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Recombination energy for excitonic trions in quantum dots

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Abstract. A theoretical study of excitonic trions, X^- and X_2^+, in semiconductor quantum dots is presented. The model of a spherical quantum well of finite depth is applied to determine the influence of the three-dimensional quantum confinement on the recombination energies of the excitonic trions. A new type of variational wave function, expanded in a Gaussian basis, has been proposed. It is shown that the blue-shift of the recombination induced by the quantum confinement is much stronger for the positive trion X_2^+ than for the negative trion X^-.

Excitonic trions (charged excitons) are electronic excited states of semiconductors, which are created when an additional electron or a hole is bound to a pre-existing exciton. The existence of negatively (X^-) and positively (X_2^+) charged excitons in bulk semiconductors was predicted theoretically [1–5] and observed experimentally in Ge [6], Si [7], and CuCl [8, 9] bulk crystals. In the bulk crystals, the recombination energies of neutral and charged excitons are very close. Moreover, the binding energies of charged excitons are small compared to the thermal excitation energies. Therefore, the identification of the excitonic trions in the bulk materials is rather difficult. In quasi-two-dimensional quantum wells (QWs), a strong increase of both the binding energy of the charged excitons and the energy separation between the neutral- and charged-exciton recombination lines has been theoretically shown by Stébé *et al* [10]. The charged excitons have been experimentally observed in CdTe/CdZnTe [11] and in GaAs/GaAlAs [12–14] semiconductor QWs. The negatively charged excitons have been observed [15] in InAs self-assembled quantum dots (QDs). The binding energies of charged excitons in pyramidal QDs have been calculated by Lelong and Bastard [18]. Wójs and Hawrylak [19] have studied the X^- confined in a two-dimensional harmonic potential in an external magnetic field. It is well known that the quantum confinement results in a blue-shift of the exciton-related photoluminescence lines [20, 21].

In the present paper, we study the influence of the three-dimensional quantum confinement on the recombination energy of excitonic trions X^- and X_2^+ in QDs. We take into account the fully three-dimensional character of the Coulomb interaction, which has been recently shown to be important even for quasi-two-dimensional QDs [22].

The effective-mass Hamiltonian for the confined negatively charged exciton (X^-) can be written as follows:

$$H = -\frac{\hbar^2}{2m_e^*}(\nabla_1^2 + \nabla_2^2) - \frac{\hbar^2}{2m_h^*}\nabla_h^2 + V_e(\boldsymbol{r}_1) + V_e(\boldsymbol{r}_2) + V_h(\boldsymbol{r}_h) + \frac{e^2}{\varepsilon}\left(\frac{1}{r_{12}} - \frac{1}{r_{1h}} - \frac{1}{r_{2h}}\right) \quad (1)$$

where m_e^* (m_h^*) is the effective electron (hole) band mass, ε is the effective dielectric constant, V_e (V_h) is the confinement potential for the electrons (holes), $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, and $\boldsymbol{r}_h$ are the position

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vectors of the two electrons and the hole with respect to the dot centre, r_{12}, r_{1h}, and r_{2h} are the electron–electron and electron–hole distances. The energy of the electrons (holes) is measured from the conduction band minimum (valence band maximum) of the QD material. We assume that the effective masses as well as the dielectric constants are the same in the well and barrier materials. The Hamiltonian for the positively charged exciton X_2^+ can be obtained from (1) by interchanging the electron and hole masses and the confinement potentials.

The confinement potentials result from the conduction and valence band offsets at the QD/barrier interface. Therefore, we have approximated them by spherically symmetric quantum wells of radius R. The barrier height is equal to V_0^e for the electrons and V_0^h for the holes. The present model is fully three-dimensional and applies to confinement potentials of finite range and depth, i.e., it is adequate for QD nanocrystals embedded in an insulating medium, e.g., GaAs [23] and InAs [24]. Contrary to the usually applied harmonic oscillator model potential [19,25], the quantum-well potential does not commute with the kinetic energy operator of the centre-of-mass motion. Therefore, Hamiltonian (1) cannot be separated into the centre-of-mass and relative-motion Hamiltonians. Hence, the ground-state wave function for the trion confined in the spherical quantum well has to be dependent on the six distances appearing in Hamiltonian (1). In the present paper, we propose the following variational trial wave function for the singlet ground state of the X^- trion:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_h) = \psi_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_h) + \psi_2(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_h) \tag{2}$$

where ψ_1 and ψ_2 are expanded in the following two Gaussian bases with N_1 and N_2 elements, respectively:

$$\psi_1(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_h) = \exp(-br_{1h}^2 - br_{2h}^2)(1 + P_{12}) \sum_{i_1 i_2 i_3}^{N_1} c_{i_1 i_2 i_3} \exp(-\alpha_{i_1}^e r_1^2 - \alpha_{i_2}^e r_2^2 - \alpha_{i_3}^h r_h^2) \tag{3}$$

and

$$\psi_2(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_h) = \exp(-a^e r_1^2 - a^e r_2^2 - a^h r_h^2)(1 + P_{12}) \times \sum_{j_1 j_2 j_3}^{N_2} d_{j_1 j_2 j_3} \exp(-\gamma_{j_1} r_{12}^2 - \beta_{j_2} r_{1h}^2 - \beta_{j_3} r_{2h}^2). \tag{4}$$

In equations (3) and (4), P_{12} is the permutation operator interchanging the electron indices $1 \leftrightarrow 2$; $c_{i_1 i_2 i_3}$, $d_{j_1 j_2 j_3}$, α_i^e, α_i^h, β_j, γ_j, a^e, a^h, and b are the variational parameters. The trial wave function for the positively charged exciton X_2^+ has been chosen in a similar way.

Trial wave function ψ_1 describes the trions in a strong-confinement regime [26], for which the interparticle correlations are weak. In the weak-confinement regime (bulk limit) [26], the correlations between the three particles are of crucial importance. They are described by trial wave function ψ_2. The choice of the double basis in formula (2) enables us to obtain reliable energy estimates in both the limiting cases, i.e., in the strong- and weak-confinement regimes. The applicability of the Gaussian basis to the few-particle problem for the spherically symmetric quantum dot of finite depth has been discussed in detail by Bednarek *et al* [27]. The Gaussian basis was proved to be useful in the variational calculations of bulk and confined exciton complexes [28, 29]. Moreover, we have performed test calculations with the use of variational wave function (2) and obtained a ground-state energy equal to -0.2611 (in double atomic rydbergs: 2 Ryd = 27.2116 eV) for X^- in a bulk material with $m_e^* = m_h^*$. For comparison, the 'exact' value obtained by Frost *et al* [30] is equal to -0.2620.

The three-dimensional nanocrystals of nearly spherical shape were fabricated from GaAs in organic solvents [23] and other three-dimensional GaAs/GaAlAs nanostructures were experimentally studied by Ugajin *et al* [31]. In the present paper, we consider the excitonic

trions in the spherical GaAs quantum dot embedded in the $Ga_{0.8}Al_{0.2}As$ matrix. We apply the GaAs effective masses and dielectric constant for the confined charged excitons and neglect the discontinuities of both the parameters at the QD boundary. In our previous paper [32], we have shown that the influence of effective-mass discontinuity on the ground-state energies of electrons and neutral donor impurities is negligibly small for the spherical GaAs/$Ga_{0.8}Al_{0.2}As$ QDs. The neglect of the dielectric constant discontinuity is justified by the similarity of the dielectric properties of the GaAs and $Ga_{0.8}Al_{0.2}As$ materials. Throughout the present paper, we use the following values of the barrier heights [33]: $V_0^e = 140.1$ meV for the electron and $V_0^h = 105.7$ meV for the hole; and the effective masses [34]: $m_e^*/m_0 = 0.0665$ for the electron and $m_h^*/m_0 = 0.34$ for the hole, where m_0 is the electron rest mass, and the dielectric constant [35] $\varepsilon = 12.5$.

We have performed systematic test calculations with an increasing number of basis elements in expansions (3) and (4). The results of table 1 show that convergence is nearly reached for N_1 and $N_2 \simeq 100$. In the following calculations, we have used the trial wave function with $N_1 = 75$ and $N_2 = 84$ terms, which provides quite reliable estimates.

Table 1. Test of the convergence of the variational basis (equations (2)–(4)) with N_1 and N_2 terms in ψ_1 and ψ_2, respectively. The results are given for the GaAs/$Ga_{0.8}Al_{0.2}As$ quantum dot with $R = 2\ a_D$. The calculated ground-state energy of the X^- (X_2^+) trion is quoted in the third (fourth) column and the corresponding recombination-energy shifts are listed in the fifth and sixth columns. In this quantum dot, the electron, hole, and exciton confinement energies are equal to 1.021 77, 0.218 92, and 0.256 70, respectively. The energy is expressed in double donor rydbergs ($2R_D = 11.4$ meV) and the length in donor Bohr radii ($a_D = 99.47$ Å).

N_1	N_2	$E(X^-)$	$E(X_2^+)$	$\Delta E(X^-)$	$\Delta E(X_2^+)$
40	42	1.12290	0.37539	0.15556	0.10023
75	84	1.10928	0.36788	0.16918	0.10773
126	144	1.10230	0.36284	0.17616	0.11278
196	225	1.09914	0.35663	0.17932	0.11899

The energy estimates obtained with the use of only ψ_1 or ψ_2 are quoted in table 2. These results enable us to give a physical interpretation of both the trial wave functions. Wave function ψ_1 yields the dominant contribution to the ground-state energy in the strong-confinement regime, while ψ_2 yields that in the weak-confinement regime. In the intermediate-confinement regime, the contributions originating from the two wave functions are comparable. Table 2 also provides the test of the reliability of the present results for the intermediate-confinement regime.

Table 2. Ground-state energy of the X^- complex confined in the GaAs/$Ga_{0.8}Al_{0.2}As$ quantum dot as a function of quantum-dot radius R calculated with the use of trial wave functions ψ_1, ψ_2, and Ψ. The units are the same as for table 1.

R/a_D	ψ_1	ψ_2	Ψ
20	−0.3087	−0.4220	−0.4308
10	−0.2937	−0.3676	−0.4054
5	−0.1615	−0.0907	−0.2609
2	1.2114	1.3021	1.0928
1	5.8065	8.2818	5.7016

We have determined the amount of energy released in an electron–hole recombination process for the positive (X_2^+) and negative (X^-) trions confined in a QD. The recombination energy is the difference between the energies of the initial and final states. The ground state of

the trion is the initial state. The final state, after the electron–hole recombination, corresponds to the confined hole (electron). Thus, the recombination energies are given by

$$h\nu_{X_2^+} = \epsilon_g + E_{X_2^+} - E_h \tag{5}$$

$$h\nu_{X^-} = \epsilon_g + E_{X^-} - E_e \tag{6}$$

for the positive and negative trions, respectively, where ϵ_g is the energy gap of the QD, $E_{X_2^+}$ and E_{X^-} are the ground-state energies of the confined charged excitons, E_e and E_h are the energies of the confined electron and hole. The recombination energy of the neutral exciton $h\nu_X = \epsilon_g + E_X$, where E_X is the ground-state energy of the exciton confined in the QD. We define the recombination-energy shifts

$$\Delta E_{X_2^+} = h\nu_X - h\nu_{X_2^+} \tag{7}$$

$$\Delta E_{X^-} = h\nu_X - h\nu_{X^-}. \tag{8}$$

The calculated energy shifts are shown in figure 1 as functions of the inverse square of the dot radius R for the weak-confinement regime of the GaAs/GaAlAs QDs. In the bulk crystal, i.e., for $R \to \infty$, the recombination-energy shift for the X_2^+ is larger than that for the X^-, which agrees with the results of the previous studies [3–5]. This results from the fact that the binding energy of X_2^+ is larger than that of X^- for $m_e^*/m_h^* < 1$. However, figure 1 shows that the quantum confinement changes the order of the recombination-energy shifts for the dot radius $R \sim 12\,a_D$, which—for small QDs—leads to the recombination-energy shift for the X^- being up to ∼50% larger than that for the X_2^+. In figure 2, we have plotted the energy shifts for a wider range of QD radii, which includes the strong-confinement regime. The energy shift ΔE_{X^-} for the negative trion increases with the decreasing QD radius. The behaviour of the energy shift for the positive X_2^+ trion is more complex. In the weak-confinement regime,

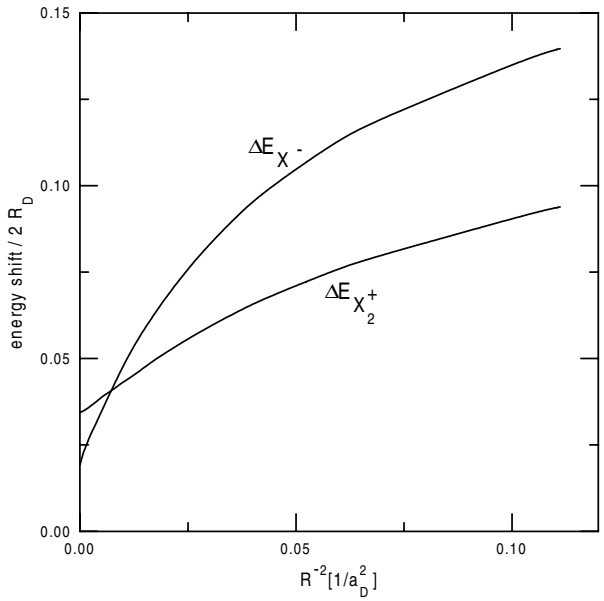

Figure 1. Calculated recombination-energy shifts for the trions X^- and X_2^+ confined in a $GaAs/Ga_{0.8}Al_{0.2}As$ quantum dot as functions of the inverse square of the dot radius R in the weak-confinement regime. The unit of energy is twice the donor rydberg ($2R_D$), the unit of length is the donor Bohr radius (a_D) for GaAs.

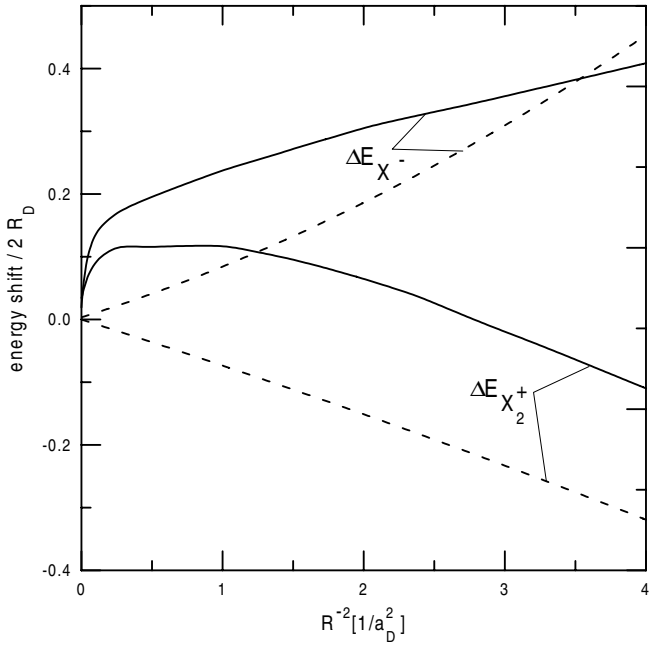

Figure 2. Recombination-energy shifts for the trions X^- and X_2^+ confined in a GaAs/$Ga_{0.8}Al_{0.2}As$ quantum dot as functions of the inverse square of the dot radius R in the intermediate- and strong-confinement regimes. The units are the same as for figure 1. Solid (dashed) curves show the variational (perturbation theory) results.

the energy shift $\Delta E_{X_2^+}$ increases if the QD radius decreases. In the intermediate-confinement regime ($a_D \leqslant R \leqslant 2\ a_D$), this shift is almost independent of the dot size. In the strong-confinement regime, i.e., for $R < a_D$, $\Delta E_{X_2^+}$ decreases, which leads to the blue-shift of the X_2^+ line with respect to the neutral-exciton line.

In order to get physical insight into this surprising behaviour of the confinement-induced shift of the X_2^+ recombination line, we have used the first-order perturbation theory. In the strong-confinement limit, the Coulomb interactions between the charge carriers can be treated as a perturbation when determining the qualitative properties of the confined electron–hole systems [26]. According to the first-order perturbation approach, energy shifts (7) and (8) result from the Coulomb interactions only and can be expressed as follows:

$$\Delta E_{X_2^+} = V_{eh} - V_{hh} \tag{9}$$

$$\Delta E_{X^-} = V_{eh} - V_{ee} \tag{10}$$

where V_{eh}, V_{hh}, and V_{ee} are the Coulomb integrals

$$V_{eh} = \langle \varphi_e(r_1)\varphi_h(r_2)|\frac{1}{r_{12}}|\varphi_e(r_1)\varphi_h(r_2)\rangle \tag{11}$$

$$V_{hh} = \langle \varphi_h(r_1)\varphi_h(r_2)|\frac{1}{r_{12}}|\varphi_h(r_1)\varphi_h(r_2)\rangle \tag{12}$$

and

$$V_{ee} = \langle \varphi_e(r_1)\varphi_e(r_2)|\frac{1}{r_{12}}|\varphi_e(r_1)\varphi_e(r_2)\rangle. \tag{13}$$

Here, φ_e and φ_h are the exact wave functions of the electron and the hole confined in spherical potential wells of depths V_0^e and V_0^h, respectively. Integrals (11)–(13) can be evaluated in a semi-analytical way. The localization of the hole in the quantum well is—due to the larger effective mass—much stronger than the localization of the electron. This leads to the following inequalities:

$$V_{ee} < V_{eh} < V_{hh} \tag{14}$$

and

$$\Delta E_{X_2^+} < 0 < \Delta E_{X^-}. \tag{15}$$

Finally, we obtain the following blue-shift:

$$h\nu_{X^-} < h\nu_X < h\nu_{X_2^+}. \tag{16}$$

The energy shifts calculated with the help of the first-order perturbation theory have been plotted in figure 2 as dashed curves. We see that—in the strong-confinement regime—the qualitative predictions of the perturbational and variational methods agree with each other. We can therefore conclude that the predicted blue-shift of the X_2^+ recombination line with respect to the lines for the neutral exciton and negatively charged exciton is caused by the strong localization of holes in the QD.

Recently, evidence for both the X^- and X_2^+ trions in CuCl QDs has been claimed by Kawazoe and Masumoto [16, 17]. Due to the use of the donor units of energy and length, the present results (figures 1 and 2) can also be applied to these QDs (although in a rather qualitative sense because of the ionic character of these structures). The authors of [16, 17] have argued that they observed the confined excitonic trions in CuCl quantum cubes embedded in a NaCl crystal in a luminescence hole-burning experiment. The interpretation in [16, 17] is based on the application of energy-conservation formulae [16] to the measured recombination-energy shifts [16]. Unfortunately, in the formulae used by the authors of [16], the energies of the confined electron and hole have been omitted in the final states. If we include these energies, which are necessary for the energy conservation, we obtain dramatic changes of the slopes of the Stokes shift versus burning-energy dependence (cf. figure 4 in reference [16]). The accurate slopes are 3.88 and 26.5 times greater than those calculated in reference [16] for lines *A* and *B*, respectively. The correct application of the energy-conservation law leads to a complete disagreement with the experimental data in [16] and to the change of order of the lines attributed to the X_2^+ and X^- trions. In view of the above arguments, the lines in [16, 17] cannot be interpreted as resulting from the excitonic trions, but could be tentatively attributed to the excited-state recombination of neutral excitons or neutral-exciton complexes [36]. Therefore, experimental evidence for trions in these QDs awaits further research.

Finally, we briefly discuss the influence of different material parameters on the present results. The change of the electron and hole confinement potentials fundamentally changes the recombination energies. However, the recombination-energy shifts, calculated as energy differences (7) and (8), change only slightly. The recombination energies of X, X^-, and X_2^+ tend to the same value if dielectric constant ε increases. For equal electron and hole band masses, i.e., for $m_e^* = m_h^*$, the X^- and X_2^+ recombination energies are equal to each other.

In summary, we have calculated for the first time the ground-state and recombination energies for X^- and X_2^+ excitonic trions confined in spherical quantum dots. We have predicted a confinement-induced change of order of the X^- and X_2^+ recombination lines and a strong blue-shift of the X_2^+ recombination line.

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