

Jožef Stefan International Postgraduate School

Theory of Nanomaterials

Excitons in Semiconductor Quantum Dots

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Abstract

In the seminar I give a short review of the effects of confinement to the excitonic levels and fluorescence in semiconductor quantum dots. Excitons are formed when an electron is excited from the valence band to the conduction band and then binds to the formed hole through Coulomb interaction. If a particle is confined in a potential well its motion becomes quantized and its energy increases. The same happens to the excitons in semiconductor quantum dots thus changing the energy levels. This influences the optical properties like fluorescence. By changing the size of the quantum dot one can tune the absorption and emission spectrum.

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1 Introduction

In recent times there has been enormous interest and development in the field of zero-dimensional semiconductor systems. The advances in material science brought the possibility to synthesize crystals with very small sizes in one or more dimensions. Particles that have sizes in the nanometer or subnanometer range in all three dimensions are called nanocrystals or *quantum dots* (QDs). Their physical characteristics are somewhere in between molecular and bulk material and can be tuned by changing the size of the QDs. The interesting electrical and optical properties of QDs arise from the quantum confinement imposed by the physical size of QDs. One of these useful characteristics is the luminescence which can be tuned in a broad spectral range from IR to UV.

2 Particle in an Infinite Potential Well

The simplest case of particle confinement in quantum mechanics is a 1D infinite square potential well (Figure 1). To find out the wave function and the energy of a confined particle we must solve

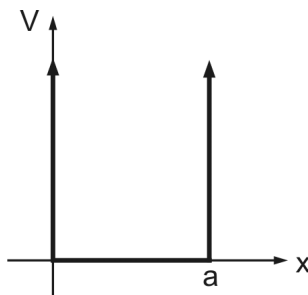


Figure 1: Infinite square potential well.

time-independent Schrödinger equation in one dimension:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x)\psi(x) = E\psi(x). \quad (1)$$

Outside the well $V = \infty$ so the only possible solution is $\psi = 0$. Inside the well we can take $V = 0$ and the equation becomes

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E\psi(x) \quad (2)$$

and the solution is

$$\psi(x) = A \sin kx + B \cos kx. \quad (3)$$

The wave function must be continuous and therefore zero at the edges of the well ($\psi(0) = 0$ and $\psi(a) = 0$). This implies $B = 0$ and $k = \frac{n\pi}{a}$. By normalizing the wavefunction across the well we also get the constant A and the final solution is

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad (4)$$

and

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}. \quad (5)$$

For 3D infinite potential well the energy of the particle is

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left[\left(\frac{n_x}{a_x} \right)^2 + \left(\frac{n_y}{a_y} \right)^2 + \left(\frac{n_z}{a_z} \right)^2 \right]. \quad (6)$$

However the quantum dots are usually of a spherical shape rather than square. The wave functions and the energies for a particle in a sphere of a radius R are

$$\phi_{n,l,m}(r) = Y_{l,m} \sqrt{\frac{2}{R^3}} \frac{J_l(\chi_{n,l} \frac{r}{R})}{J_{l+1}(\chi_{n,l})} \quad (7)$$

and

$$E_{n,l} = \frac{\hbar^2 \chi_{n,l}^2}{2mR^2} \quad (8)$$

where J_l are Bessel functions, $Y_{l,m}$ are spherical harmonic functions and $\chi_{n,l}$ is the n^{th} zero of the spherical Bessel function of order l .

3 Excitons in Bulk

If photons of energy comparable to the band gap are incident on a semiconductor, then they can excite an electron from the valence band across the band gap into the conduction band. Now we have an electron in the conductive band and a positively charged hole in the valence band. The attractive potential between the electron and the hole leads to a reduction in the total energy of the electron and hole forming a bound electron-hole pair called an *exciton*. Let us now calculate the energy of such electron-hole pair. The hamiltonian is a sum of electron and hole kinetic energy, energy of electrostatic interaction between the two and the interaction of the electron and the hole with the atomic lattice:

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{4\pi\epsilon\epsilon_0 |\vec{r}_e - \vec{r}_h|} + V_e(\vec{r}_e) + V_h(\vec{r}_h). \quad (9)$$

According to the Bloch theorem we can reduce the periodic potential of the atomic lattice $V_e(\vec{r}_e)$ and $V_h(\vec{r}_h)$ to the effective mass of the electron (m_e^*) and the hole (m_h^*). The effective mass is obtained from the band curvature near the minimum and maximum:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \left. \frac{\partial^2 E(k)}{\partial k^2} \right|_{k=0}. \quad (10)$$

The new hamiltonian is

$$H = -\frac{\hbar^2}{2m_e^*} \nabla_e^2 - \frac{\hbar^2}{2m_h^*} \nabla_h^2 - \frac{e^2}{4\pi\epsilon\epsilon_0 |\vec{r}_e - \vec{r}_h|}. \quad (11)$$

To calculate the electron-hole pair energy we use the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e^*}\nabla_e^2 - \frac{\hbar^2}{2m_h^*}\nabla_h^2 - \frac{e^2}{4\pi\epsilon\epsilon_0|\vec{r}_e - \vec{r}_h|}\right)\psi(\vec{r}_e, \vec{r}_h) = E_{ex}\psi(\vec{r}_e, \vec{r}_h). \quad (12)$$

Sometimes we can take the approximation that the hole mass is much larger than the mass of the electron. However in the semiconductors the two masses are of the same order of magnitude. We define the position of the center of mass

$$\vec{R} = \frac{m_e^*\vec{r}_e + m_h^*\vec{r}_h}{m_e^* + m_h^*}, \quad (13)$$

the relative position between the electron and the hole

$$\vec{\rho} = \vec{r}_e - \vec{r}_h, \quad (14)$$

total mass

$$M = m_e^* + m_h^*, \quad (15)$$

and the reduced mass

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}. \quad (16)$$

The Schrödinger equation now becomes

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{4\pi\epsilon\epsilon_0|\vec{\rho}|}\right)\psi(\vec{R}, \vec{\rho}) = E_{ex}\psi(\vec{R}, \vec{\rho}). \quad (17)$$

We can separate the variables

$$\psi(\vec{R}, \vec{\rho}) = \chi(\vec{R})\varphi(\vec{\rho}) \quad (18)$$

and get

$$-\frac{\hbar^2}{2M}\frac{1}{\chi(\vec{R})}\nabla_R^2\chi(\vec{R}) - \frac{1}{\varphi(\vec{\rho})}\left[\frac{\hbar^2}{2\mu}\nabla_\rho^2\varphi(\vec{\rho}) + \frac{e^2}{4\pi\epsilon\epsilon_0|\vec{\rho}|}\varphi(\vec{\rho})\right] = E_{ex}. \quad (19)$$

The two separate equations are

$$-\frac{\hbar^2}{2M}\nabla_R^2\chi(\vec{R}) = W\chi(\vec{R}) \quad (20)$$

and

$$-\left[\frac{\hbar^2}{2\mu}\nabla_\rho^2 + \frac{e^2}{4\pi\epsilon\epsilon_0|\vec{\rho}|}\right]\varphi(\vec{\rho}) = E_n\varphi(\vec{\rho}) \quad (21)$$

where

$$E_{ex} = W + E_n. \quad (22)$$

Total energy of an exciton E_{ex} is the sum of the kinetic energy of the exciton W and the self energy E_n . Equation (20) describes the free motion of the electron-hole pair center of mass

$$\chi_x(x) = Ae^{ikx} + Be^{-ikx} \quad (23)$$

and

$$W = \frac{\hbar^2k^2}{2M}. \quad (24)$$

The equation for self energy (21) is similar to the equation for the energy of H-atom. The only two differences are the reduced mass μ instead of electron mass and the dielectric constant of the semiconductor. The self energy of the exciton is therefore

$$E_n = E_{Hatom} \frac{\mu}{m_e} \frac{1}{\epsilon^2} = -\frac{\mu e^4}{32\pi^2 \hbar^2 \epsilon^2 \epsilon_0^2 n^2}. \quad (25)$$

The Bohr radius for exciton is equal to

$$r_{ex} = \frac{4\pi\epsilon\epsilon_0\hbar^2}{\mu e^2}. \quad (26)$$

and electron (hole) radius is

$$r_{e(h)} = \frac{m_{e(h)} r_{ex}}{m_e + m_h}. \quad (27)$$

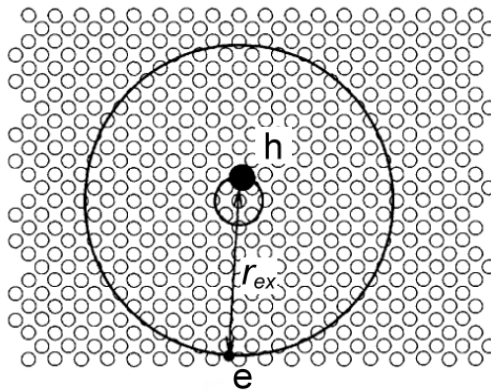


Figure 2: Graphical illustration of a exciton. A electron (e) and a heavier hole (h) are orbiting around their center of mass. The trajectory circumnavigates many atoms of the semiconductor material[1].

Let calculate the radii and energy of excitons in CdSe¹. From its material parameters (Table 1) we get $\mu = 0.10m_e$, $E_1 = -16$ meV, $r_{ex} = 4.9$ nm, $r_e = 3.7$ nm and $r_h = 1.2$ nm. The Bohr radius of the exciton is much bigger than the lattice constant. Therefore it was correct to take the bulk dielectric constant in between the electron and the hole. This kind of exciton is called *Mott-Wannier exciton*. Apart from the very big Bohr radius we also note the small self energy of the exciton.

In the case when the material has low dielectric constant the electrostatic interaction between the electron and the hole is strong. The exciton radius becomes very small and it is of the order of the lattice constant. The binding energies are around 1 eV. This kind of exciton is called *Frenkel exciton* or *molecular exciton*. To calculate the energy of Frenkel excitons we must employ a different approach than describe above.

In the description of excitons the spin of the electron and the hole is also important. We get one singlet state of total spin 0 and three triplet states with total spin of 1. The two states have different energies and must be taken into account when calculating the energy levels of excitons.

¹CdSe is a widely used semiconductor material for fluorescent quantum dot production.

Parameter	Parameter value
Static dielectric constant $\varepsilon(0)$	9.2
Band gap E_g	1.84 eV
Lattice constant a	6.052 Å
Electron effective mass m_e^*	$0.13m_e$
Hole effective mass m_h^*	$0.41m_e$

Table 1: Material parameters for bulk CdSe[2].

4 Confined Excitons and Confinement Regimes

Now we want to know what happens to the energy of an exciton if it is in a small volume of semiconductor material i.e. quantum dot. First we must find out what 'small' means by comparing the size of the quantum dot (r_{QD}) with some typical scale of the exciton. The typical length that we need to compare to the quantum dot size is previously calculated Bohr radius of the exciton r_{ex} . The exciton as a whole also has de Broglie wavelength defined by its thermal movement:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2\pi M k_B T}}. \quad (28)$$

For CdSe at room temperature the de Broglie wavelength of the exciton is $\lambda = 8.6$ nm. With respect to λ and r_{ex} we have four confinement regimes.

4.1 Bulk ($r_{QD} \gg \lambda$)

When the size of a quantum dot is couple of times larger than de Broglie wavelength of the exciton, there is no confinement effect. The energy of the excitons are calculated using Equation (22).

4.2 Weak Confinement ($r_{ex} < r_{QD} \sim \lambda$)

Weak confinement corresponds to the case when the size of the quantum dot is comparable with the de Broglie wavelength of the exciton but larger than the Bohr radius of the exciton. The exciton can be described as a single uncharged particle with mass $M = m_e^* + m_h^*$ in a spherical potential (7,8). We assume that the potential does not change the relative motion of the electron and the hole. We can treat the exciton as a quasiparticle as long as its self energy is larger than the quantization energy posed by the confinement. In this case the total energy of the exciton is

$$E = E_n + \frac{\hbar^2 \chi_{n,l}^2}{2MR^2}. \quad (29)$$

4.3 Intermediate Confinement ($r_{QD} \sim r_{ex}$)

If the quantum dot radius is comparable to the radius of the exciton, we talk about intermediate confinement. In this case the situation is more complicated and we can not use any simple approximation. We need to solve Schrödinger equation for electron and hole (12) taking into account the potential caused by the confinement. The equation is solved numerically.

If the radii of the electron and hole are quite different the influence of confinement on electron and hole is substantially different. In this case a approximation can be used to derive analytical solutions.

4.4 Strong Confinement ($r_{QD} \ll r_{ex}$)

In strong confinement regime the size of the quantum dot is much smaller than Bohr radius of exciton. As a result the kinetic energy of electron and hole is higher than the exciton self energy. Therefore no bound state exists and we can not talk about excitons any more. The electron and the hole are confined separately. We can also neglect the Coulomb interaction. The energy is quite different in comparison to exciton in bulk and is calculated using (8) for electron and hole

$$E = \frac{\hbar^2 \chi_{n,l}^2}{2m_e^* R^2} + \frac{\hbar^2 \chi_{n,l}^2}{2m_h^* R^2}. \quad (30)$$

5 Optical transitions

To find out optical properties of QDs we need to understand the optical transitions between energy levels in the QDs. First we will try to describe the situation in bulk material and then the effects of confinement.

5.1 Bulk

In Section 3 we calculated the self energy of exciton E_n given by equation (25). This energy lies just beneath the conduction band (Figure 3). When a photon hits the material it excites a electron from valence band to conduction band. The electron than binds to the hole creating an exciton. The energy produced in this transition from conduction band to excitonic level is thermally dissipated in the system. Finally the electron jumps back to the valence band producing a photon. The process is known as fluorescence. The energy of the photon is equal to the new energy gap $E_g^* = E_g - |E_n|$.

5.2 QD

In the case of QDs we need to consider the effect of confinement on the excitonic energy levels. For weak confinement the gap is bigger because of the quantization of the exciton as a whole (29)

$$E_g^* = E_g + \frac{\hbar^2 \chi_{1,0}^2}{2MR^2} - \frac{\mu e^4}{32\pi^2 \hbar^2 \epsilon^2 \epsilon_0^2} \quad (31)$$

where $\chi_{1,0} = \pi$. For strong confinement the gap energy is the sum of the gap energy in bulk plus the lowest energies of quantization for the electron and the hole (30)

$$E_g^* = E_g + \frac{\hbar^2 \chi_{1,0}^2}{2m_e^* R^2} + \frac{\hbar^2 \chi_{1,0}^2}{2m_h^* R^2} = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2}. \quad (32)$$

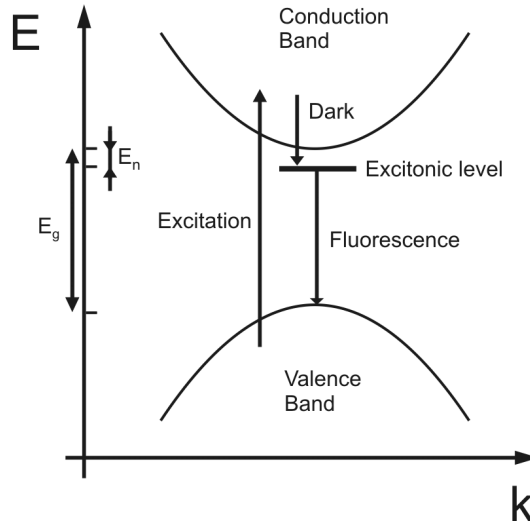


Figure 3: Electronic levels and transitions in bulk semiconduction material.

Here we can neglect the Coulomb interaction.

Both bandgap energies for weak and strong confinement were calculated for CdSe QDs of three different radii. The results are given in the last two columns in Table 2.

We can now compare the calculated energies with experimental ones. In Figure 4 there are absorption and emission spectra of CdSe QDs of different sizes. The absorption spectra was obtained by measuring the intensity of the transmitted light through a dispersion of QDs at different wavelengths. The emission spectra was measured when the dispersion was irradiated with blue light (~ 450 nm).

The emitted light is distributed in a broad symmetrical peak. The emission maximum shifts with different sizes of the QDs, with smaller QDs emitting at shorter wavelengths. This trend qualitatively matches our theoretical model. At smaller sizes we have stronger confinement and therefore higher energies. In the second column in Table 2 there are the experimental emission maximum energies for CdSe QDs of three different radii. The emission peak is broad mainly because the monodispersity of the QDs is not perfect. Other reasons for broadening are the natural line width and the existence of more excitonic levels.

The absorption spectrum is more complicated. It is also dependent of QDs size in a similar way than the emission spectrum. At shorter wavelengths the absorption is stronger than at longer wavelengths. There is a peak near the emission maxima that corresponds to the excitonic level. The absorption ends at the so called edge. This edge energy should correspond to the bandgap energy, because this is the minimal energy the photon can have to excite an electron. The experimental edge energies for CdSe QDs of three different radii are given in the third column in Table 2. Apart from the energy levels the absorption spectrum is also dependent of the electron density of states.

Let's now compare the theoretical and experimental data. In the Section 3 we calculated, that the excitonic radius for CdSe is 4.9 nm. Our QDs have radii from 1.2 nm to 4.3 nm and are therefore smaller than the excitonic radius. So we are in a strong confinement regime. However the calculated

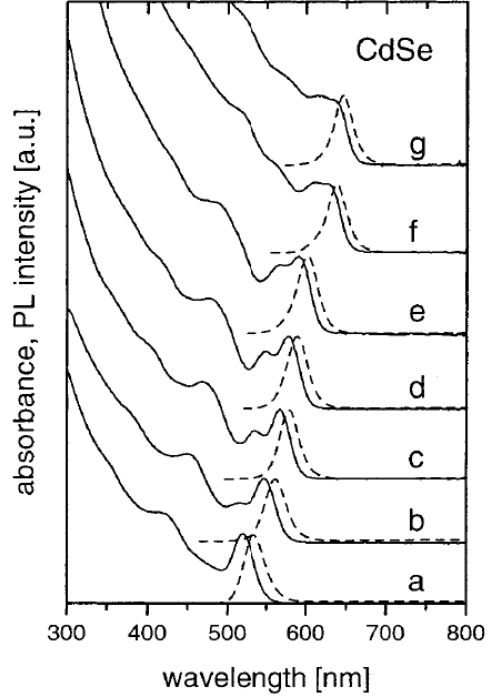


Figure 4: Absorption spectra (solid line) and emission spectra (dashed line) of CdSe QDs of different sizes. The diameters of the QDs from a) to g) are 1.2, 1.4 1.8, 2.2, 2.7, 3.1 and 4.3 nm.[3]

QD radius	Emission maximum	Edge energy	Strong Conf. Appr.	Weak Conf. Appr.
1.2 nm	2.34 eV	2.16 eV	4.43 eV	2.31 eV
2.2 nm	2.12 eV	1.98 eV	2.60 eV	1.97 eV
4.3 nm	1.91 eV	1.82 eV	2.05 eV	1.86 eV

Table 2: In the first two columns are the energies of the emission maxima and edge energies for three CdSe QDs of different sizes calculated from spectra in Figure 4. In the third and fourth column there are the calculated excitonic energies in strong and weak approximation.

energies in strong confinement regime do not match the experimental values of edge energy (3rd and 4nd column in Table 2). The matching should be better with smaller QDs where our approximation works best, but it is just the opposite. The explanation to this discrepancy most probably lies in our approximation of infinite quantum well whereas the real QDs have finite potential. With smaller QDs the energies are close to the work function of CdSe of ~ 5 eV [4]. Therefore the wavefunction is spilling out of the finite well thus reducing the energy. If we also compare the calculated results in weak confinement approximation and the measured edge energies (3rd and 5nd column in Table 2) we get very good agreement. However this is probably just a coincidence.

6 Conclusion

Because their properties QDs have can be used in a broad range of application such as more efficient solar cells, LEDs and diode lasers, for biological imaging and as all-optical switches in the future optical computers. QD are already commercially available at reasonable prices. Mass production will bring the prices much lower, so they will become a industrial material used in everyday products.

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