Module-2: Excitons and excitonic Bohr radius, energy levels, splitting

1.1 Semiconductors and excitons

In atomic and molecular systems, energy transfer can occur within a molecule via intramolecular vibrational energy redistribution and electronic state coupling. Energy transfer between molecules can occur through coupling of rotations, vibrations, or electronic excitation. In all of these energy transfer mechanisms, the probability for the coupling depends on the relative energies of the states being coupled. Within a molecule, the energy between the first excited state and the ground state depends on the build up of atomic orbitals to form molecular bands, the highest occupied molecular orbital (HOMO) being the ground state, and the lowest unoccupied molecular orbital (LUMO) being the first exited state. In solid state systems, the magnitude of the energy difference between the HOMO and LUMO, referred to as the band gap or Eg, can be separated into one of the following three types: metals, semiconductors, and insulators. In a metal the energies of the HOMO and LUMO orbitals overlap, and electron promotion occurs with very little or no impetus. In insulators, Eg is very large and electronic excitation is a weak or unlikely process. Semiconductors, as their name suggests, have a measurable band gap but not so significant as to limit electronic excitation. The states that lie at or below the HOMO are in the valence band (VB) and the states that lie at or above the LUMO are in the conduction band (CB). In large-scale semiconductor materials, the build up of the atomic orbitals in forming the molecular orbitals includes many, many atoms each with slightly different energies.

Electronic excitation can occur in a semiconductor when a photon with energy equal to or greater than Eg is absorbed. The promoted electron leaves behind a vacancy; the electron deficient region behaves as a positively charged particle and is referred to as a hole. The energy and distribution of the photogenerated electrons and holes are described quantum mechanically by their wavefunctions, probability distributions, and permitted energies. The
breadth of the probability distributions of the electrons and holes determine their effective size and are referred to as the electron a_e and hole a_h Bohr radii. As for all charged particles, there are Coulombic interactions between the electrons and holes, and the strength of these interactions determine if the electrons and holes can be treated separately or as coulombically bound electron-hole pairs, termed excitons. There is a preferred separation distance between the electron and hole probability distributions in an exciton, and this distance is termed the exciton Bohr radius, a_B.

1.2 Quantum confinement

Decreasing the size of a semiconductor particle in one, two or all three physical dimensions can change the electronic structure of the material by confining the spatial distribution of the exciton, electron, or even hole wavefunctions. Since there is a continuum of states for each of the dimensions that do not exhibit quantum confinement, therefore, the density of states depend on the dimensionality of the material, as shown in Figure 1. The states of a QD become discrete with energies of a few hundred meV between the quantized states, Figure 1D, and there is a similar shift of the band gap to higher energy than the bulk Eg. In a 2D system (Figure 1 C), the states resemble a saw-like quasi-continuum, the energy between these states can be a few hundred meV, and the band gap can also shift a few hundred meV above Eg.

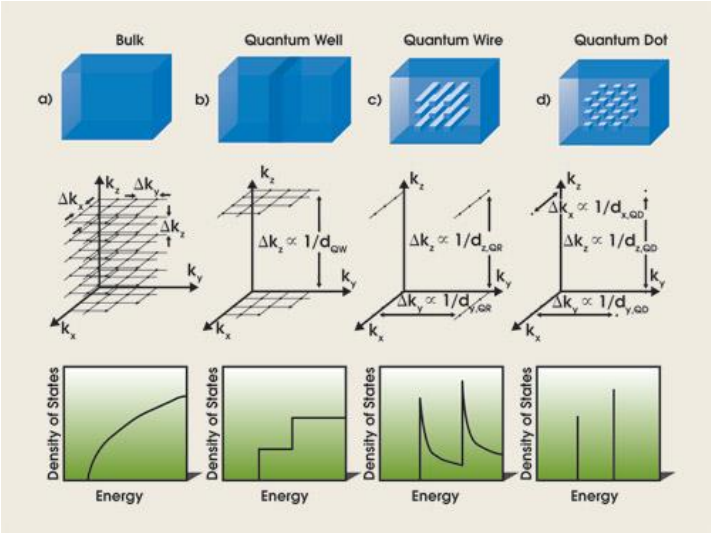

Figure 1-1. The density of states in energy for a semiconductor as the degree of quantum confinement increases. On the left, a), shows the continuous nature of the bulk material, b) depicts confinement in 1 dimension, c) in two and d) the density of states becomes discrete for confinement in all three dimensions.

The strong, medium, and weak confinement terms mentioned are a result of the specific size in each dimension relative to a_B, a_e, and a_h. In the case of strongly-confined systems, the restricted dimension(s) are smaller than both a_e and a_h in an intermediate-confinement regime, the size of the confined dimension is smaller than a_e but greater than ah. In a weakly confined system, the restricted dimension(s) are larger than both ae and ah but small enough that the wavefunction of the exciton is perturbed, and an energetic shift of this state to higher energy results.

The extent of confinement also affects the spatial overlap of the electron and hole wavefunctions and the Coulombic interactions between them. Bound electron-hole pairs, or excitons, should also be treated as quantum-mechanical systems with wavefunctions that resemble this simple H-atom system. The photogenerated electron-hole interactions are weak in bulk semiconductors, and the binding energies are sufficiently small that the electron-hole pairs are not bound at room temperature. Instead, they dissociate into separate electrons and holes. The dependence of the oscillator strength and the binding energy depends on how many degrees of confinement there are. The energy interactions due to quantum confinement are often large compared to the coulomb interaction term. Furthermore, the dimensionality may not permit the electrons and holes to be stabilized at a preferred length within the coulombic potential, and excitons may not be formed. Such is the case for small QDs, where the electrons and holes are forced to occupy the same volume and the electrons and holes weakly interact and can be considered as independent systems. QDs are novel nanocrystalline semiconductor materials whose electrical as well as optical properties strongly depend upon the size and shape of the dots. The diameter of QDs can vary from ~2 to 10 nm, or on the order of 10-50 atomic lengths. Due to their small size, QDs have very large

surface-to-volume ratios. As a result, they have properties somewhere between the individual atoms/molecules and the bulk materials. QDs can be produced either from a single element (e.g., silicon, germanium, and so on) or from more than one element (such as CdSe, CdS, and so on).

Quantum Dots & Nanoparticles

The materials with their dimensions in the nanometer scale are called nanoparticles and they are frequently investigated by the researchers to study novel properties at this scale, the majority of the quantum dots are prepared from semiconducting materials like silicon, germanium, cadmium selenide, cadmium sulphide, etc.

Since the size of quantum dots is of the order of nanometers, they are not single atoms, rather they are comprising several atoms. The quantum dots can produce different colors depending on its size. **Figure 2** shows different light being emitted from nanoparticles having varying sizes.

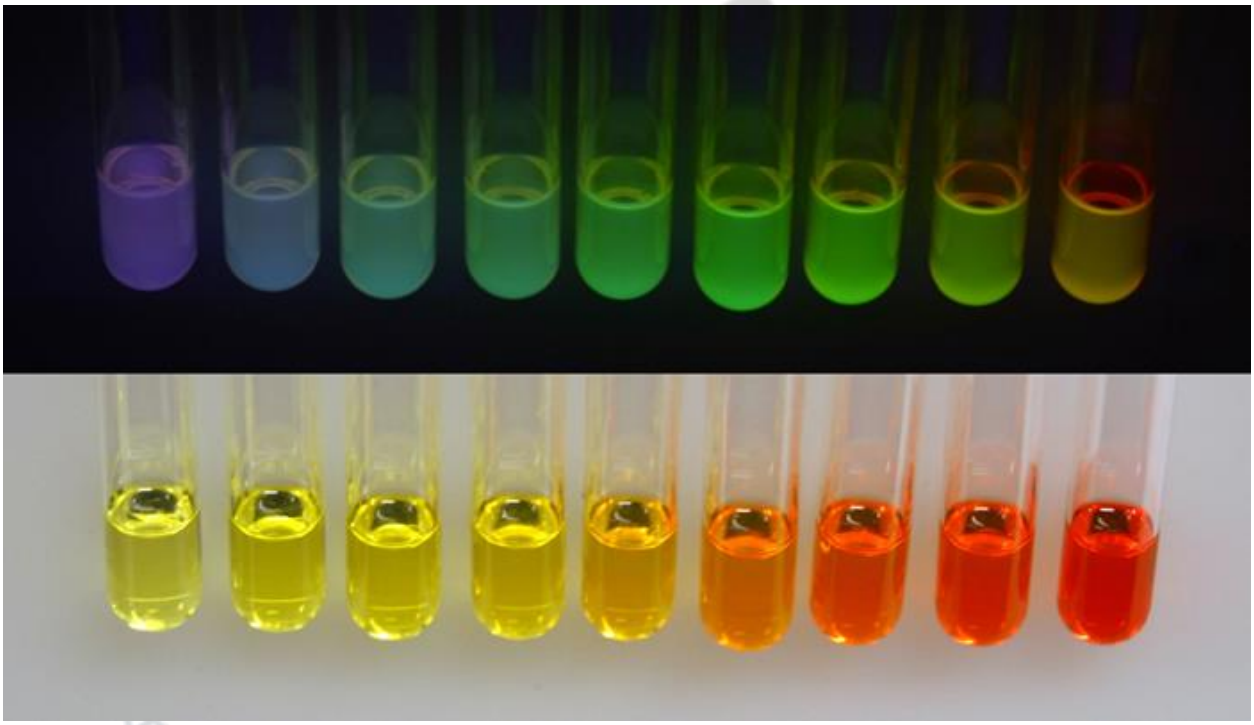

Figure 2 Top: Long wave UV illumination. Bottom: Ambient illumination. Solutions are in order of increasing particle size (longer growth time).

As the QDs are irradiated with UV light, some of the electrons absorb adequate energy in order to break free from the atoms. Thus, these electrons become free to move around the nanoparticle, thereby creating the conduction band wherein the electrons freely move through the material and conduct electricity.
When the electrons return back to the original orbit around the atom (or the valence band), light is emitted whose color depends upon the difference in conduction band energy and the valence band energy (see **Figure 3**).

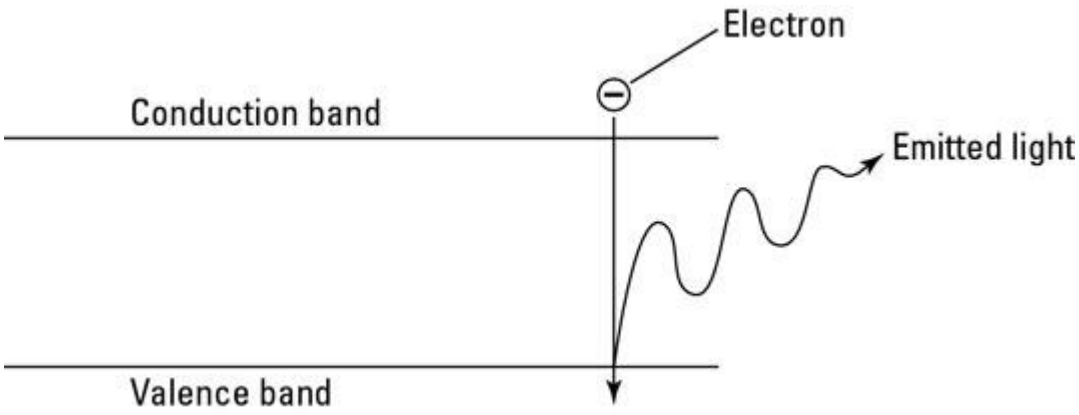

Figure 3 Electrons in a quantum dot generating light.

The smaller the nanoparticle is, higher is the energy difference between the valence and conduction bands, resulting in the deeper blue color. For a larger nanoparticle, the energy difference between the valence band and the conduction band is lower, which shifts the glow toward red.

Almost all the semiconductor materials can be used to prepare QDs. Nanoparticles of all semiconductor materials behave as QDs. The gap between the valence and conduction bands (present in all semiconductors) causes the QDs to fluoresce. Following figures (**Figure 4 & 5**) show images of gold nanoparticles and bulk.

Figure 4 Gold nanoparticles of different sizes demonstrating different colors.

Figure 5 A coin having gold in bulk form.

Figure 6 shows the size dependence of the optical and electrical behavior of QDs. The following sections provide the theoretical explanation for this behavior.

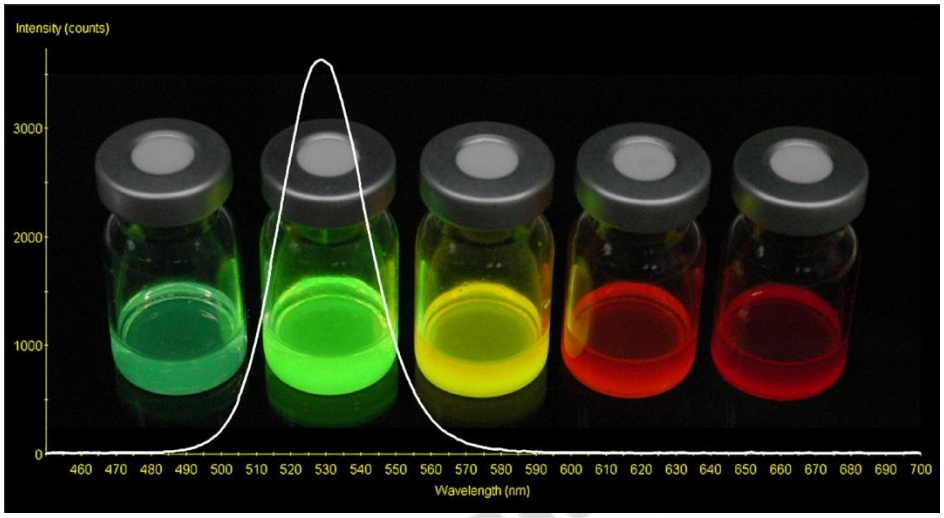

Figure 6 The electronic and optical properties of quantum dots can be fine-tuned due to their dependent relationship on size.

Theoretical Understanding

Quantum confinement is experienced by the semiconductor crystals with size less than twice the Bohr radius of the excitons (i.e., electron-hole pairs). The particle-in-a-box model is often employed to model the energy levels and their dependency on the dimensions of the potential well. The following situations may be considered:

1. **Strong Confinement:** Strong confinement is experienced by the excitons when the radius of the QD is less than the Bohr radius of the exciton (electron-hole pair).
2. **Moderate Confinement:** In occurs when the radius of the QD is less than the Bohr radius of either the electron or the hole, and not both.
3. **Weak Confinement:** In this case the QD radius is greater than the Bohr radius of both electron and hole.

The total energy involved with the QDs comprises three energies: band gap energy, confinement energy, and the energy of the bound exciton. This total energy can be written as:

$$E = E_{bandgap} + E_{confinement} + E_{exciton}$$

We will not consider these three energies individually.

Band Gap Energy

Band theory in solids tell us about the allowed (energy bands) and disallowed (forbidden band or the band gap) energy states. Numerous models have been developed to model the band structure of the solids, such as Kronig-Penney model, Density Functional Theory, etc.

In strong confinement region, the bad gap increases when the QD is smaller than exciton Bohr radius, owing to the splitting of energy bands. Total emitted energy increases, and the emission occurs at various wavelengths, resulting in white light.

Exciton Bohr radius can be expressed as:

$$a_b^* = \varepsilon_r \left(\frac{m}{\mu}\right) a_b$$

where, ε_r is the dielectric constant (relative permittivity), m is the mass, μ is reduced mass, and a_b represents the Bohr radius (~0.053 nm).

Confinement Energy

Particle-in-a-box model can be used to model an exciton. The variations in particle size allow to control the confinement energy, and solution of particle-in-a-box model represents the exciton energy as follows:

$$E_{confinement} = \frac{\hbar^2 \pi^2}{2a^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) = \frac{\hbar^2 \pi^2}{2\mu a^2}$$

Bound Exciton Energy

Coulombic attractions occur between the electron (having negative charge) and hole (having positive charge). The energy of these attractions is directly proportional to Rydberg's energy, and varies inversely with the square of the dielectric constant. This term assumes significance as the semiconductor crystal becomes smaller than the Bohr radius of exciton, and is given by:

$$E_{exciton} = -\frac{1}{\varepsilon_r^2}\frac{\mu}{m_e} R_y = -R_y^*$$

Substituting the values of these energies in the expression for total energy, we obtain:

$$E = E_{bandgap} + E_{confinement} + E_{exciton}$$

$$\therefore E = E_{bandgap} + \frac{\hbar^2 \pi^2}{2\mu a^2} - R_y^*$$

Optical Properties

Wavelength of the emitted light in a QD depends upon its size. With decreasing the size of the dot, the wavelength of the emission shortens and demonstrates a blue shift in the electromagnetic spectrum of the visible light. Similarly, when the size of the QD is increased, the wavelength experiences a red shift.

Using de Broglie relation, energy can be written as:

$$E = \frac{hc}{\lambda}$$

This shows that a particular wavelength of the emitted light can be determined. This makes QDs very useful to finely tune specific properties, like the wavelength of the emitted light.

Electronic Properties

Small-sized crystals have large electronic band gaps, implying the occurrence of a larger energy difference between energy states. In these cases, larger energy is required to promote the electron to the excited state, and also, more energy is emitted when electrons return to their original energy level. When a semiconductor is incident with a light photon having more energy than its band gap, an electron is excited from the valence band to the conduction band (**Figure 7**). The excitation of electron to a higher energy state results in the creation of a hole in the valence band. A hole can be simple described as the absence of an electron and it has opposite charge to the electron, i.e., it is positively charged. The electron and hole experience Coulombic attractions and form an exciton.

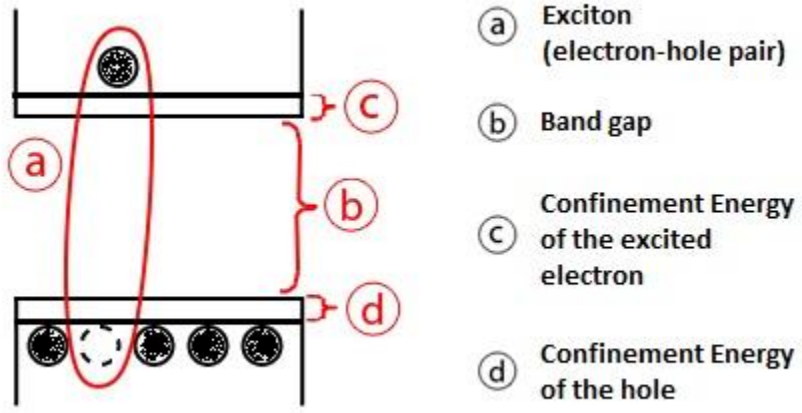

Figure 7: Generation of exciton from an electron-hole pair.

The exciton, itself, is an electrically neutral quasiparticle, and it can be found in semiconductors, insulators, and also in some liquids. Yakov Frenkel first introduced the concept of exciton in 1931 during a discussion regarding the excitation of atoms in an insulator lattice.

Brus Equation

Brus equation is used to describe the emission energies of QDs as a function of the band gap energy, Planck's constant h, the radius of the QD r, and the effective masses of electron and hole:

$$\Delta E(r) = E_{gap} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

QD Production

Quantum dots linked together can form the basic building blocks of a variety of crystalline and non-crystalline nanostructures. The quantum dots can be linked together as molecules to form more complex structures, e.g., lattices, polymeric backbones, and can also be incorporated into thin polymer films (**Figure 8**).

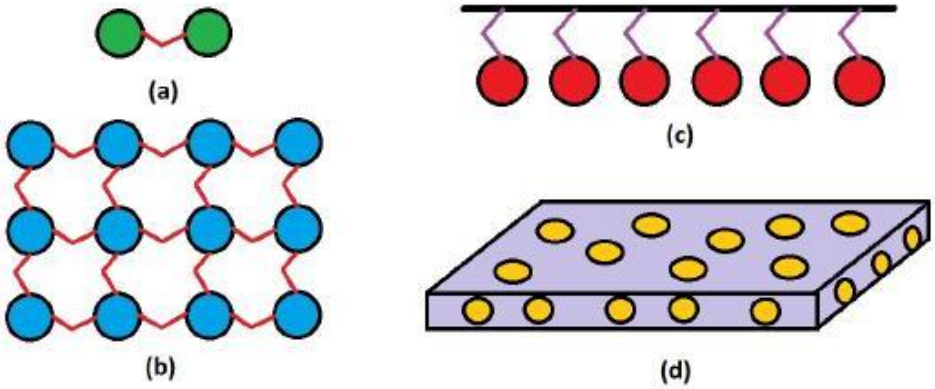

Figure 3: Quantum dots utilized in a variety of structures, including (a) molecular, (b) crystalline, (c) polymeric, and in (d) thin films.

The QDs can be prepared by a variety of different techniques, such as:

- Colloidal Synthesis
- Electrochemical Assembly
- Fabrication
- Viral Assembly

Questions

(1) Considering the particle in a box model, the strong confinement scenario occurs when the radius of the quantum dot is:

A) More than the Bohr radius of both the electron and hole.

B) More than the Bohr radius of only one of the electron or hole.

C) Less than the Bohr radius of both the electron and hole.

(2) Using the below information, please determine the emission energy of the photon of light emitted from the CdSe nanocrystals:

$E_{gap} = 1.74eV$

$m_e^* = 0.13m_e$

$m_h^* = 0.45m_e$

$r = 5.6nm$

(3) Briefly describe an exciton.

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