Anisotropy-induced exchange splitting of exciton radiative doublet in CdSe nanocrystals

S. V. Goupalov

A.F. Ioffe Physico-Technical Institute, 26 Polytechnicheskaya, 194021 St. Petersburg, Russia

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It is shown that reduction of the symmetry of the shape of almost spherical nanocrystals to that of a three axial ellipsoid or lower leads to a splitting of the exciton radiative doublets into linearly polarized components. The splitting is a result of a combined action of the distortion of the boundary conditions and the electron-hole exchange interaction. Both the short-range and the long-range parts of the exchange interaction are equally important for the splitting.

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Since the experiment of Gammon *et al.*[1] and theoretical studies of Refs. 2 and 3 it is well known that, in anisotropic quantum dots with weak confinement, exciton radiative doublets are split by the long-range electron-hole exchange interaction (also known as nonanalytical exchange or annihilation interaction) into linearly polarized components (see also Refs. 4 and 5). The anisotropy in these systems originates from the fact that epitaxially grown quantum dots tend to be elongated along certain crystallographic directions. In the weak confinement regime (when quantum dot size exceeds the exciton Bohr radius) the exciton envelope function factorizes into a product of a function, describing relative motion of the electron and the hole, and a function dependent on the coordinates of the exciton center of mass. The latter function (and, therefore, its Fourier transform) reflects anisotropy of the quantum dot shape. In bulk semiconductors or quantum wells the long-range electron-hole exchange interaction affects only optically active exciton states and is sensitive to relative orientation of the exciton dipole moment (associated with the interband optical transition) and its wave vector. For quantum dots with weak confinement, contribution of each wave vector to the exchange energy is weighted with the corresponding squared Fourier component of the envelope function describing the motion of the exciton center of mass. When this function is anisotropic the long-range electron-hole exchange interaction splits the exciton radiative doublet.

Nanocrystals (NCs) of CdSe synthesized in glass matrices or grown by organometallic chemistry are typical examples of the strong confinement regime. They are believed to possess almost perfect spherical shape. Only deviations of the NC shape preserving cylindrical symmetry (so that a NC has the shape of either prolate or oblate ellipsoid of revolution) have been so far discussed in literature.[6] However, plausible interpretations of recent experiments on polarized four-wave mixing[7] and resonant photoluminescence of CdSe NCs in magnetic fields[8] require an assumption of the existence of a (zero-field) splitting of the exciton radiative doublet. In the present paper we propose a mechanism of such a splitting. This mechanism is different from the mechanism responsible for the splitting of radiative doublets in quantum dots with weak confinement.

In the strong confinement regime the exciton wave function factorizes into a product of functions dependent on only electron and only hole coordinates, respectively. The ground exciton state ($1S_e 1SD_{3/2}$) in a perfectly spherical CdSe quantum dot is formed by the s-wave electron and the hole characterized by the total angular momentum $\frac{3}{2}$ whose orbital motion is contributed by orbital angular momenta 0 and 2. The fine structure of the exciton ground state can be described by the effective Hamiltonian[9]

$$H = -\frac{\Delta}{2}\left(J_z^2 - \frac{5}{4}\right) - \bar{\eta}(\boldsymbol{\sigma}\mathbf{J}). \tag{1}$$

Here σ_α ($\alpha = x, y, z$) are the Pauli matrices, J_α are the matrices of projections of the $J = \frac{3}{2}$ angular momentum operator, z axis is along the C_6 axis of wurtzite. The first term in Eq. (1) describes the crystal-field induced splitting associated with the wurtzite structure of CdSe, the second one is due to the electron-hole exchange interaction. The parameter Δ is size independent while $\bar{\eta}$ scales as R^{-3} with the NC radius R.[9] Note that the parameter $\bar{\eta}$ is determined by both the long-range and the short-range parts of the exchange interaction.[9–12]

The effective Hamiltonian (1) was first used for a description of the fine structure of excitonic levels in CdSe NCs in Ref. 13. However, only the short-range (analytical) contribution to the electron-hole exchange interaction was taken into account, and the value of $\bar{\eta}$ was underestimated. This makes quantitative analysis of Ref. 13 invalid. The issue of a necessity to account for the long-range part of the electron-hole exchange interaction was first raised by Goupalov and Ivchenko[10] in the framework of the effective mass method. Their results were later confirmed by Ajiki and Cho.[14] A large long-range contribution to the electron-hole exchange interaction in semiconductor quantum dots was also obtained by using a many-body approach based on atomistic pseudopotential wave functions.[15] A detailed quantitative account for the exciton ground state splittings in CdSe NCs along with comparison to experimental data was made in Ref. 9. An additional justification for the importance of the electron-hole long-range exchange interaction was made within the empirical tight-binding method[12] and from consideration of resonant Rayleigh scattering of light by a quantum dot.[11,16] It is worth noting, however, that the ongoing discussion concerns only the value of the parameter $\bar{\eta}$ and its dependence on the NC size while both the short-range and the long-range electron-hole exchange contributions to the effective Hamiltonian (1) have the same symmetry.

Now consider a NC of the ellipsoidal shape whose surface is described by the equation

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{R^2}=1. \tag{2}$$

Suppose that this NC has the same volume as a sphere of radius R. The NC of this shape can be obtained from a spherical quantum dot if we first squeeze the quantum dot in the x direction so that it expands in the y and z directions; and then stretch it in the y direction so that it shrinks in the x and z directions. If these two deformations are of the same magnitude then the size in the z-direction remains as it had been before any strain was introduced. Assume that anisotropy of the resulting three-axis ellipsoid is small. Then, on symmetry grounds, one should expect that the new effective Hamiltonian is given by

$$H=-\frac{\Delta}{2}\left(J_z^2-\frac{5}{4}\right)-\bar{\eta}(\boldsymbol{\sigma}\mathbf{J})+\frac{C}{\sqrt{3}}(J_x^2-J_y^2), \tag{3}$$

where $C\propto R^{-2}$, $C\propto\mu=(a-b)/R$, and μ is the parameter of the perturbation theory which should be employed in order to calculate the energy C explicitly (see below). Diagonalization of the Hamiltonian (3) reveals linear in C splittings of the radiative doublets. In particular, energies of the components of the lowest radiative doublet probed in the experiments[7,8] are

$$E_{1^L_{x,y}}=\frac{\bar{\eta}}{2}-\frac{1}{2}\sqrt{16\bar{\eta}^2+\Delta^2-4\bar{\eta}\Delta+4C^2\pm 8\sqrt{3}\bar{\eta}C}. \tag{4}$$

The energies of the other states are given by

$$E_{2a}=-\frac{3\bar{\eta}}{2}-\frac{\sqrt{\Delta^2+4C^2}}{2},$$

$$E_{2b}=\frac{\bar{\eta}}{2}-\frac{\sqrt{16\bar{\eta}^2+\Delta^2+8\bar{\eta}\Delta+4C^2}}{2},$$

$$E_{1^U_{x,y}}=\frac{\bar{\eta}}{2}+\frac{1}{2}\sqrt{16\bar{\eta}^2+\Delta^2-4\bar{\eta}\Delta+4C^2\pm 8\sqrt{3}\bar{\eta}C},$$

$$E_{0^L}=-\frac{3\bar{\eta}}{2}+\frac{\sqrt{\Delta^2+4C^2}}{2},$$

$$E_{0^U}=\frac{\bar{\eta}}{2}+\frac{\sqrt{16\bar{\eta}^2+\Delta^2+8\bar{\eta}\Delta+4C^2}}{2}.$$

Here the states are labeled by the quantum numbers which become good in the limit when $C\to 0$ and NC assumes spherical shape. In this limit 0, 1, and 2 are the absolute values of the projections of the exciton total angular momentum onto the wurtzite axis. When $C\neq 0$, the states with the total angular momentum projection ± 2 mix with the states with the total angular momentum projection 0 (0^L and 0^U).[17] The electron-hole exchange interaction lifts degeneracy of all the doublets.

The splitting of the lowest radiative doublet is given by

$$\Delta_{xy}\approx-\frac{4\sqrt{3}\bar{\eta}C}{\sqrt{16\bar{\eta}^2+\Delta^2-4\bar{\eta}\Delta}}. \tag{5}$$

This splitting is exchange-induced and vanishes for $\bar{\eta}=0$. For small NCs ($\bar{\eta}\gg\Delta$), $\Delta_{xy}\approx-\sqrt{3}C$ (here $|C|\ll\bar{\eta}$) and scales as R^{-2} with the NC size. For large NCs ($\bar{\eta}\ll\Delta$), $\Delta_{xy}\approx-4\sqrt{3}\bar{\eta}C/\Delta$ and scales as R^{-5} with the NC size.

Let us express the energy C through the small parameter $\mu=(a-b)/R$ and parameters of the NC. To that end we will use the perturbation theory of boundary conditions proposed by Migdal.[18] In this theory a new coordinate system is introduced in such a way that the surface (2) in the new coordinates transforms into a sphere. In our case the new coordinates are

$$x'=xR/a,\quad y'=yR/b,\quad z'=z. \tag{6}$$

When the system Hamiltonian (essentially, the kinetic energy) is expressed through the new coordinates, it receives an addition which can be treated by a conventional perturbation theory. Since the electron in the exciton ground state has zero orbital angular momentum, only the hole kinetic energy is essential. Due to the high symmetry of wurtzite crystals in the plane perpendicular to the hexagonal axis, the hole kinetic energy in the zeroth approximation can be described by the spherical Luttinger Hamiltonian

$$\hat{H}_L(\hat{\mathbf{p}})=\left(\gamma_1+\frac{5}{2}\gamma_2\right)\frac{\hat{\mathbf{p}}^2}{2m_0}-\frac{\gamma_2}{m_0}(\hat{\mathbf{p}}\mathbf{J})^2.$$

Here m_0 is the free electron mass, γ_1 and γ_2 are the Luttinger parameters, and $\hat{\mathbf{p}}=-i\hbar\nabla$ is the momentum operator. The crystal-field induced splitting of the valence band is taken into account in the first order of the perturbation theory which results in the first term in the effective Hamiltonian (1).[19] Since we assumed that the ellipsoid (2) has the same volume as a sphere of radius R, in the linear in μ approximation we have $a\approx R(1+\mu/2)$, $b\approx R(1-\mu/2)$. Let us express the Luttinger Hamiltonian through the coordinates (6) up to the terms linear in μ. We obtain

$$\hat{H}_L(\hat{\mathbf{p}})=\hat{H}_L(\hat{\mathbf{p}}')+\mu\hat{V}(\hat{\mathbf{p}}'),$$

where

$$\hat{V}(\hat{\mathbf{p}})=\left(\gamma_1+\frac{5}{2}\gamma_2\right)\frac{\hat{p}_y^2-\hat{p}_x^2}{2m_0}+\frac{\gamma_2}{m_0}\Big[\hat{p}_x^2J_x^2-\hat{p}_y^2J_y^2 +\frac{1}{2}\hat{p}_z\hat{p}_x(J_xJ_z+J_zJ_x)-\frac{1}{2}\hat{p}_z\hat{p}_y(J_yJ_z+J_zJ_y)\Big]. \tag{7}$$

Using the unperturbed hole wave function from Ref. 9 we find that the effect of this perturbation reduces to a contribution to the effective Hamiltonian (1) in the form $(J_x^2-J_y^2)C/\sqrt{3}$ with

$$C=\frac{\sqrt{3}}{2}\mu v(\beta)E_h(\beta). \tag{8}$$

Here $\beta=(\gamma_1-2\gamma_2)/(\gamma_1+2\gamma_2)$ is the light-to-heavy hole effective mass ratio, $v(\beta)$ is the function introduced in Ref. 6, $E_h(\beta)=\hbar^2\varphi_h^2/2m_{hh}R^2$ is the energy of the hole level of size quantization in a perfectly spherical NC of radius R, $m_{hh} = m_0/(\gamma_1 - 2\gamma_2)$ is the heavy hole effective mass, φ_h is the first root of the following equation:

$$j_0(x)j_2(\sqrt{\beta}x) + j_2(x)j_0(\sqrt{\beta}x) = 0,$$

and $j_l(x)$ is the spherical Bessel function of order l. We would like to emphasize that, in the present model, the dependence of the energy C on the light-to-heavy hole effective mass ratio β is described in terms of the same functions which were employed in Ref. 6 to describe NCs having the shape of an ellipsoid of revolution with the cylindrical axis along the wurtzite axis. In the latter case nonsphericity of the NC shape results in a size-dependent renormalization of the parameter Δ in Eq. (1).

To summarize, we have shown that reduction of the symmetry of the NC shape to that of a three-axis ellipsoid or lower leads to splittings of radiative doublets into linearly polarized components. We have managed to construct a model where such anisotropy is described by a single perturbation parameter. The splittings of the radiative doublets are due to a combined action of the distortion of the boundary conditions and the electron-hole exchange interaction. The proposed mechanism is different from that responsible for the splittings of the radiative doublets in quantum dot systems in the weak confinement regime.[2,3] The obtained analytical expression for the splitting of the lowest radiative doublet can be used to estimate the degree of the NC anisotropy from experimentally measured splittings.

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