1D Exciton Spectroscopy of Semiconductor Nanorods

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We have theoretically shown that optical properties of semiconductor nanorods are controlled by 1D excitons. The theory, which takes into account anisotropy of spacial and dielectric confinement, describes size dependence of interband optical transitions, exciton binding energies. We have demonstrated that the fine structure of the ground exciton state explains the linear polarization of photoluminescence. Our results are in good agreement with the measurements in CdSe nanorods.

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There is growing interest in nano-size crystalline semiconductor structures of various shapes such as nanocrystals (NCs) 1, nanorods (NRs) 2 and nanowires (NWs) 3 created by the "from the bottom up" technological approach. Size-tunable control of their optical and transport properties combined with the ability to move these nano-size objects around with precise control opens the exciting possibilities for the creation of new functional materials which can be used in unlimited applications. Among these nanostructures, the NCs are the most heavily studied and one can find a broad description of their properties and their potential applications in the reviews of Brus 4 and Alivisatos 5.

The optical properties of NRs, however, differ significantly from those of NCs. Compared to NCs, the NRs show higher photoluminescence (PL) quantum efficiency 2, strongly linear polarized PL 6-8, an increase of the global Stokes shift 6, and significantly faster carrier relaxation 6. The Auger processes in NRs are strongly suppressed relative to those in NCs 6,10, which subsequently decreases the optical pumping threshold for stimulated emission 11,12. The size and shape dependence of the optical and tunneling gaps measured in CdSe NRs 12 shows an unexpectedly large difference that cannot be explained by the electron-hole Coulomb correction to the optical gap used for NCs. To describe their measurements Katz et al. 12 applied the four-band theory developed by Sercel and Vahala 13. The most important result of the latter paper was the prediction of an inverse order of light and heavy hole subbands in NWs, which was later confirmed by semiempirical pseudopotential calculations 6,14,15 and numerical calculations within the 6 band model 16. An anisotropy of the light hole-to-electron optical transition matrix element predicts some degree of the PL linear polarization parallel to the NW 15,15.

The dielectric confinement connected with the difference between dielectric constants of semiconductor crystallites, κs, and surrounding medium, κm, (for example, see 12) usually does not affect the optical spectra of NCs because the charge distributions of an excited electron and hole practically compensate each other at each point of the NC. This leads to a complete screening of an electric field of the total charge from penetration into the surrounding medium. This is not the case, however, in NRs where the electron and hole are at a distance larger than a NR radius and interact predominantly through the surrounding medium, which usually has a small dielectric constant, κm ≪ κs. This should lead to a formation of 1D excitons (1DEs) with large binding energy similar to that in NWs 21. In addition, the dielectric confinement of anisotropic crystallites leads to strong PL polarization and PL polarization memory that was observed in NWs 21 and in porous Si 22. This dielectric model, however, does not explain the strong linear polarization of NRs 6.

In this letter, we have developed a theory that describes energy spectra and polarization properties of 1DEs in NRs. Our theory takes into account both spatial and dielectric confinement and allows one to describe optical properties of elongated NRs with quasi-cubic and zinc-blende lattice structure. The calculation for CdSe NRs surrounded by a dielectric with κm = 2.0 has shown that the 1DEs control optical properties of NRs even at room temperatures and has described the difference between the optical and tunneling gaps 12. We have shown that the fine structure of 1DE explains the observed 87% polarization degree of PL 6 and leads to the fast radiative decay in NRs at room temperatures.

In what follows, we consider the NR as a crystalline that has the shape of an ellipsoid of revolution with major semi-axis b (the NR axis) much larger than the minor semi-axis a (the NR radius). The motion of electrons and holes is analyzed within the 6-band model that has successfully described optical spectra of CdSe NCs 23. The significant elongation of NRs (b ≫ a) makes it possible, by using an adiabatic approximation, to separate the parallel motion from the motion perpendicular to the NR axis. Within this approximation we initially neglect the slow motion of carriers parallel to the NR axis. Assuming that the momentum of the parallel motion k∥ ≈ 0, we find the spectrum of carriers in 2D confinement perpendicular to the NR axis. Next, we consider the parallel motion by averaging the Hamiltonian over the fast motion of carriers strongly confined in 2D.

Each electron state in NRs is characterized by the
angular momentum projection on the NR axis, \( m = 0, \pm 1, \ldots \). The wave functions of the electron motion perpendicular to the NR axis can be written as \( \sim e^{i\rho \phi} J_{m}(k \rho) \), where \( \phi \) is the azimuthal angle, \( \rho \) is the distance from the NR axis, and \( J_{l}(x) \) is the Bessel function of the \( l \)-th order. The momentum \( h \rho \) is connected to the kinetic energy of the electron motion perpendicular to the NR, \( E_{n} = \frac{\hbar^{2} k^{2}}{2m_{0} E_{c}(E_{0})} \), where \( m(E) = m_{0}/[1 + 2f + (E_{p}/3)[(E + E_{g}) + (E + E_{g} + \Delta)] \) is the electron effective mass that depends on the electron energy, \( E, m_{0} \) is the free electron mass, \( E_{g} \) is the band gap, \( \Delta \) is the spin-orbit splitting of the valence band, \( E_{p} \) is the Kane energy parameter, and the parameter \( f \) includes the contribution of remote bands. Assuming that the wave function vanishes at the NR surface, we find the momentum \( h \rho \) which satisfies the boundary condition: \( h \rho J_{n}[\rho] = h \alpha_{n}[\rho] / a \), where \( \alpha_{n}[\rho] \) is the \( n \)-th root of the Bessel function of the \( [n] \)-th order. This gives the following energy of electron subbands \( E_{n}[\rho] \) with the corresponding wave functions \( \Psi^{(c)}(\rho, \phi) \) for the motion perpendicular to the NR axis, with total angular momentum projection, \( j_{z} \), as written

\[
E_{n}[\rho] = \frac{\hbar^{2} \alpha_{n}[\rho]}{2a^{2} m(E_{n}[\rho])}, \quad \Psi^{(c)}(\rho, \phi) = \frac{J_{n}[\alpha_{n}[\rho] \rho] e^{i \rho \phi}}{\sqrt{\pi a J_{n}[\alpha_{n}[\rho]]}}, \quad (1)
\]

where \( \rho = \rho / a \) and the three smallest \( \alpha_{n}[\rho] \) are \( \alpha_{10} \approx 2.41, \alpha_{11} \approx 3.83, \alpha_{12} \approx 5.14 \).

Due to a strong spin-orbit coupling in the valence band, each hole state in the NR is characterized by the total angular momentum projection on the NR axis \( j_{z} = m + J_{z} \) which is the sum of angular momentum projection and the projection of the hole spin \( J = 3/2 \) \( (j_{z} = \pm 1/2, \pm 3/2, \ldots) \). The energy spectrum of holes is found within the 6-band model, which takes into account the nonparabolicity of light hole spectrum \( 24 \). In this model, the hole wave function of the motion, perpendicular to the NR axis, with total angular momentum projection, \( j_{z} \), can be written

\[
\Psi^{(h)}(\rho, \phi) = \sum_{\mu = -3/2}^{3/2} C_{\mu}^{3/2} J_{j_{z} - \mu}(x_{1} \rho) e^{i(\mu - \mu) \phi} \sqrt{2\pi} u_{3/2, \mu}^{(h)}(\rho),
\]

where \( u_{3/2, \mu}^{(h)} \) and \( u_{3/2, \mu}^{(e)} \) are the valence band Bloch functions \( 24 \). For every value of the hole energy \( E \), there are dimensionless momenta \( x_{1} \) and the sets of coefficients \( C_{\mu}^{3/2} \) corresponding to the three branches in the dispersion law of the valence band \( (l, h, s) \):

\[
\begin{align*}
\chi_{h}^{2} &= \frac{\varepsilon}{\gamma_{1}^{L} - 2\gamma_{L}^{L}} = \frac{\eta(\varepsilon) + (-\xi(\varepsilon))}{(\gamma_{1}^{L} - 2\gamma_{L}^{L})(\gamma_{1}^{L} + 4\gamma_{L}^{L})}, \\
\eta(\varepsilon) &= 2e(\gamma_{1}^{L} + \gamma_{L}^{L}) - \delta(\gamma_{1}^{L} + 2\gamma_{L}^{L}), \\
\xi(\varepsilon) &= \sqrt{\eta(\varepsilon)^{2} - 4\varepsilon(\varepsilon - \delta)(\gamma_{1}^{L} - 2\gamma)(\gamma_{1}^{L} + 4\gamma_{L}^{L})},
\end{align*}
\]

where \( \varepsilon = E/E_{0}, \delta = \Delta/E_{0}, E_{0} = \hbar^{2}/2m_{0} a^{2} \), and the energy dependent Luttinger parameters \( \gamma_{1}^{L} \) and \( \gamma_{L}^{L} \) are connected with the contributions from remote bands, \( \gamma_{1} \) and \( \gamma_{L} \), by the relationships: \( \gamma_{1}^{L} = \gamma_{1}^{0} + E_{p}/[3(E_{g} + E)] \) and \( \gamma_{L}^{L} = \gamma_{1}^{0} + E_{p}/[6(E_{g} + E)] \) \( 24 \). At \( k_{z} = 0 \), the 6-band Hamiltonian can be decomposed into two 3-band Hamiltonians and the wave functions \( \Psi^{(j_{z})}(\rho) \) in Eq. (2) are described by the set of only three coefficients: \( C_{l}^{3/2, 1/2}, C_{s}^{3/2, 1/2}, C_{s}^{1/2, 1/2} \). For the heavy hole and for the mixture of the light- and spin-orbit split holes, these coefficients are \( C_{l}^{3/2, 1/2} = (\sqrt{3}, 1, 0) \) and \( C_{s}^{(l)} = (1, -\sqrt{3}, \chi_{s}(l)/1/2) \) respectively, with \( \chi_{s}(l) = 1 - \delta(\rho) + (-\sqrt{2}/4 - \gamma_{L}^{L}(\delta)_{l} + (3\gamma_{L}^{L}(\delta)_{l})^{2}) = \gamma_{L}^{L}(\delta)_{l}^{2} \).

**FIG. 1:** Size dependence of the electron and hole energy spectrum in CdSe NRs \( (E_{0} = 1.839 \text{ eV}, E_{p} = 19 \text{ eV}, \Delta = 0.42 \text{ eV}, f = -1.035, \gamma = 0.55, \gamma_{1} = 2.1) \). Arrows show optically allowed interband transitions. Inset: Size dependence of the hole effective mass at the 1$\Sigma_{1/2}$ subband.
The size dependence of the electron and hole QSLs calculated for CdSe NRs is shown in Fig.1, where we use level notations adopted from molecular physics. For the electron levels it is \( n\Lambda_e \), where \( \Lambda = \Sigma, \Pi, \Delta, \ldots \) for the states with angular momentum projection on the NR axis \( |m| = 0, 1, 2, \ldots \). The energy shift \( \delta \) (see Ref.\[23\]). The energy shift \( \delta \) due to the first hole subband effective mass, \( \Lambda = \Sigma_1/2 \) is above the \( 1\Sigma \) level with \( |m| = 1/2 \) is above the \( 1\Sigma_3/2 \) level with \( |m| = 3/2 \) in accordance with previous predictions of the reverse order of the light and heavy hole QSLs in NRs. The arrows in Fig.1 show the accurately allowed transitions between the electron and hole QSLs, which have been obtained by the calculation of the overlap integral \( K_{n\Lambda_e,n'\Lambda_e'} = \int d^2r \Psi_n^{(i)}(\rho)\Psi_{n'}^{(i)}(\rho) \) (see Ref.\[22\]). The energy shift \( \delta \) of each 1D hole subband at finite \( k_z \) can be described in terms of the 1D effective mass: \( \delta \) of the first hole subband effective mass, \( m_{1\Sigma_1/2} \), on the NR radius is shown in the inset of Fig.1.

The calculated optical spectra, however, does not include the electron-hole Coulomb interaction enhanced by the penetration of an electric field into a surrounding medium. These e-h interaction can be written

\[
U(r_e, r_h) = -\frac{e^2}{(\kappa_e |r_e - r_h|)} - e V_s (r_e, r_h) + e V_s (r_h, r_e) / 2 + e V_s (r_h, r_h) / 2, \tag{6}
\]

where the first term is the direct e-h interaction in a semiconductor, the second term is the e-h interaction mediated by the surface separating the NR from the surrounding dielectric, and the last two terms are self-interactions of each particle with the surface. For an ellipsoid, the potential \( V_s \) can be written in the following form \[23\]

\[
V_s (r, r') = \frac{e}{\kappa_e} \sum_{n=0}^{\infty} \frac{(-1)^n (2 - \delta n_0)(2n + 1) S_n^m}{\sqrt{b^2 - a^2}^n / |(n + m)! / (n - m)!|^2} \times \epsilon_n P_n^m (\eta') \epsilon_n P_n^m (\xi') \cos (\phi' - \phi), \tag{7}
\]

where \( P_n^m, Q_n^m, \tilde{P}_n, \) and \( \tilde{Q}_n \) are Legendre functions of spheroidal coordinates \( (\eta, \xi) \) and their derivatives, \( \delta_{ij} \) is the Kronecker symbol, and

\[
S_n^m = \frac{(\kappa_m - \kappa_s) Q_n^m (\eta_s) \tilde{Q}_n^m (\eta_s)}{\kappa_s P_n^m (\eta_s) \tilde{Q}_n^m (\eta_s) - \kappa_m Q_n^m (\eta_s) P_n^m (\eta_s)}. \tag{8}
\]

The spheroidal coordinates are connected with cylindrical coordinates \( (z, \rho) \) by the relationships:

\[
\eta \sqrt{b^2 - a^2} = z \quad \text{and} \quad (1 - \xi^2) (\eta^2 - 1) (b^2 - a^2)^{1/2} = \rho.
\]

At the spheroidal surface of the NR \( \eta \) becomes \( \eta_s = b / \sqrt{b^2 - a^2} \).

In the adiabatic approach, one averages the potential \( U(r_e, r_h) \) in Eq.6 over the electron and hole wave functions of the fast motion perpendicular to the NR axis (Eq.1 and Eq.4). The procedure leads to the 1D potential of e-h Coulomb interaction and the shift of the electron and hole QSLs due to their interaction with the "mirror forces" described by the last two terms in Eq.6. The 1D potential \( U_{1\Sigma_e - 1\Sigma_h}(z) \) for the lowest \( 1\Sigma_e \) electron and \( 1\Sigma_1/2 \) hole subbands can be approximated as

\[
U_{1\Sigma_e - 1\Sigma_h}(z) \approx U_{\text{eff}} (z) = -e^2 / [k_m (|z| + \rho_{\text{eff}})], \tag{9}
\]

where \( \rho_{\text{eff}} = 0.7a \) for \( \kappa_e = 6.1 \). This approximation is valid only if the distance \( |z| = |z_e - z_h| \) between two charges is much smaller than the NR length \( 2b \).

In the 1D adiabatic potential, 1DEs are formed under each pair of e-h subbands. These 1DEs strongly modify the absorption and PL spectra of NRs. The approximation of the 1D potential in Eq. 9 makes it possible to analytically find energy spectra and wave functions of 1DEs. The wave function of the 1DE is \( \Phi_{\text{ex}} (z) = A W_{\alpha,1/2} (\tilde{z}) \), where \( W_{\alpha,1/2} \) is the Whittaker function \[24\]. A is the normalization constant, and \( \tilde{z} = \pm (|z| + \rho_{\text{eff}}) / (a_1 \rho_0) \) with \( a_1D = e^2 \kappa_m / h^2 \mu \), where \( \mu = [1 / (m(E) + 1) / n_{n\Lambda_e}]^{-1} \) is the reduced electron and hole effective mass. The plus sign is for positive \( z \) and the minus sign is for negative \( z \). Each state of the 1DE is characterized by its parity. For "even" states, including the ground state, the derivative of the wave function must turn to zero at \( z = 0 \). The wave function of "odd" states becomes zero itself at \( z = 0 \). The boundary conditions determine the \( n \)-th value of \( \alpha_n \), and the energy spectrum of 1DEs as \( E_n = -h^2 / (2m_1D \alpha_n^2) \).

The size dependence of the CdSe NR transport gap, which is determined by the energy between the lowest \( 1\Sigma_e \) electron and \( 1\Sigma_1/2 \) hole subbands, is shown in Fig.2 for the bare QSLs (dotted line) and for the QSLs shifted by the "mirror forces" (dashed line). One can see that the "mirror forces" corrections to the transport gap of NRs are significant. The optical gap in NRs is determined by the 1DEs. The size dependence of the first two "even" 1DE states (only "even" states are optically active) is shown in Fig.2 by solid lines. Even in thick NRs, the binding energy of the ground and excited states is higher than 150meV and 50 meV, respectively. As a result, 1DEs should completely control the absorption and PL of CdSe NRs even at room temperature. Given the good agreement with the experimental data for the transport and optical gaps in CdSe NRs \[12\], formation of the 1DEs in NRs explains the substantial difference (~ 240 – 300 meV) between the two gaps in NRs with \( a = 1.8 - 2.0 \) nm.

The above results for 1DEs in NRs can be applied directly to NWs. Unlike in NWs, however, the radius of NRs decreases and causes a rise of the electron and hole QSLs energy. Both electrons and holes tend to be at those parts of the NR where the radius is larger. In NRs of ideal ellipsoidal shape, this leads to the parabolic potential, acting on the 1DE center of mass motion, whose minimum is at the NR center and
The calculation of the 1DE localization energy, $\bar{\Omega}$, shows how the 1DE localization energy, $\bar{\Omega}$, is similar to Ref. [27] and it depends on two values of the NR radius.

The PL properties of NRs are determined by the fine structure of the ground exciton state. Two solid lines show the optical transition frequency for the two first optically active 1DEs. Experimental data for the transport and optical gap measured in CdSe NRs from Ref. [12] are shown by empty circles and filled squares. Insets a: Dependence of the 1DE localization energy, $\bar{\Omega}$, shows that the ground 0 exciton state is similar to Ref. [27] and it is the angle between the polarization analyzer and the NR axis, the observation angle $\theta$ is measured from a direction parallel to the NR. At room temperature and $\theta = \pi/2$, the polarization is modulated at 87%, which is in very good agreement with the experiment.

Our calculations show that the anisotropy of dielectric and spatial confinement shortens the radiative lifetime at room temperatures down to 500 ps in reasonably elongated NRs relative to ~20 ns measured in CdSe NCs.

The 1DE is localized at the NR center only if the NR thickness decreases to the edges. Any nonmonotonic variations of NR thickness, NR bending, and localized charges at the NR surface should lead to 1DE localization at different parts of the NR. This results in inhomogeneous broadening of 1DEs, even in a single NR.

To summarize, we have described the structure of the 1D excitons in NRs, which control practically all aspects of the NR PL properties even at room temperatures.

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