

A. Experiment #1, Quantum Dots– A Particle in a Box Study

Objectives:

1. Relate the wavelength of the maximum absorbance in the visible region of the electromagnetic spectrum to the size of CdSe quantum dot “boxes”.
2. Investigate how well the one-dimensional “particle-in-a-box” quantum mechanical model predicts the average diameter of the quantum dots.

Background:

In this experiment you will use UV-vis absorption and photoluminescence emission spectroscopy to evaluate the size-dependent electronic and optical properties of colloidal CdSe nanocrystals (“quantum dots”) in solution. From these studies you will determine quantum dot size and concentration and compare your results to prediction from a simple “particle in a box” quantum system.

Quantum mechanics captures the underlying physics of the microscopic world and therefore describes the behavior of quantum objects (electrons, atoms, molecules and crystallites in the nanometer size regime). Since the behavior of single or small numbers of quantum objects is in, most cases, very different from their cumulative ensemble behavior (macroscopic world), many results and predictions of quantum mechanics are difficult to relate to our everyday observations and appear strange. The so-called “particle in a box” system (e.g., a quantum particle with mass m in a potential box with length L) is an excellent example of quantum behavior. Not only does such a system have discrete energy levels, E_n , in terms of the quantum number n , but the spacing between these quantized energy levels ($E_{n+1} - E_n$) is a function of the size of the box (eqs. 1 and 2). The smaller the box, the larger then energy spacing and vice versa (a.k.a. “quantum confinement” or “quantum size effect”).

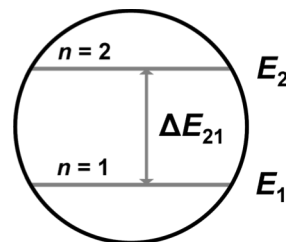


Figure 1. Schematic energy level presentation of an ideal particle in a box quantum system.

$$E_n = \frac{h^2 n^2}{8mL^2} \quad n = 1, 2, 3, \dots \quad h \text{ is the Planck constant} \quad (1)$$

$$\Delta E_{n+1 \leftarrow n} = E_{n+1} - E_n = \frac{h^2}{8L^2} \frac{1}{m} (2n+1) \quad n = 1, 2, 3, \dots \quad (2)$$

Semiconductor nanocrystals, so-called “quantum dots” are real-world examples of particle in a box systems. Quantum dots are spherical crystallites with diameters ranging from 1 to ~10 nm, consisting of hundreds to a few thousands of atoms. Due to their small size and defined shape, these crystallites act as the “box” confining a delocalized electron (the “particle”) within it. In this experiment you will investigate quantum confinement effects by studying the optical (absorption and emission) properties of CdSe quantum dots. Since these optical properties are the direct result of transitions between quantized energy levels, analysis of their wavelength positions will allow you to evaluate the spacing of these levels. Furthermore, conducting these studies with CdSe quantum dots having different diameters (i.e. varying “box” length), will enable you to determine the dependence of energy level spacing with “box” size. This means you will directly measure a “particle in a box” quantum phenomenon in a real system!

Compared to an *ideal* particle in a box model, the energy level situation in most *real* systems is more complicated. For example in CdSe quantum dots the lowest energy level ($n = 1$) is split into two sub-levels (see Fig. 2). This splitting is due to spin-orbit coupling interactions and the energy difference is called spin-orbit coupling energy ΔE_{SO} . As indicated in Fig. 2, we can evaluate the spin-orbit coupling energy by optical absorption and photoluminescence spectroscopy. Here, the difference in the absorption and emissions energies (Ab and Em respectively) gives us directly the spin-orbit coupling energy. Knowing ΔE_{SO}

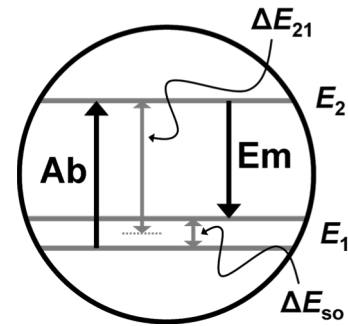


Figure 2. Schematic energy level presentation of a CdSe quantum dot (a real particle in a box quantum system).

enables you to experimentally determine the “mean” transition energy, ΔE_{21} , corresponding to a transition between the two lowest quantum dot energy levels ($n = 1$ and $n = 2$). A further modification from an ideal particle in a box system is that the position and spacing of quantized energy levels have to be modified for quantum dots. A true quantitative description has to take into account that, in real systems, an electron created by optical excitation is not a *free* delocalized electron as in an ideal particle in a box model. Instead it has to be considered together with the positively charged “hole” that it left behind in the lower energy level. This *bound* (or combined) electron-hole state is also called an “exciton”. Therefore the mass of the “particle” in eq. 1 has to be replaced by an *effective* mass for both electron and hole ($m_{e,eff}$ and $m_{h,eff}$ respectively) in their bound state in which eq. 1 becomes eq. 3.

$$E_n = \frac{h^2 n^2}{8L^2} \left(\frac{1}{m_{e,eff}} + \frac{1}{m_{h,eff}} \right) \quad n = 1, 2, 3, \dots \quad (3)$$

For our further discussion we will utilize the fact that the effective hole mass is in general much larger than the effective electron mass. The second $1/\text{mass}$ term in eq. 3 is therefore much smaller than the first one, which allows us to simplify eq. 3 into an approximated form (eq. 4).

$$E_n = \frac{h^2 n^2}{8L^2} \frac{1}{m_{e,eff}} \quad n = 1, 2, 3, \dots \quad (4)$$

Using eq. 4, an expression for the energy spacing between adjacent energy levels of a quantum dot can be derived which is eq. 5 (analogous to eq. 2).

$$\Delta E_{n+1 \leftarrow n} = E_{n+1} - E_n = \frac{h^2}{8L^2} \frac{1}{m_{e,eff}} (2n+1) \quad n = 1, 2, 3, \dots \quad (5)$$

Unfortunately effective electron masses in quantum confined semiconductors can differ significantly from the free electron mass. Calculating these effective masses is rather complicated and requires sophisticated quantum chemical calculations. However for certain quantum dots (such as the CdSe nanocrystal quantum dots used in this experiment) we can use a semi-empirical approach that will allow us to determine quantum dot sizes directly from optical absorption transitions without prior knowledge of the effective electron mass. This semi-empirical correlation directly relates the wavelength-position and strength of the first optical absorption transitions (i.e., the peak occurring at the highest wavelength position) of quantum dots to their size and concentration respectively.

In more detail, by knowing the wavelength position of the first optical absorption peak of a given quantum dot sample, which corresponds to the absorption transition “Ab” in Fig. 2, the size of these quantum dots can be calculated by eq. 6.

$$D = (1.6122 \times 10^{-9} \text{ nm}^{-3}) \cdot \lambda^4 - (2.6575 \times 10^{-6} \text{ nm}^{-2}) \cdot \lambda^3 + (1.6242 \times 10^{-3} \text{ nm}^{-1}) \cdot \lambda^2 - (0.4277) \cdot \lambda + (41.57 \text{ nm}) \quad (6)$$

In this equation, D (in nm) is the diameter of a given quantum dot and λ (in nm) is the wavelength position of the first optical absorption peak of the corresponding sample. Knowing the quantum dot diameter, it is then possible to determine the molar extinction coefficient, ε , using experimentally obtained data. For CdSe, the relevant expression of ε (in $\text{L mol}^{-1} \text{ cm}^{-1}$) as a function of the quantum dot diameter (in nm) is eq. 7.

$$\varepsilon = (5857 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{nm}^{-2.65}) \cdot D^{2.65} \quad (7)$$

The calculated molar extinction coefficient can then be used to determine the quantum dot concentration in solution by the Beer-Lambert law (eq. 8).

$$A = \varepsilon \cdot C \cdot I \quad (8)$$

in which A is the absolute absorbance at the peak position of the first absorption peak of the quantum dot absorption spectrum, C is the molar concentration (in mol/L) of the quantum dot solution, and I is the path length (in cm) of the radiation beam used for recording the absorption spectrum (for the cuvettes used in this lab, I is fixed at 1 cm).

Procedure:

1. There is only one good cuvette available to make these measurements so care has to be taken not to break the cuvette and to *thoroughly* clean it in between measurements different quantum dots samples.
2. Using a glass pipette and bulb, transfer about 2 mL (or half of the cuvette volume) of toluene into the cuvette.
3. On the absorption instrument, measure the solvent background.
 - a. Turn on the PC (password is 3000hanover)
 - b. Turn on Agilent spectrometer
 - c. Open software: UV-Vis
 - d. Task→Spectrum/Peaks→Setup→Abs
 - e. Set the display range to 350 nm – 850 nm
 - f. Put in the sample and hit “blank”
4. Empty the toluene into a waste container and transfer ~2 mL of one of the quantum dot solutions into the cuvette and measure the absorbance.
 - a. Put in the cuvette and hit “sample”
 - b. Click on the spectrum to select it and then export the data to Excel by clicking File→Export→CSV.
5. Measure the fluorescence spectra of the quantum dots
 - a. Turn on the instrument in the order indicated by the hand written numbers followed by the PC. No password is required to access the PC.
 - b. Start the data collection program (password is “pti”)
 - c. Navigate to Acquire→New Acquisition→Emission Scan. Excite the QDs at 300 nm, measure the emission from 350 nm – 850 nm, and use a 1 nm step size.
 - d. Manually adjust the source and spectrometer slit widths to 1.0 mm for the source and 0.15 mm for the spectrometer. The power on the source should be halfway between min and max.
 - e. When the acquisition is complete, take note of the emission maximum, display the grid view for the data then copy and paste the data into Excel for later processing/plotting.

6. Measure the excitation spectrum of the quantum dots. Details in the absorption spectra are partially washed out by the size distribution of the quantum dots. By measuring how the emission intensity, over a narrow wavelength range, changes with excitation wavelength we can probe a single size of QD in solution.
 - a. On the same instrument start a new acquisition and select excitation scan.
 - b. Manually adjust the slit widths to 0.10 mm on both the source and spectrometer.
 - c. Turn the power on the source up to the maximum.
 - d. Excite the QDs from 350 nm up to the emission maximum. Measure the emission 5 nm past the maximum (i.e. if the emission max was 543 nm then measure at 548 nm).
 - e. When the acquisition is complete, display the grid view and copy and paste the data into Excel.

Safety Notes:

1. Handle all quantum dot samples with gloves and do not bring them into direct contact with any parts of your body. CdSe as well as most of the solvents used are toxic compounds!
2. Turn off the power supply of the photoluminescence excitation source before changing the lamps.
3. Do not look directly into the photoluminescence excitation light.
4. Do not direct the end (output) of any optical fiber into your eyes.

Report:

1. For each absorption spectrum, determine the wavelength position (in nm) of the first absorption peak maximum. Convert all of the peak positions from nm to Hz (s^{-1}). This is a more convenient unit for spectroscopy since quantities in Hz are proportional to energy but quantities in wavelengths are not.
2. Using the particle in a box equation, estimate the size of the quantum dots using the free electron mass and the energy corresponding to your 1st absorption peak.
3. For each of the quantum dot samples use the wavelength position of the first absorption peak (in nm) to calculate the corresponding quantum dot size (diameter), D .
4. Knowing the quantum dot diameter, compute the molar extinction coefficient and molar quantum dot concentration for each sample.

5. Determine the wavelength position (in nm) of the photoluminescence emission peak maximum for each of the quantum dot samples. Convert all of the peak positions from nm to Hz.
6. For each quantum dot sample, use the energy values of the first absorption peak and photoluminescence emission peak positions to calculate the energy of the spin-orbit coupling energy, ΔE_{SO} .
7. Compute the “mean” transition energy, ΔE_{21} . Here, the position of the lower-lying energy level, E_1 , is taken as the halfway point between the spin-orbit split energies.
8. Plot the calculated values of ΔE_{21} vs. $1/L^2$ ($\equiv 1/D^2$) for the two samples and fit the data points to a line. Determine the slope of the line.
9. Use the slope of the fitted line and eq. 5 to determine the effective electron mass, $m_{e,eff}$, of quantum confined CdSe.
10. Combine all quantities that you determined for the two quantum dot samples (including error estimates!) into a single table. Plot the Abs spectrum and Excitation spectrum on a graph making sure it is normalized so that the 1st excitation peak is equal to 1.
11. In the discussion section of your paper you should compare your results (calculated quantum dot sizes vs. absorption and emission peak position) with values from the literature or authoritative sources. Also try to find values for the effective electron mass for CdSe quantum dots and compare it to the value you obtained. Comment on various approximations and possible sources of errors used in your studies and how they may have affected your final results. In addition look up values for the effective hole mass of semiconductor quantum dots (CdSe, CdS, ...) and estimate the magnitude of “inaccuracy” that we induced by ignoring the $1/\text{mass}$ term for the hole. Give a short discussion on the differences of *ideal* and *real* particle in a box quantum systems. Finally, comment on the difference between the excitation spectrum and absorption measurement. Which method provides more detailed information? Why? Speculate on the interpretation of the additional peaks in the excitation spectrum.