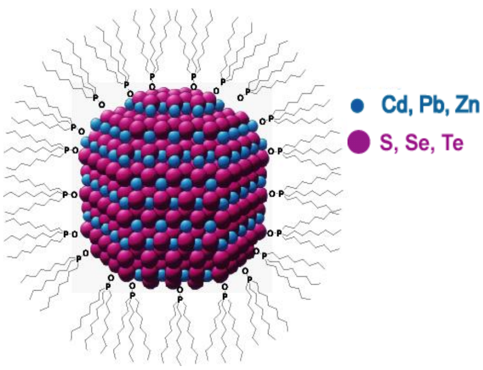
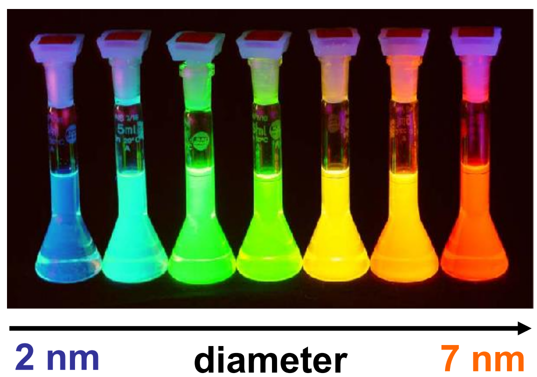
Particle in a Box applied to Quantum Dots

Useful constants and conversions:
1 eV = $1.60*10^{-19}$ J
h = $6.626*10^{-34}$ Js
c = $3.00*10^{8}$ ms^{-1}

Quantum dots are small particles of semiconductors such as CdSe, CdS, etc. These particles usually have diameters of < 10 nm, and each particle has on the order of 1,000-10,000 atoms. You can think of them as giant spherical molecules, such as the one in the picture on the left. The exciting thing about quantum dots is that fluorescence emission wavelength depends on the particle size, as shown on the figure on the right for CdSe. This is called the *quantum size effect*. The physical model used to predict the emission and absorption wavelength is essentially a *particle in a spherical box* model. The goal of this problem-solving session is to investigate how the particle in a spherical box model is applied to quantum dots and examine the behavior of wave functions and energies.





When a quantum dot absorbs a photon, an electron is excited into a specific orbital and it leaves behind a positive charge, called a *hole*. When the semiconductor particle is "large", the electron and the hole have energies defined by the semiconductor composition, and the difference in the energies is called the *band gap* (E_g). For CdSe, E_g is 1.75 eV. However, when the particle is "small", both the electron and the hole are confined in a spherical box, and their energies increase compared to energies in a "large" particle. This increase is called the *confinement energy*.

The potential inside the quantum dot is not zero because there are nuclei and electrons exerting electrostatic forces on each other. To account for the non-zero potential, we introduce the concept of *effective mass*, expressed in units of mass of an electron (m0). The electron and the hole often have different effective masses, abbreviated as m_e and m_h respectively. The concept of effective mass is extremely useful because it allows us to use the simple equations derived when the potential is zero inside the box by only changing the mass of the particle.

Use the Mathematica file called "Quantum Dots" to answer the questions below (read the instructions on the top of the notebook first). The TISE for the particle in a sphere has been solved (wavefunctions and energies determined) already, and your job is to investigate how those wavefunctions and energies behave as you change parameters. To simplify further, you will only consider the lowest energy (equivalent of n=1) wavefunctions for the electron and the hole. Due to the spherical symmetry of the particle, it is convenient to plot the wavefunctions in the radial direction.

1. Infinite potential outside the box

First, let's assume the potential outside the quantum dot is infinite, just like we have done for the other PIB problems. The confinement energy is given as:

$$E_{e,h} = \frac{\pi^2\hbar^2}{2m_{e,h}r_{QD}^{\ 2}}$$

Effective masses for the electron and the hole for CdSe are already in the Mathematica notebook. Note that confinement energies for electron and hole are different because they have different masses.

(a) What is the particle diameter at which the confinement effects become important, meaning that total confinement energy (E_e + E_h) is on the order of 10% of the band gap energy (E_g)? You can figure this out by varying the radius of the quantum dot (r_{QD}) in the Mathematica notebook and examining the resulting confinement energies.

(b) What is the value of the wavefunction at the surface of the dot ($r = r_{QD}$)? Does this make sense and why?

2. Finite potential outside the box

As you can see in the figure above, quantum dots usually have organic molecules on their surfaces to make them soluble in organic solvents. We can ask whether the organic molecules present an infinite potential barrier, or whether a finite one is more appropriate. When finite barrier is introduced, the math becomes a lot more cumbersome, and is hidden in the Mathematica file. In Part 2 of the notebook, you can plot electron and hole wavefunctions and calculate confinement energies for a finite barrier case, but you have to enter the value of the potential in the "constants and parameters" section.

(a) What are the values of confinement energies for the essentially infinite (V=1000 eV) potential outside the box with r_{QD} = 2.5 nm? How do these values compare to the ones obtained using an infinite potential?

(b) Repeat (a), but use a potential outside the sphere that is more representative of the organic molecules on the surface (V=3 eV).

(c) Take a look at the electron and hole wave functions with the outside potential of 3 eV. How do the wave functions behave near $r=r_{QD}$? What do you think is going on?

(d) Compare the electron and hole wave functions near $r=r_{QD}$. Describe any difference you notice and propose/guess a reason for the difference. Explain your reasoning.

3. Comparison of the particle in a spherical box model with experimental data

The lowest energy of photons emitted by quantum dots is a sum of the E_g of a "large" semiconductor particle (1.75 eV for CdSe) and the confinement energies of the electron and the hole.

$$E_{emission}^{(QD)} = E_g^{(large)} + E_e + E_h$$

(a) Using this equation and your results from parts 1 and 2, calculate the emission wavelength of CdSe quantum dots with radius of 2.5 nm to complete the table below.

	Infinite potential outside (Part 1)	3 eV potential outside (Part 2)
Calculated emission wavelength (nm)		

(b) An emission spectrum of CdSe quantum dots with radius of 2.5 nm is shown below. The emission peak is centered at 550 nm. Compare your predictions with this experimental value and comment on which model (infinite potential outside or finite potential outside) is more appropriate and whether the difference is sufficiently large to notice.