Quantum Nature of the Nanoworld

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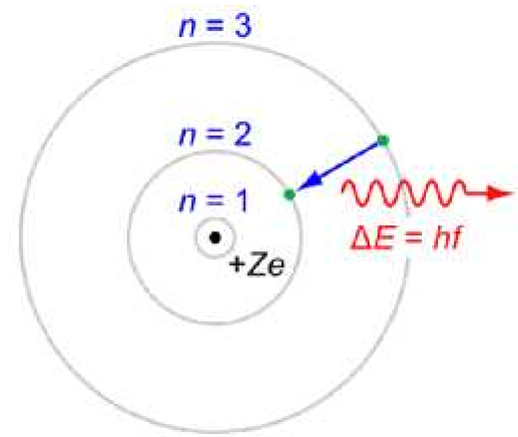
1- Bohr’s Model of the Nuclear Atom



$$E = -kZe^2/2r$$

- Where Z is the atomic number, e is the electron charge, e is the electron charge and r is the radius of the orbit

- This classical relation predicts collapse (of atoms, of all matter): for small r the energy is increasingly favorable (negative). So the classical electron will spiral in toward r = 0, giving off energy in the form of electromagnetic radiation.

All chemical matter is unstable to collapse in this firm prediction of classical physics.

All of the spectroscopic observations of anomalous discrete light emissions and light absorptions of the one-electron atom were nicely predicted by the simple quantum condition

$$h\nu = hc/\lambda = E_o(1/n_1^2 - 1/n_2^2). \quad (4.4)$$

- Where:

$$E_o = mk^2e^4/2\hbar^2 = 13.6 \text{ eV}.$$

The energy of the light is exactly the difference of the energy of two electron states, n_1, n_2 in the atom. This was a breakthrough in the understanding of atoms, and stimulated work toward a more complete theory of nanophysics which was provided by Schrodinger in 1926 [2].

The Bohr model, which does not incorporate the basic wavelike nature of microscopic matter, fails to precisely predict some aspects of the motion and location of electrons. (It is found that the idea of an electron orbit, in the planetary sense, is wrong, in nanophysics.)

2- Particle-wave Nature of Light and Matter, DeBroglie Formulas λ= h/p, E = hν

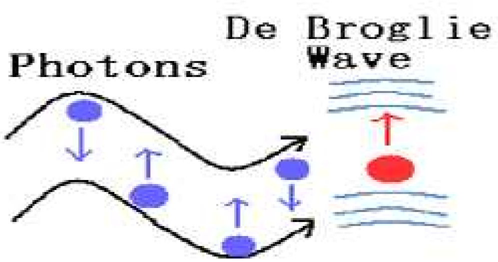
- The first prediction of a wave nature of matter was given by Louis DeBroglie. This young physics student postulated that since light, historically considered to be wavelike, was established to have a particle nature, it might be that matter, considered to be made of particles, might have a wave nature. The appropriate wavelength for matter, DeBroglie suggested, is

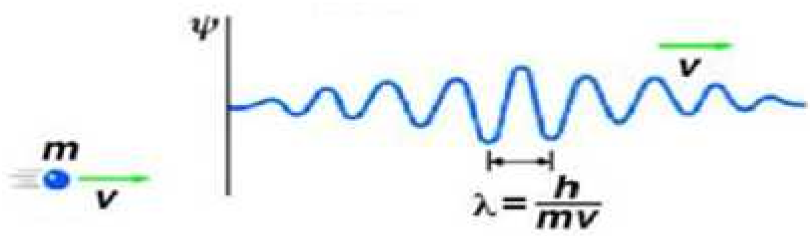
$$\lambda = h/p, \tag{4.6}$$

where h is Planck's constant, and $p = mv$ is the momentum. For light $p = E/c$, so the relation $\lambda = h/p$ can be read as $\lambda = hc/E = c/\nu$. Filling out his vision of the symmetry between light and matter, DeBroglie also said that the frequency ν associated with matter is given by the same relation,

$$E = h\nu, \tag{4.7}$$

as had been established for light by Planck.

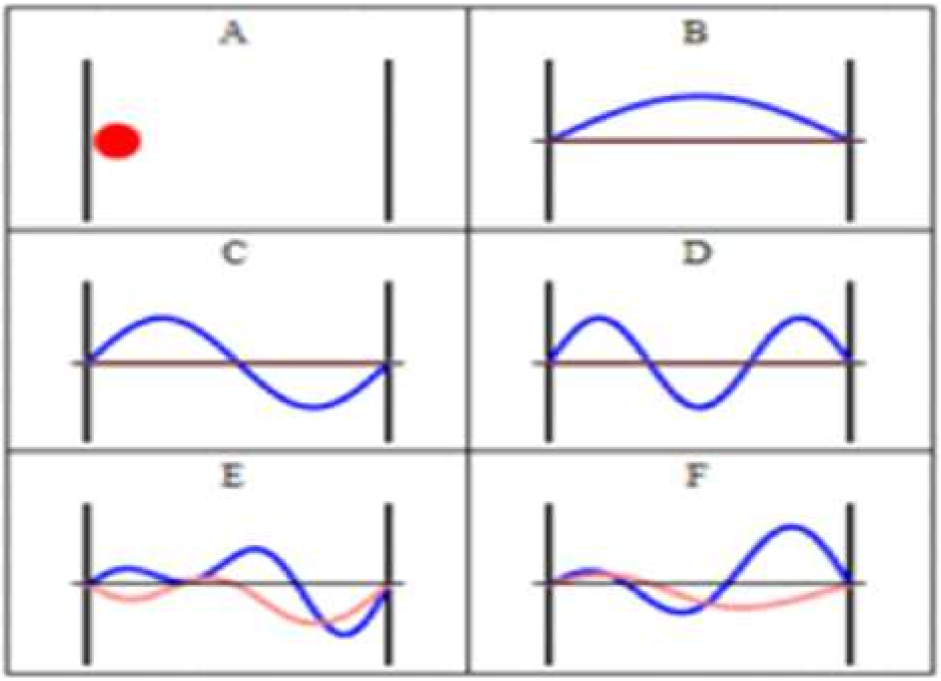




3- Trapped Particle in a box Three Dimensions (3 D)

$$E_n = [h^2/8mL^2](n_x^2 + n_y^2 + n_z^2). \quad (4.67)$$

These simple results can be easily adapted to two-dimensional boxes and also to boxes of unequal dimensions L_x L_y L_z.



- Some trajectories of a particle in a box according to

A) Newton's laws of classical mechanics

B-F) Schrödinger equation quantum mechanics.

In (B-F), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B,C,D) are energy eigenstates, but (E,F) are not.

4 - Trapped Particle in a Two-dimensional Box (2D)

- A scanning tunneling microscope image, shown in Figure 4.5, reveals some aspects of the trapping of electrons in a 2D rectangular potential well. The well in this case is generated by the rectangular array of iron atoms (silver-colored dots in this image), which reflect electrons

- The energy scale can be suggested as,

$$E_n = [h^2/8mL^2](n_x^2 + n_y^2)$$

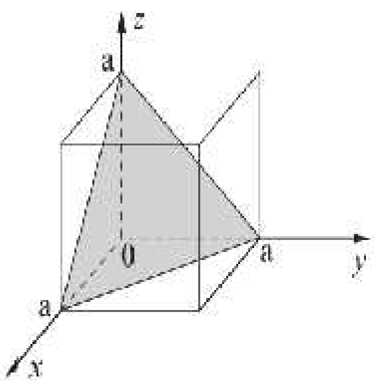


Figure 4.6 Geometry of a (111) plane, shown shaded. Copper is a face-centered cubic crystal, but only if the surface is cut to consist of the indicated (111) plane will the 2D electron effects be present.

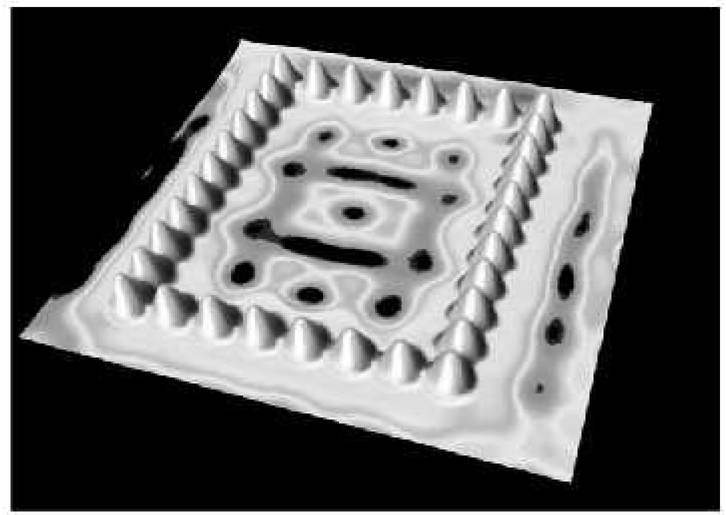


Figure 4.5 Electrons trapped in a small two-dimensional box on the (111) surface of copper. A rectangular array of iron atoms serves as a barrier, reflecting electron waves [6].

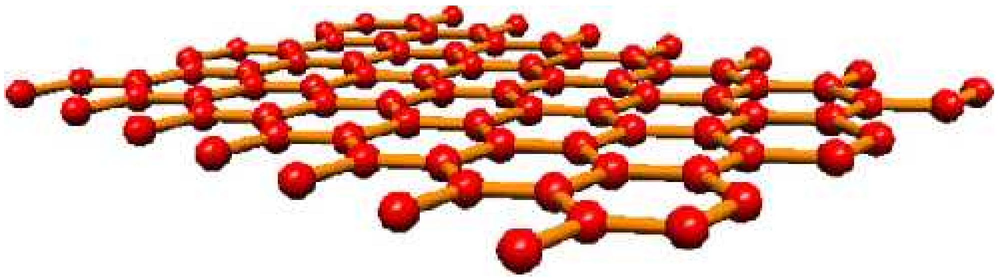
4-1 2D Bands (Quantum wells)

- A second physical situation that often arises in modern semiconductor devices is a carrier confined in one dimension, say z, to a thickness d and free in two dimensions, say x and y. ***This is sometimes called a quantum well.***

- The energy of the carrier in the n^{th} band is

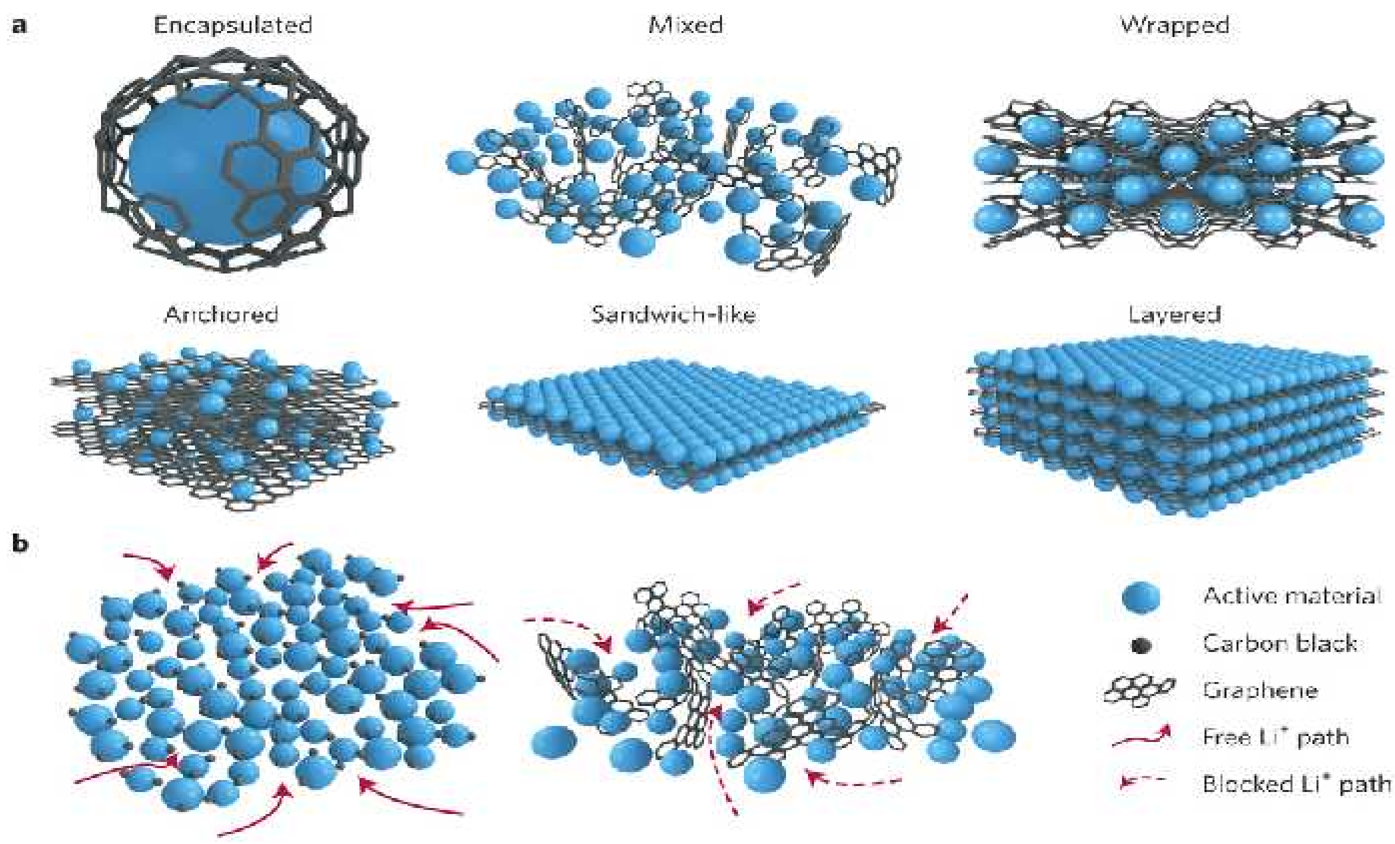
$$E_n = (h^2/8md^2)\, n_z^{\,2} + \hbar^2 k_x^{\,2}/2m + \hbar^2 k_y^{\,2}/2m. \qquad (4.70)$$

- In this situation, the quantum number n_z is called the sub-band index and for n = 1 the carrier is in the first sub-band. We discuss later how a basic change in the electron's motion in a semiconductor band is conveniently described with the introduction of an effective mass m*.



Monolayer graphene structure with one-atom thickness.

4.2- The role of graphene for electrochemical energy storage



5- The Energy Scale for Trapped Particle in one Dimension (1 D)

$$k = (2mE/\hbar^2)^{1/2} = 2\pi/\lambda. \quad (4.40)$$

The infinite potential walls at $x = 0$ and $x = L$ require $\psi(0) = \psi(L) = 0$, which means that $B = 0$. Again, the boundary condition $\psi(L) = 0 = A\sin kL$ means that

$$kL = n\pi, \quad \text{with } n = 1,2\ldots \quad (4.41)$$

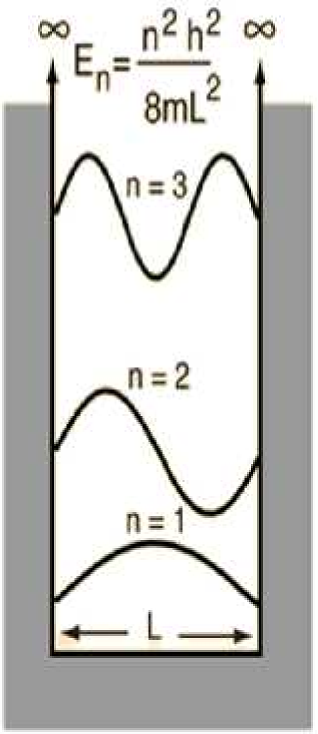
This, in turn, gives

$$E_n = \hbar^2 (n\pi/L)^2/2m = n^2h^2/8mL^2, \quad n = 1,2,3,\ldots \quad (4.42)$$

The condition for allowed values of $k = n\pi/L$ is equivalent to

$$L = n\lambda/2, \quad (4.44)$$

the same condition that applies to waves on a violin string.



a_0 = Bohr radius = 0.0529 nm

5.1- Quantum Wires (1D)

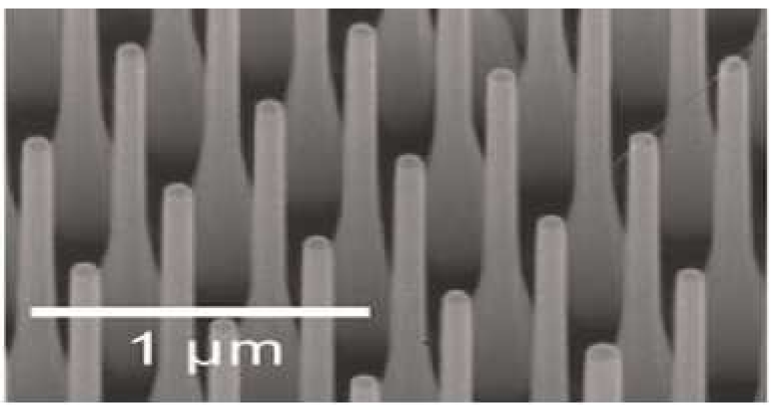
- The term Quantum Wire describes a carrier **confined in two dimensions, say z and y, to a small dimension d** (wire cross section d^2) and **free to move along the length of the wire, x**.

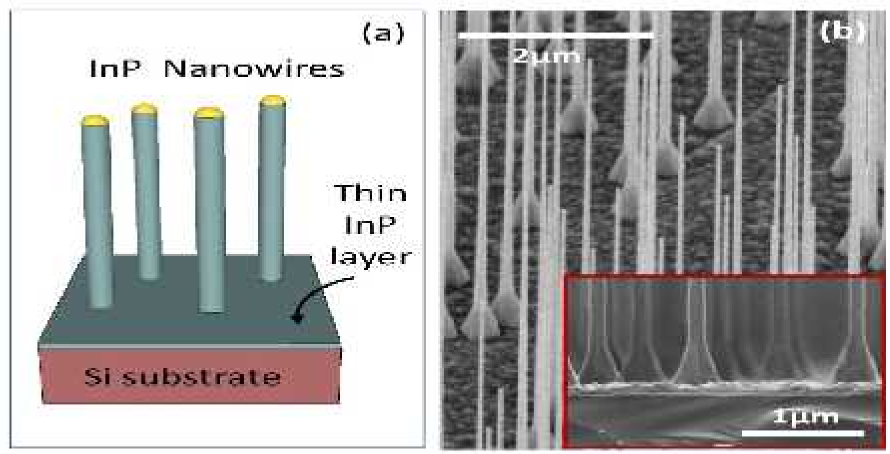
- (Qualitatively this situation resembles the situation of a carrier moving along a **carbon nanotube**, or **silicon nanowire**, although the details of the bound state wavefunctions are different.)

- In the case of a quantum wire of square cross section, the energy is

$$E_n = (h^2/8md^2)\,(n_y{}^2 + n_z{}^2) + \hbar^2 k_x{}^2/2m. \qquad (4.72)$$

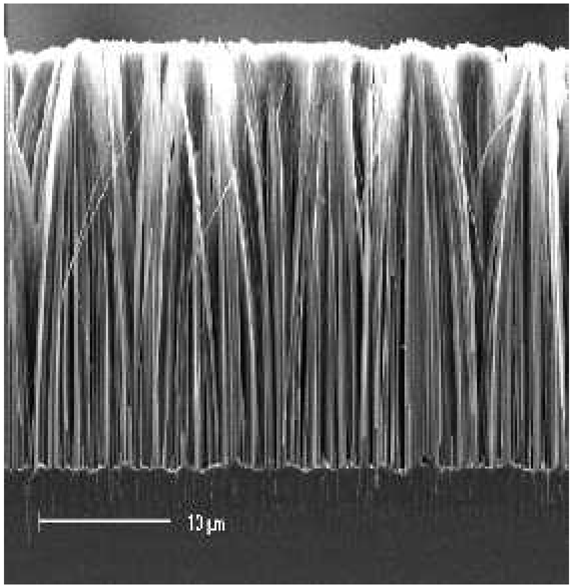
- It is possible to grow nanowires of a variety of semiconductors by a laser assisted catalytic process, and an example of nanowires of indium phosphide.



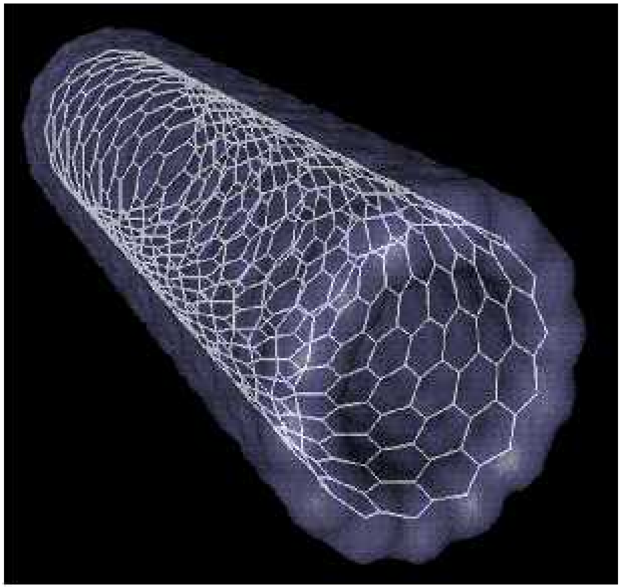


5.2- Basic Applications

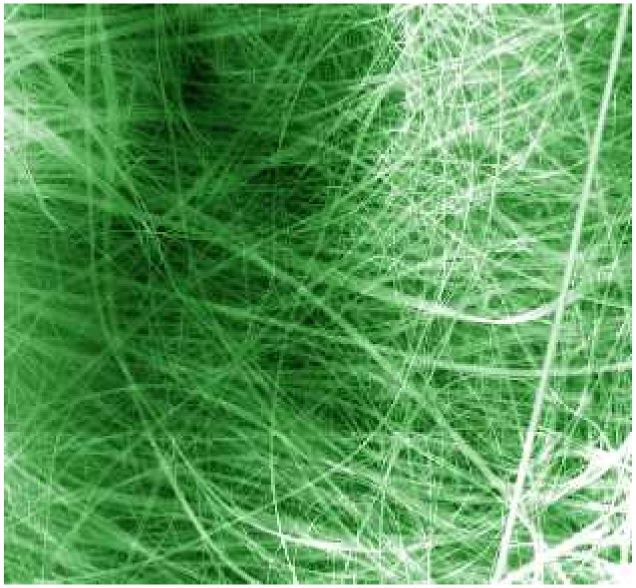
- Since these wires have one long dimension, **they do not behave like quantum dots, and the light energy is not shifted from the bandgap energy.** It is found that the nanowires can be doped to produce electrical conductivity of N- and P-types, and they can be used to make electron devices.



Silicon Nanowires



Carbon Nanotubes



vanadium oxide and lead

6- Quantum Dots (0 D)

- The rules of nanophysics that have been developed so far are also applicable to holes in semiconductors. To create an electron-hole pair in a semiconductor requires an energy at least equal to the energy bandgap, E_g, of the semiconductor.

- This application to semiconductor quantum dots requires L in the range of 3–5 nm, the mass m must be **interpreted as an effective mass m*, which may be as small as 0.1 m_e**. The electron and hole particles are generated by light of energy

$$hc/\lambda = E_{n,\text{electron}} + E_{n,\text{hole}} + E_g. \quad (4.68)$$

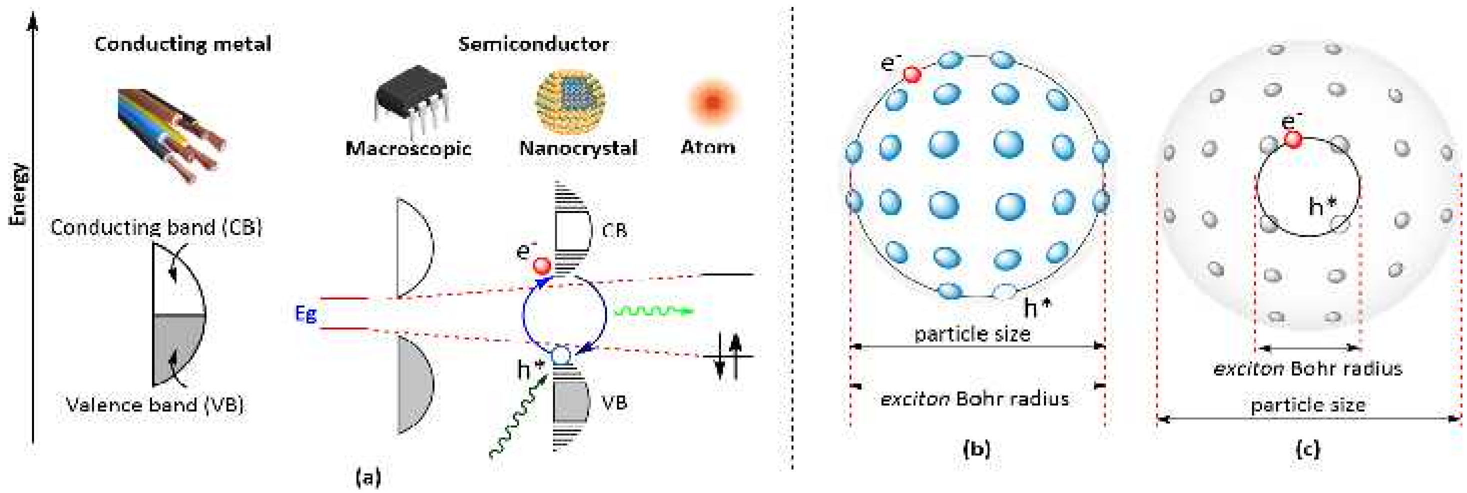
- Here the first two terms depend strongly on particle size L, as L^{-2}, which allows the color of the light to be adjusted by adjusting the particle size.

- The bandgap energy, E_g is the minimum energy to create an electron and a hole in a pure semiconductor.

$$E_g(eV)=1240/\lambda\ (nm)$$

- The electron and hole generated by light in a bulk semiconductor may form a bound state along the lines of the Bohr model, described above, **called an exciton.**

- However, as the size of the sample is reduced, the Bohr orbit becomes inappropriate and the states of the particle in the 3D trap, as described here, provide a correct description of the behavior of quantum dots.



Energy levels in macroscopic, nanocrystal and atomic semiconducting materials (a), and related dimensions of exciton Bohr radius and particle size (b, c).

What are Quantum Dots?

- Quantum dots are semi-conductors that are on the nanometer scale.
- Obey quantum mechanical principle of quantum confinement.
- Exhibit energy band gap that determines required wavelength of radiation absorption and emission spectra.
- Requisite absorption and resultant emission wavelengths dependent on dot size.

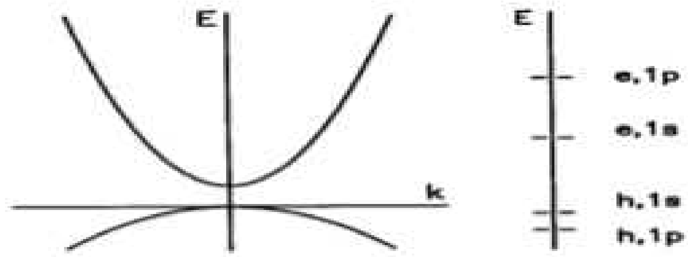
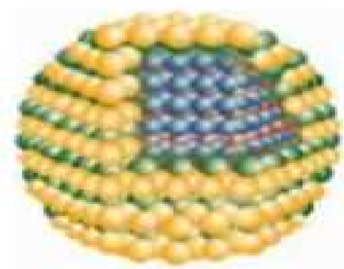
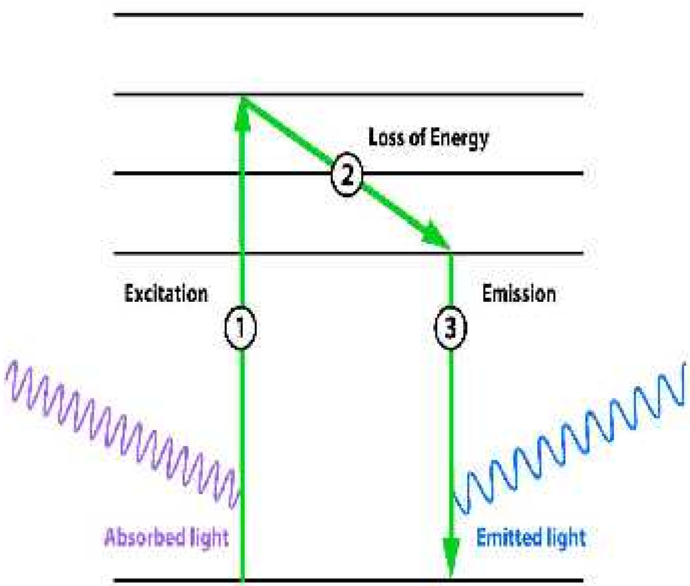
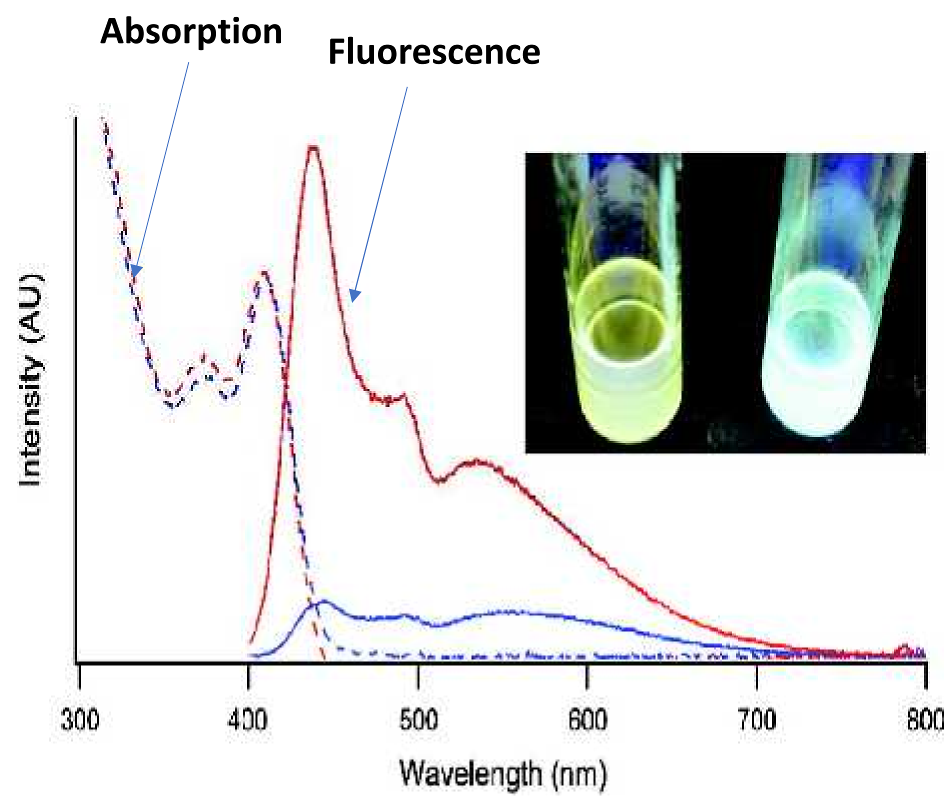


Figure: Schematic plot of the single particle energy band gap. The upper parabolic band is the conduction band, the lower the valence.



- Nanocrystals
- 2-10 nm diameter
- semiconductors

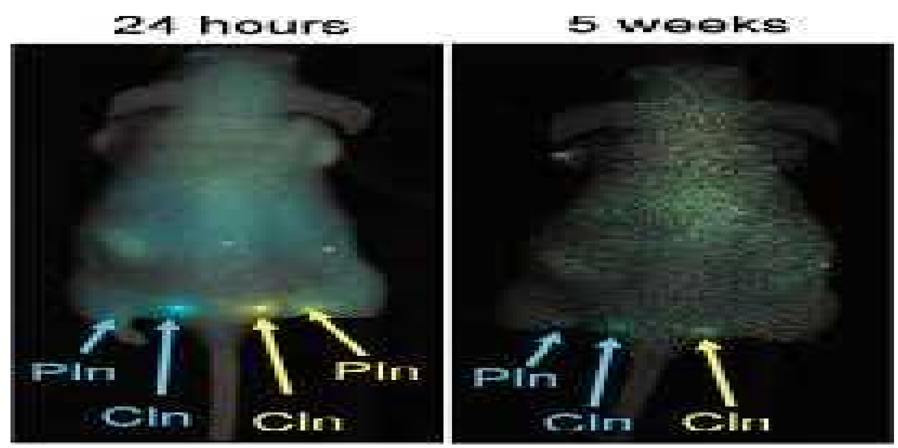




Absorption (dashed) and fluorescence (solid) of CdSe QDs

- The Bohr model is also useful in analyzing the optical spectra of semiconductors exposed to radiation, having energy $E = hc/\lambda > E_g$ which produces electron–hole pairs. (E_g is the symbol for the "energy gap" of a semiconductor, which is typically about 1 eV.)

- A relevant topic in nanophysics is the alteration, from the exciton spectrum, of the fluorescent light emitted by a semiconductor particle as its size, L, is reduced. It is found that the correct light emission wavelengths for small sample sizes L, are Quantum Nature of the Nanoworld obtained from **<u>the energies of electrons and holes contained in three-dimensional potentials</u>**, using the Schrodinger equation. This understanding is the basis for the behavior of **<u>"quantum dots",</u>** marketed as fluorescent markers in biological experiments, as will be described below.

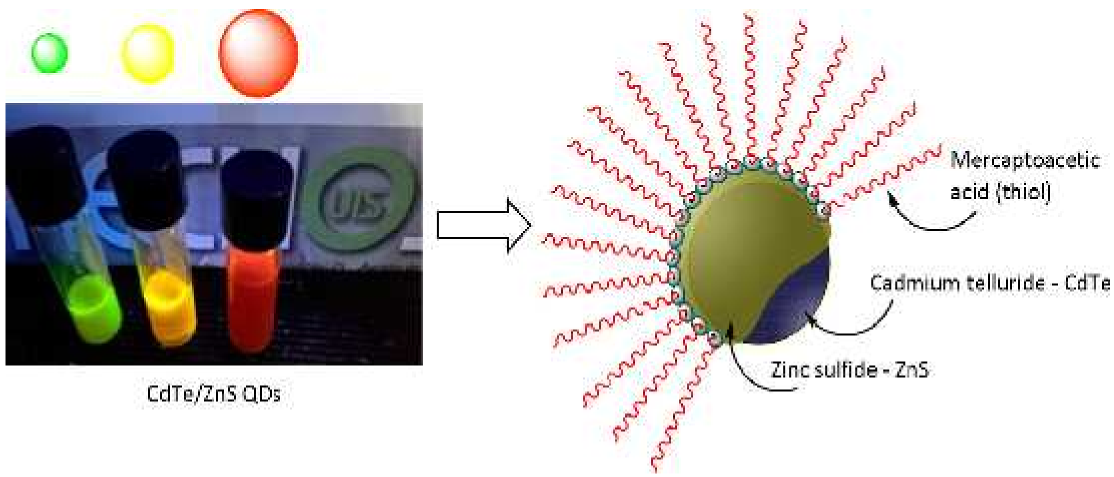


<u>Fluorescent QDs markers</u>

General Features of QDs

- A discrete level refers to finite separation between energy levels due to the quantum confinement effects of **electrons and holes** in QDs with smaller sizes than its **exciton Bohr radius.**

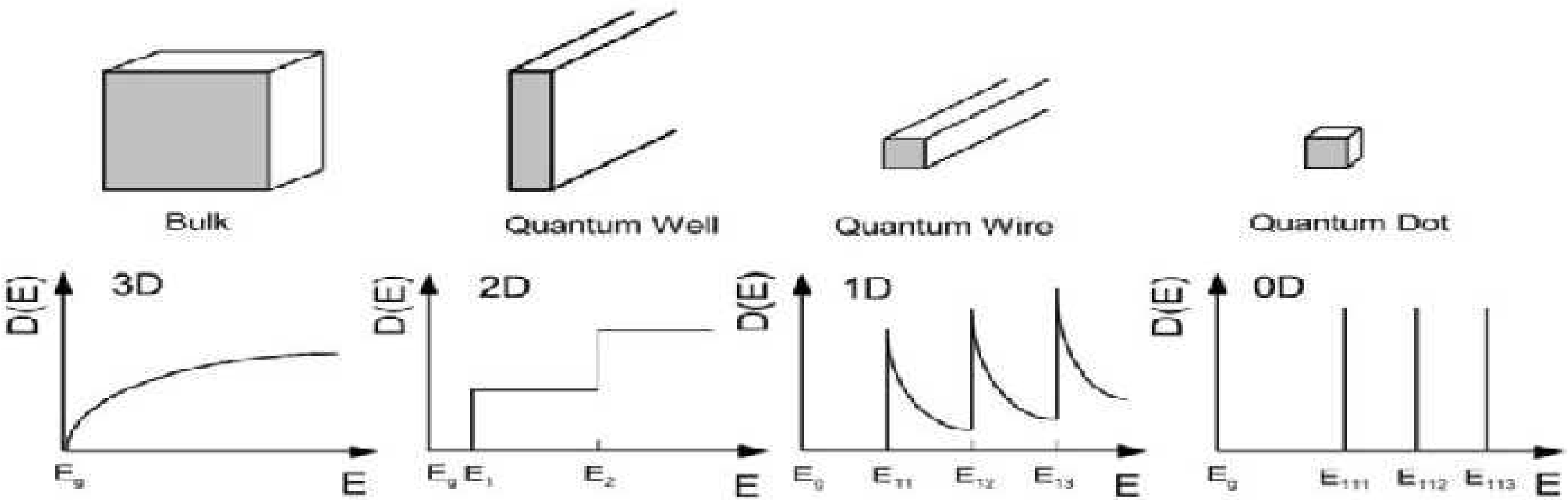
- Their **emission colors** depend on **their size** and can be tuned from the ultraviolet to the visible wavelengths. QDs have nanoproperties in all three dimensions, whereas other nanoparticles as nanowire or single thin layers have ordinary properties along the wire and two dimensions, respectively.



Emission colors of ZnS-capped CdTe QDs excited under a UV lamp (365 nm).

Summary About The Concept of System Dimensionality

(a) Bulk semiconductors (3D);
(b) Thin film, layer structure, quantum well (2D);
(c) linear chain structure, quantum wire (1D);
(d) cluster, colloid, nanocrystal, quantum dot (0D).



The corresponding density of states D(E) versus energy (E) diagram (for ideal cases).