

Quantum Confinement

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Abstract

Quantum Confinement is the spatial confinement of electron-hole pairs (excitons) in one or more dimensions within a material and also electronic energy levels are discrete. It is due to the confinement of the electronic wave function to the physical dimensions of the particles. Furthermore this can be divided in to three ways: 1D confinement (free carrier in a plane) -Quantum Wells, 2D confinement (carriers are free to move down) - Quantum Wire and 3D-confinement (carriers are confined in all directions) are discussed in details. In addition the formation mechanism of exciton, quantum confinement behaviour of strong, moderate and week confinement have been discussed below.

Keywords: Quantum dots; Energy level; Exciton; Confinement; Bohr radius;

1. Introduction of Quantum confinement

The term 'quantum confinement' is mainly deals with energy of confined electrons (electrons or electron-hole). The energy levels of electrons will not remain continuous as in the case of bulk materials compare to the nanocrystal. Moreover, obtains the confined electron wave functions, they become a discrete set of energy levels as shown in the figure 1. Such kinds of effects appear when the dimensions of the potential approach nearly to de Broglie wavelength of electrons and resulting in the changes or discreteing levels of energy. The effects are defined as quantum confinement and consequently, for nano-crystals are often called quantum dots (QDs). Furthermore, this quantum dot effect influence into the nanomaterial properties such as electrical, optical as well as mechanical behavior of material . It is due to the peculiar nature in nano material possess higher energy electrons than the bulk material's. Depending on the QDs size, confined electrons have higher energy than the electrons in bulk materials.

The semiconductor nanomaterials exhibit fascinating properties when reducing their dimensionality from 2D to 1D or 1D to 0D. Perhaps, the quantum confinement effect occurs when reducing the size and shape of nanomaterials is less than 100-10nm or even lesser. These changes due to discrete set of electron energy level and that lead to size confinement [1-3] figure 1&2.

To know more about quantum confinement it is necessary to understand the phenomenon of quantum dots (QDs). QDs are the new class of materials in which quantum confinement effects can be evident. QDs are very tiny semiconductor crystals in the order of nanometer size and also molecules are tightly confined electrons or electron-hole pairs called “excitons” (explained in the next section) in all three dimensions. QDs are a subatomic group in the family of nanomaterials, which comprises metals, insulators, semiconductors, and organic materials. It’s well known, the quantum confinement occurs only in semiconductors quantum dots and because of their tunable bandgap nature than zero band gap in metals respectively. As mentioned before the peculiar tunable band gap properties QD are composed only group such as II-VI, III-V, and IV-VI based materials. The optical, electrical and bandgap are tunable with respect to changes in particle size that leads to different multiple application.

The main discussion is that, how bandgap can be tuned with respect to size? For that we need to understand the formation of discrete energy levels and the formation of excitons.

2. Formation of discrete energy level

To understand or recall the formation of discrete energy level, when atoms are brought together in a bulk material the number of energy states increases substantially to form nearly continuous bands of states. And also decreasing trend was occurred in the amount of atoms in material and energy states were delocalized with confinement nature. Furthermore, electron-hole pairs converting spatially confined nature when the particle towards natural de-Broglie wavelength of electrons in the conduction band. As a result the energy difference between energy bands is increased with decreasing in particle size dimension as shown in the figure 3.

Particle behaves like a free particle when the dimensions of the confining structure are very large in comparison to the de Broglie wavelength. On this stage, the energy states are continuous and the bandgap is comes to its original position and another energy spectrum does not remain continuous and becomes discrete in nature when the dimensions of confining structure are decreased towards nanoscale. Therefore, the bandgap exhibits size dependence properties, and eventually causes a blue shift in the emitted light as the particle’s size is decreased. However, this effect demonstrates the consequences of confining the electrons and electron-hole pair (or the excitons) within a dimension which approaches the critical quantum limit, often termed as the Bohr exciton radius.

In this view, a quantum dot confines in all the three dimensions; a quantum wire (nanowire) confines in two dimensions; and a quantum well confines only in one dimension. The corresponding structures are also termed as zero dimensional (0D), one dimensional (1D), and two dimensional (2D) potential wells, respectively, with regard to the number of dimensions in which the confined particle has freedom of movement. The below figure 4 shows the overview of quantum confinement in nanostructures.

- Electrons confined in one direction: i.e **Quantum Wells** (thin films): Electron can easily move in 2 dimensions (**2D**) so, one dimensional is quantized.
- Electrons confined in two directions: i.e **Quantum Wires**: Electrons can easily move in 1 dimension (**1D**) so, two dimensional is quantized.
- Electrons confined in three directions: i.e. **Quantum Dots**: electrons can easily move in zero dimensions (**0D**), hence three dimensional is quantized.

In conclusion, each confinement direction changes a continuous k component to a discrete component characterized by a quantum number n .

3. Formation of Excitons

It is very important and necessary to understand the concept of excitons as it is the primary steps to understand QDs and as well as quantum confinement in semiconductors. In the case of semiconductor, electron where shifted from valence band to conduction band when emitting light falling on it and consequently recombination effect impose or create the photon particle. The electron and hole were occupied or created from conduction band and valence band respectively. However, charge of hole is equivalent to the electron charge which is helping to implementation of one particle named as excitation. Above mentioned charges and Coulomb exchange interaction there is an attractive connection between the electron and the hole. Such kind of electron-hole pair is some time expressed in simple term quasiparticle which is named exciton. It is an electrically neutral quasiparticle that occurs in insulators, semiconductors and some liquids.

In solid state physics, the band gap/energy band gap is separated between the finite energy level of conduction and valence band. When an electron from the valence band attains sufficient energy to overcome the energy gap, due to thermal excitation or absorption of a photon, and its goes to the conduction band, a hole is created on the left behind on the valence band. The created hole is moving to conduction band this is formed as an excited electron, the charge carrier in semiconductor device or recombines with hole after time the release of energy. The combination between the electro and hole pair combination leads to the formation of excitons.

Because of the different polarity charges and the Coulomb force exchange interaction there is an attractive connection between the electron and the hole and by simple way the electron-hole pair is were called as a quasiparticle which is named exciton. Due to combination of electron-hole resulting neutral quasiparticle nature were exists into different material nature like semiconductor, insulator and some of the liquid. Furthermore this exciton is transport the energy without compromising net electric charge as per condensed matter theory.

However, there is a major difference. Excitons have an average physical separation between the electron and hole, referred to as the Exciton Bohr Radius this physical distance is different for each material. In the case of semiconductor nanocrystal (QDs) the size of the particles is lesser than the Bohr radius, the electron excited by an external energy source tends to form the weak bond with its hole. This bound state of electron and electron hole, which are attracted by the electrostatic Coulomb force if often called an exciton which was shown in figure 5A&B.

Thus, the Bohr radius is the distance in an electron-hole exciton, also called the exciton Bohr radius [4]. Every semiconductor material has a characteristic exciton Bohr radius (Fig. 5C&D) below which the quantum confinement effect is realized. This unique

confinement property causes the “band” of energies to turn into discrete energy levels in QDs (fig 6.)

3.1 Excitons

To understand the quantum mechanical behaviour of semiconductor particle, let consider materials in an electron which is stimulated from valance band to conduction band (figure 7).

From the valance band left behind electron is a ‘hole’, which can be thought of as a particle with its own charge (+1) and effective mass. The bound state of electron and hole are considered to be quasiparticles is then known or called as ‘exciton’. The pair of electron and hole formation due to Columbic attraction. The exciton can be considered as hydrogen like system, and the exciton radius is easily compare with Bohr radius approximation which is used to calculate the spatial separation of the electron-hole pair,

$$r = \frac{\epsilon h^2}{\pi m_r e^2} \dots\dots\dots (1)$$

Where, r - is the radius of three dimensional sphere containing excitation, m_r - is the reduced mass of the excitation, ϵ -is the dielectric constant of the given material, and e - is the charge of the electron and h - is plank’s constant. Ion cyclotron resonance is a powerful technique to find the effective mass of hole and electron and are range were 0.1-3 m_e (m_e -is the mass of the electron) .Furthermore, the empirical radius and mass calculation suggests that the electron-hole pair spatial separation is around about 1-10 nm for most the semiconductors.

4. Quantum confinement effect:

In literature, semiconductor quantum dots are also known as semiconductor nanocrystals or nanoparticles. A semiconductor nanocrystal (SNC) or quantum dot (QD) is a semiconductor whose excitons are confined in all three spatial dimensions. As a result, they have properties that are between bulk semiconductors and those of discrete molecules. Size effects are observed in semiconductor crystals measuring 10-100 nm, whereas quantum size effects are usually the characteristics of nanocrystallites measuring less than 10 nm. The physico chemical properties of nanocrystalline particles different from those of bulk materials for two specific reasons. First, the high surface to volume ratio that results in many atoms at the surface in the crystalline lattice. And secondly, the electronic bands are spilt up in to discrete energy levels as the result three dimensional confinement of the charge carriers occurs. This leads to quantum confinement of charge results in the increase bandgap with decreasing particles size.

The quantum confinement effect in low dimensional semiconductor systems was described about 25 years ago. The bulk crystalline structure is preserved in a nanocrystal. However, due to quantum confinement, nanocrystals have molecule-like discrete electronic states which exhibit strong in size dependent properties. In the last decade, comprehensive investigations were made to explore size dependent properties of semiconductors with emphasis on optical properties, including absorption and luminescence.

Detail knowledge of the optical properties of the nanostructured materials is important for understanding the photophysical and photochemical process that follow the absorption of light quanta. Steigewald and Brus (1990)[5] used quantum mechanical molecular orbital calculations to explain quantum confinement effect on optical absorption, accounting the well established blue shift in the absorption spectra with decreasing particle size. Bawendi (1995) [6-7] has also provided a recent overview of this field. As explaining observed spectral shifts during the early stages of inorganic semiconductor particle growth, molecular orbital (MO), and linear combination of atomic orbital coupled with molecular orbital (LCAO-MO) procedures provide information for the construction of energy level diagrams for clusters of several molecules up to size characteristic of bulk semiconductor.

By addition of the filled and empty orbitals of the multiple energy levels can increase the molecules level in a cluster. This decreasing trend in energy differences between the not only filled orbitals and as well as empty orbitals too. Also, decreasing trend into the energy gap was observed between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). For a bulk semiconductor, the filled and empty state form separated continuums i.e., the valence and conduction bands. However, for Quantum Dot (Q-size) regime region energy levels were within the empty and filled states remain discrete and the band gap energy levels were higher states of between the HOMO and the LUMO than of the bulk materials as shown in the schematic diagram (Figure 8).

The band gap, E_g , increases in magnitude as the semiconductor particle radius decrease in size to the point where it becomes comparable or smaller than the exciton radius. These properties have led to the applications in a wide range of fields i.e., semiconducting quantum well and super lattice devices, nonlinear optical materials, photocatalysis and imaging systems. For II-VI compounds, maximum radii for the onset of quantum confinement effect (Q-size effects) leading to the bandgap increase have been determined by Bawendi (1995)[7] to be 10 to 100 Å. Wide band photoconductors such as, TiO_2 (rutile) and ZnO undergo increase in band gap as radii approach in the range of 50 Å. It is interesting to note that a blue shift in the long wavelength optical absorption edge with decreases in particle size was first observed by Berry (1967)[8] for AgBr samples with radii of 65 Å and 350 Å. It's very clear that Quantum confinement effect based semiconductor nanocrystals were produced tremendous optical and electrical properties than of the bulk materials which are due to the reduced behavior of characteristic length which is called as exciton Bohr diameter. This peculiar characteristic length is usually in the range of few nanometers when the material reveals size dependent of optical and electrical properties.

One of the most important consequences of the spatial confinement effect is an increase in energy of the band-to-band excitation peaks (blue shift) as the radius R of a microcrystallite semiconductor is reduced in relation with the Bohr radius. However due to significant spatial confinement effect there is an increase in energy of band-to-band excitation peaks which is called blue shift. In terms, microcrystallite of Radius (R) ranges in semiconductor having less relation with than of the Bohr Radius. Some of minor difference would have happen between the theoretical and experimental of confine effect it is due to electron electron-hole interaction energy, in coulomb term and the confinement energy of the electron and hole in the kinetic energy.

4.1 Weak confinement regime

To observe this regime, the radius R of a crystallite should be greater than the bulk exciton Bohr radius a_B . In this region of weak confinement, the dominant energy is the Coulomb term and they already occur in size quantization of the exciton motion. The exciton energy states are shifted to higher energies by confinement and shifts in energy ΔE is proportional to $1/R^2$. The shift ‘ ΔE ’ of the exciton ground state is given approximately by

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2MR^2} \text{-----(2)}$$

Where, M is the mass of the exciton, and it is give by $M = m_e^* + m_h^*$, with m_e^* and m_h^* being the effective masses of the electron and hole respectively.

4.2 Moderate confinement regime

Quantum confinement taking another point of view, especially II-VI semiconductor region the bohr radius equal (a_B) to the material radius (R) which is called moderate confinement regime and also following terms condition should satisfy $a_h < R < a_e$ for moderate confinement regime process. The overall process were observed in small QD and its well the well restricted motion of a photo excited hole.

4.3 Strong confinement regime

Finally, the strong confinement regime were confirmed by satisfying the following condition such that $R \ll a_B$, and $R \ll a_h$. Due to these conditions excitations are not formed and separate size quantization of an electron and hole is the dominant factor. For strong confinement regime must need two different reason first one is the Coulomb term of electron-hole interaction is small it’s acted as perturbation and another one is independent behavior of electron and holes when above condition is apply. Following the optical spectra should then consist of a series lines due to transition between subbands. This factor was confirmed experimentally, and the simple model gives shift in energy as a function of crystallite size as,

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2\mu R^2} \text{-----(3)}$$

in which the exciton mass M is replaced by reduced exciton mass μ , where,

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \text{-----(4)}$$

The electrons and holes in QDs are treated as independent particles, and for the excited state there exist a ladder of discrete energy levels as in molecular systems.

5. Summary

Recently quantum dots based nanomaterials play a major role in the applications many filed such as Q-LEDs, transistors, solar cells, laser diodes, displays, medical imaging and quantum computing etc. Especially the QDs exhibit significant role in the optoelectronic application, its changes because of precisely controlling the size, shape, emission of color and bandgap tuning. These properties are changing inside the quantum dots and that leads to different applications from energy harvesting to biomedical application. This entire physical and chemical phenomenon could be explained through theoretical model by using quantum confinement behavior.

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Conflict of Interest

The authors declare no conflict of interest

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