal for optoelectronic application at high excitation intensity.

#### Acknowledgment

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#### Appendix A. Effective interactions

The effective electron-hole, hole-hole and electron-electron interactions that are defined as

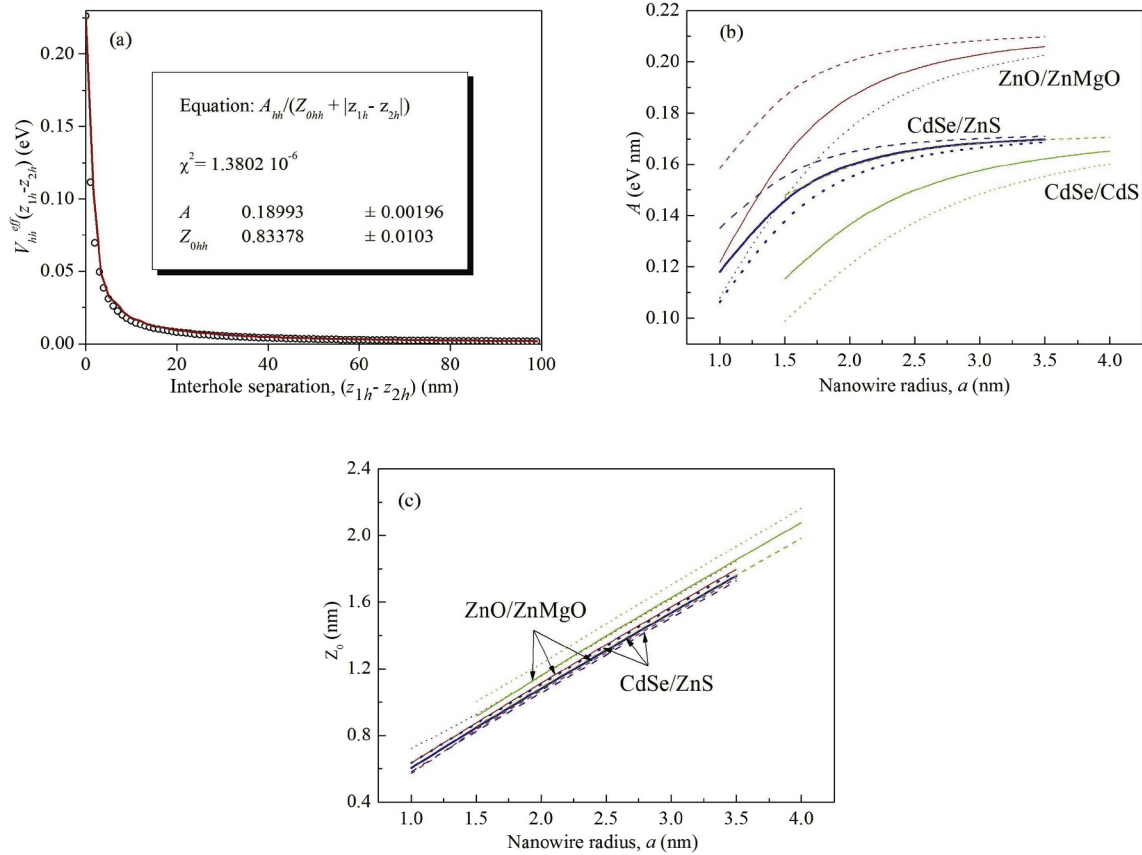
$$V_{eh}^{eff}(z_e - z_h) = - \int_0^{a+b} \int_0^{2\pi} \varphi_e d\varphi_e d\varphi_e \int_0^{a+b} \int_0^{2\pi} \varphi_h d\varphi_h d\varphi_h |\psi_e(\rho_e, \varphi_e)|^2 \times V(\mathbf{r}_e, \mathbf{r}_h) |\psi_h(\rho_h, \varphi_h)|^2 \quad (A.1)$$

$$V_{hh}^{eff}(z_{1h} - z_{2h}) = \int_0^{a+b} \int_0^{2\pi} \varphi_{1h} d\varphi_{1h} d\varphi_{1h} \int_0^{a+b} \int_0^{2\pi} \varphi_{2h} d\varphi_{2h} d\varphi_{2h} \times |\psi_{1h}(\rho_{1h}, \varphi_{1h})|^2 V(\mathbf{r}_{1h}, \mathbf{r}_{2h}) |\psi_{2h}(\rho_{2h}, \varphi_{2h})|^2 \quad (A.2)$$

$$V_{ee}^{eff}(z_{1e} - z_{2e}) = \int_0^{a+b} \int_0^{2\pi} \varphi_{1e} d\varphi_{1e} d\varphi_{1e} \int_0^{a+b} \int_0^{2\pi} \varphi_{2e} d\varphi_{2e} d\varphi_{2e} \times |\psi_{1e}(\rho_{1e}, \varphi_{1e})|^2 V(\mathbf{r}_{1e}, \mathbf{r}_{2e}) |\psi_{2e}(\rho_{2e}, \varphi_{2e})|^2 \quad (A.3)$$

where  $V(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{\varepsilon |\mathbf{r}_1 - \mathbf{r}_2|}$  is the Coulomb potential. As a result of averaging of  $\frac{e^2}{\varepsilon |\mathbf{r}_1 - \mathbf{r}_2|}$  over the electron  $\psi_e(\rho_e, \varphi_e)$  and hole  $\psi_h(\rho_h, \varphi_h)$  wave functions

in the lateral directions, the effective potentials (A.1) - (A.3) are free from the singularity of the bare Coulomb potential at the origin. The modeling of the potentials (A.1) - (A.3) with the first order rational function  $\frac{A}{(z+Z_0)}$ , where  $z$  is interparticle distance in  $z$ -direction and  $A$  and  $Z_0$  are fitting parameters, provides a slight modification of the long-range Coulomb potential by a cusp-type Coulomb potential. The values of the fitting parameters  $A$  and  $Z_0$  depend on a dielectric constant  $\epsilon$  of a NW material, a NW core radius  $a$  and a shell thickness  $b$ . As an example of the fitting procedure Fig. 9a illustrates the fitted  $\frac{A_{hh}}{|z_{1h}-z_{2h}|+Z_{0hh}}$  1D potential in the case of hole-hole interaction. The calculation is performed for a ZnO/ZnMgO nanowire of radius  $a = 1.5$  nm and shell thickness  $b = 2$  nm. To find the values of the best fitting parameters  $A_{hh}$  and  $Z_{0hh}$  we use the  $\chi^2$  distribution, which is a commonly used probability distribution for hypothesis testing. The consideration of different materials leads to changes in the values of the fitting parameters, but the functional dependences, of course, remains the same. This procedure is used for the parametrization of the potentials (A.1) - (A.3) for each NW. In our particular case related to the ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS quantum NWs the dependence of the fitting parameters  $A$  and  $Z_0$  on the NW radius are presented in Fig. 9b and c. From Fig. 9b one can conclude that the fitting parameters  $A_{ee}$ ,  $A_{eh}$  and  $A_{hh}$  that indicate the strength of the cusp-type Coulomb electron-electron, and hole-hole interactions converge with the increase of NW radius. The fitting parameters  $Z_{0ee}$ ,  $Z_{0eh}$  and  $Z_{0hh}$  presented in Fig. 9c display the linear dependence on NW radius. The slopes of these dependences are almost the same for the same NW, but there are the significant differences for the slopes for ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS NW. The variation of  $Z_{0ee}$ ,  $Z_{0eh}$  and  $Z_{0hh}$  parameters with a nanowire radius in ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS NW can be explained the following way: these parameters are obtained by means of averaging of 3D Coulomb potential with radial wave functions, which describe the lateral confinement of electrons and holes. After averaging procedure Coulomb potentials depend only on the distance between carriers.  $Z_0$  should be a measure of their average lateral separation. Now it is obvious that  $Z_0$  must increase i) when barrier is decreased and/or ii) when carrier effective masses are reduced.



**Fig. 9.** The dependence of the effective potential  $V_{hh}^{eff}(z_{1h}-z_{2h})$  on the interhole separation. Open circles - the numerical value of the 1D potential obtained from Eq. (A.2), solid curve - results from the equation  $V_{hh}^{eff} = \frac{A_{hh}}{|z_{1h}-z_{2h}|+Z_{0hh}}$  with the best fitting parameters (a). Dependence of the fitting parameters  $A_{ee}$ ,  $A_{eh}$  and  $A_{hh}$  (b) and  $Z_{0ee}$ ,  $Z_{0eh}$  and  $Z_{0hh}$  (c) on the core radius for ZnO/ZnMgO, CdSe/ZnS and CdSe/CdS NWs. The shell thickness  $b = 2$  nm. Dotted curves - for electron-electron interaction; solid curves - for electron-hole interaction; dashed curves - for hole-hole interaction.

## Appendix B. Matrix elements for $J$ and $K$

The value for  $J$  and  $K$  are given by the following matrix elements

$$J = \langle \Phi_{X_1} | \frac{A_{eh}}{|z+R/2|+Z_{0eh}} | \Phi_{X_1} \rangle = \langle \Phi_{X_2} | \frac{A_{eh}}{|z-R/2|+Z_{0eh}} | \Phi_{X_2} \rangle, \quad (B.4)$$

$$K = \langle \Phi_{X_2} | \frac{A_{eh}}{|z+R/2|+Z_{0eh}} | \Phi_{X_1} \rangle = \langle \Phi_{X_1} | \frac{A_{eh}}{|z-R/2|+Z_{0eh}} | \Phi_{X_2} \rangle. \quad (B.5)$$

The matrix elements (B.4) can be treated as the total energy of the cusp-type Coulomb interaction between the hole located at  $z = -R/2$  with the electron density  $e |\Phi_{X_1}|^2$  or the hole located at  $z = R/2$  with the electron density  $e |\Phi_{X_2}|^2$ . Numerically, these two matrix elements are equal to one another. The matrix elements (B.5) correspond to the energy of the cusp-type Coulomb interaction of the overlap charge density  $e |\Phi_{X_1}\Phi_{X_2}|$  localized around the hole located at  $z = -R/2$  with the hole. By symmetry, the energy of interaction of the overlap charge density with the hole located at



$z = R/2$  has the same value. The matrix elements  $J$  and  $K$  both depend on the interhole separation  $R$  and are calculated for each fixed value of interhole distance.

### Appendix C. Matrix elements for $\mathfrak{J}$ and $\mathfrak{K}$

For the biexciton, the values for  $J$  and  $K$  are the same as for the trion and are given by (B.4) and (B.5), while  $\mathfrak{J}$  and  $\mathfrak{K}$  are the matrix elements as defined below

$$\mathfrak{J} = \left\langle \Phi_{X_1}(z_1)\Phi_{X_1}(z_1) \left| \frac{A_{ee}}{z_{12} + z_{0ee}} \right| \Phi_{X_2}(z_2)\Phi_{X_2}(z_2) \right\rangle, \quad (C.6)$$

$$\mathfrak{K} = \left\langle \Phi_{X_1}(z_1)\Phi_{X_2}(z_2) \left| \frac{A_{ee}}{z_{12} + z_{0ee}} \right| \Phi_{X_1}(z_2)\Phi_{X_2}(z_1) \right\rangle. \quad (C.7)$$

The matrix element  $\mathfrak{J}$  is the repulsion energy of the charge density  $e|\Phi_{X_1}(z_1)|^2$  of electron 1 localized around the hole located at  $z = R/2$  with the charge density  $e|\Phi_{X_1}(z_1)|^2$  of electron 2 localized around the hole located at  $z = -R/2$ , when the repulsion occurs via the cusp-type Coulomb interaction. The matrix element  $\mathfrak{K}$  presents the repulsion energy between the electrons due to the cusp-type Coulomb interaction, which is connected with the correlation in the motion of the electrons arising from the antisymmetrization of the wavefunctions in accordance with the Pauli principle. The matrix elements  $\mathfrak{J}$  and  $\mathfrak{K}$  are functions of the distance  $R$  between the holes.

Once the value of  $J$  and  $K$ , and  $\mathfrak{J}$  and  $\mathfrak{K}$  are known one can find the value of  $Q$  and  $P$  as

$$Q = E_{hh} + 2J + \mathfrak{J}, \quad P = SE_{hh} + 2SK + \mathfrak{K} \quad (C.8)$$

and obtain the biexciton energy as a function of the interhole distance  $R$  using Eqs. (26) and (27).

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