Nanophotonics

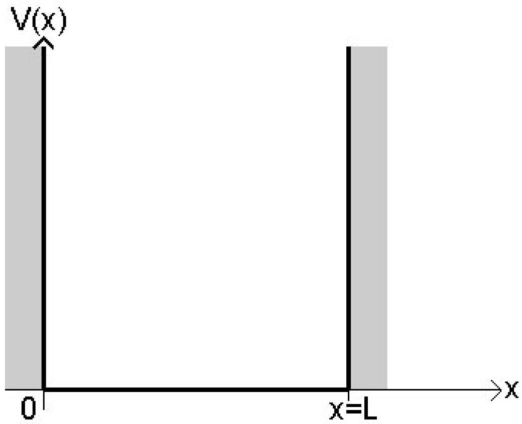
Class 5 - Rare earth ions and quantum dots

The simplest way to understand electronic quantum confinement in nanometer scale inorganic crystals (quantum dots) lies in treating quantum mechanically the motion of a particle in an infinite potential well, also known as particle in a box (PIB) model. In this assignment, we are going to solve the 1-dimensional version of the PIB model before generalizing it for the 3D confinement case of quantum dots (QD). In the second part, we will briefly review the solution of the PIB model in a spherical potential before applying it to electrons and holes in QDs to understand exciton generation in low-dimensional semiconductors.

Assignment 1: Particle in a box model

I: 1-dimensional scenario (quantum well)

In the following problem, we consider the motion of a particle of mass *m*, interacting with a potential V(x) where V=0 between x=0 and x=L and is infinite elsewhere (see figure below).



a) Without any mathematical treatment, what would be the motion of such a particle with an initial speed v_0, studied using classical mechanics?

Since the applied potential is time-independent, the time and space variables can be separated and the time-independent Schrödinger equation can be applied. Furthermore, this is a 1D problem along the x axis:

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

where E is the energy of the particle.

b) Express the possible eigenfunctions $\varphi(x)$ for all positions for the given potential function. Show that the possible eigenenergies are $E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$. Justify that *n* is positive and non-zero.

c) Make a sketch showing the $\varphi_n(x)$ eigenfunctions for *n*=1,2,3,4 of a particle in a 1D infinite well and for $0<x<L$. For clarity, you may shift each function vertically so they do not overlap with one another. What classical mechanics problem exhibits similar modes and spatial profiles? Conclude.

d) What is the probability of finding a particle of energy E_n between x and $x+dx$? What happens when $\varphi(x)=0$?

II: Generalization to 3D quantum confinement

We now consider a (L_x, L_y, L_z) box exhibiting a similar infinite potential well. In practice, this corresponds to quantum dots: nanometer-sized crystal of a low bandgap semiconductor surrounded by an isolating material or very high bandgap semiconductor.

a) Without any detailed mathematical treatment, explain why the eigenenergies are now expressed as: $E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$?

b) Considering an electron as the particle in an infinite potential, explain briefly why Quantum Dots are often considered artificial atoms.

Assignment 2: Spherical Quantum Dots

In semiconductors, absorbing a photon of energy higher than the Bandgap gives rise to the creation of an electron-hole pair, also called exciton. The excited electron reaches an energy level of the conduction band while the hole is in the valence band. If the interaction between the electron and the hole is neglected then each particle can be treated using the PIB model. However, the shape of QDs studied experimentally is often spherical and not cubic. Solving Schrödinger's equation for the PIB model in spherical coordinates is mathematically more involved than in Cartesian coordinates. The eigenfunctions are indeed expressed in terms of Bessel functions and spherical harmonics. These functions are similar to the orbitals of a spherical hydrogen atom. The eigenenergies of a particle in a spherical infinite well are given as:

$$E_{nJ} = \frac{\hbar^2}{2m}\frac{\chi_{nJ}^2}{R^2} \qquad (2)$$

where R is the radius of the QD, m the mass of the particle and χ_{nJ} is the n^{th} zero of the spherical Bessel function of order J. For instance $\chi_{10}=\pi$, $\chi_{11}=4.493$, $\chi_{12}=5.763$, $\chi_{20}=2\pi$ and χ_{nJ} increases when n and J increase.

I: Creation of an electron-hole excited state

a) The discrete levels observed in quantum dots enable them to absorb specific wavelengths in the near UV-visible part of the spectrum. Using equation (2) for the electron and the hole, express the lowest energy ΔE needed to create an electron-hole pair as a function of $E_{bandgap}$, R and μ, the reduced effective mass of the electron-hole pair ($1/\mu=1/m_e+1/m_H$).

If Coulomb interactions are taken into account between the electron and the hole, the PIB model cannot be applied because the Coulomb potential has to be included in the system Hamiltonian. Thus, no separation of variables is allowed between the spatial positions of the hole and the electron. The electron and hole are treated together as an exciton.

b) We suppose that the Coulomb interaction can be treated as a small perturbation of the exciton Hamiltonian. Give this perturbation. Without any mathematical treatment, explain briefly if the energy needed to create the electron-hole pair (ΔE) will increase or decrease.

c) What happens if the energy needed to overcome the Coulomb interaction is, on the contrary, much larger than energy term due to quantum confinement? Knowing that the Coulomb potential for an electron-hole pair scales with the inverse of the "exciton Bohr radius", R_{exc}. Give a qualitative explanation of when you expect quantum confinement of an exciton in a semiconductor nanocrystal to be feasible.

II: Size-dependent photoluminescence of QDs

The major technological interest of QDs is their high luminescence quantum yield, narrow luminescence emission and tunable luminescence wavelength with respect to their size (R). The energy of the emitted photons is lower than the absorbed photons because energy is lost in electron-phonon interaction. However this energy difference does not change significantly with the size of the QDs.

a) Using the results obtained in the previous paragraph, explain why the luminescence of large quantum dots is red-shifted with respect to the luminescence of small quantum dots.

b) We put a II-VI QD with a diameter of 2.6 nm embedded in PMMA on top of a silver layer (mirror) and we measure the number of photons per unit of time as a function of the distance (*d*) between the QD and the silver. As expected, we find that the emission rate changes due to the LDOS as we move the QD further apart from the silver. In the range of distances we measure, we find two maxima, one at 56 nm and one at 190 nm. What could be the material of the QD? Explain clearly how you came to this answer, and quote the sources you used.

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