CHAPTER - 1

Semiconductor Quantum Dots and Its Band Structure Parameters: An Introduction
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1.1 Prelude:

The combination of spectroscopy and electrochemistry has allowed us to establish novel charge transfer induced phenomena in colloidal quantum dots (Q-dots) including tuning the band structure parameters and modifying their opto-electronic properties. The main objective of the thesis is related to the determination of band structure parameters and the understand the charge transfer characteristics in colloidal Q-dots using combination of electro, spectro and spectro-electrochemical methods [1].

This chapter will review in brief on the general introduction to nanomaterials with special emphasis on semiconductor Q-dots and the charge transfer processes, therein. It includes the brief explanation of the quantum confinement or size quantization effect followed by classification of nanomaterials based on the quantization in dimensions, and a short discussion about the synthesis of the semiconductor Q-dots. The determination of band structure parameters viz. conduction band edge, valence band edge, optical band gap and quasi-particle gap using spectroscopic and voltammetric measurements has been discussed, thoroughly. A theoretical background to the determination of these parameters by different methods with special focus on semi empirical pseudopotential (SEPM) calculations as described by Zunger and co-workers [2, 3] has been illustrated. The importance of determination of band structure parameters for the potential applications of semiconductor quantum dots in varied fields are also discussed in detail. Furthermore, the processes of charge transfer and the effect of different parameters such as size, composition and spectator charge carriers have also been explained.
1.2 Introduction to Nanotechnology:

“The revolutionary promise of molecular nanotechnology has become a part of society’s expectations for the future. This technology will provide nanomedicine breakthroughs that could cure cancer and extend life space, bring abundance without environmental harm and provide clean sources of energy. These ideas are part of the vision that launched the field of nanotechnology.”

- Kim Eric Drexler

The revolutionary vision given in the above statement by one of the pioneer of Nanotechnology K. Eric Drexler (born April 25, 1955 in Alameda, California) express the power of nanoscience and nanotechnology.

Another important statement from the renowned scientist and Nobel laureate Richard Smalley is given below,

“Just wait, the next century is going to be incredible, we are about to be able to build things that work on the smallest possible length scales, atom by atom. These little nanothings will revolutionize our industries and our lives.”

The futuristic idea given in the above statement itself is an indication of the greatness of the nanoscience. What are those things and how will they change and revolutionize our lives? In the following sections, we shall discuss in brief the fundamentals and applications of these things.

1.2.1 Nanoparticles:

The nanoparticles can be defined as particles with a physical dimensions in the nanometer (i.e. $10^{-9}$ m) size range which show novel and exotic properties due to the size quantization effect. Nanoparticles can be considered as a single “crystal” of a typical size of few nanometers consisting of 100’s to 1,000,000’s of atoms. The name nanoparticle (NP) is generally given for all colloidal materials in the nanometer range, while the designation nanocrystal (NC) is used mostly for highly crystalline nanoparticles.

Nanoparticles possess a variety of properties depending on their chemical composition and their size and shape. Metal nanoparticles such as gold or silver exhibit
surface plasmon resonance absorbance bands in the visible spectral region that are controlled by the size and shape of the particles [4]. Basically, the physicochemical properties of any materials is mainly a manifestation of the electronic structure of that material. For bound charge carriers (electron and hole), the motion becomes highly confined and quantization sets in. This spatial confinement is well known as size quantization or quantum confinement effect.

For this thesis, the main emphasis has been given towards studying the electronic properties of semiconductor Q-dots with special consideration of Q-dots of CdSe, CdTe and their composites. The effect of different parameters including size, stoichiometric and non-stoichiometric composition and the added spectator charged species have been studied. So, henceforth we will focus our discussion mainly to the semiconductor Q-dots.

1.2.2 Semiconductor Nanoparticles:

![Figure 1.1: Semiconductor nanoparticles with tunable emission colors over the whole visible spectrum (i.e. from blue to red color) as a function of size. Courtesy: Photograph by Xiaohu Gao from internet source.](image)

The quantum confinement effect are investigated in very much details in case of the semiconductor nanomaterials. For example, as shown in Figure 1.1, the semiconductor nanoparticles can emit different colors over the whole visible spectrum as a function of particle size. In semiconductor materials, electrons and holes are the charge carriers responsible for the electric current. These two charge carriers are separated by the gap in the allowed energies called as band gap.

As shown in Figure 1.2, the energy gap between the allowed energies of the elec-
Figure 1.2: Energy level diagram showing separation between energy levels for different situations (a) bulk materials, (b) nanomaterials, and (c) molecular species.

Electrons in the material that separates the normally filled energy levels of the valence band (where missing electrons behave like positively charged current carriers called “holes”) and the conduction band (where electrons behave like a gas of free negatively charged carriers). The energy difference or band gap in between two bands depends on the size, shape and nature of the material at specific temperature and pressure. The absorption of energy can excite electrons from valence band to the conduction band leaving hole in the valence band. At low temperature, these two charge carriers form a weak coupled pair, which is called an “exciton” [5]. The energy of exciton lies below the energy of the band gap of semiconductor crystal because of the electrostatic Coulomb interaction.

1.3 Size Quantization Effect:

When we move from bulk material toward smaller and smaller dimensions, we realize that on reaching certain dimensions one begins to enter a new regime where the particles start to experience changes in their properties compared to the bulk material. The difference in properties between the bulk material and the isolated molecules is already known. In fact, the nanomaterial domain is a bridge in between
these two, implying that their properties lie between those of the bulk and the isolated molecules. The passage from bulk to nanomaterials is manifested when their size gets small enough that the charge carriers inside the particle start to feel the volume limitations, the “walls” of the particles [6]. As we know from elementary quantum mechanics, when the electronic particles or charge carriers (electrons and holes) are confined in a volume limited by potential barriers that are comparable or smaller than the de Broglie wavelength of the particle, their allowed energy states become discrete (quantized) rather than continuous as in the bulk material [7]. This effect of size or spatial confinement is termed as size quantization or quantum confinement effect.

There are many properties including optical and electronic that undergo changes with size due to the size quantization effect or quantum confinement effect. To understand what is the size quantization effect, first we shall make a slight glance over structure and bonding properties of the molecules.

The molecular orbital model for the evolution of continuous bands from discrete MOs in case of sp$^3$ hybridised system of Si atoms is shown in Figure 1.3 [7, 8]. The HOMO is called Fermi energy level $E_f$ for infinite situation. It is independent of size and depends only on density.
\[ \rho = \frac{n}{V} \tag{1.1} \]

Where, \( n = \) number of atoms
\( V = \) volume

The average spacing \( \delta \) between two nearer energy levels is calculated by

\[ \delta = \frac{E_f}{V} \tag{1.2} \]

i.e. \( \delta \) is inversely proportional to volume. It means that the spacing between adjacent energy levels changes in an inversely proportional with the volume.

Above relation can also be written as,

\[ \delta \propto \frac{1}{L^3} \tag{1.3} \]

or,

\[ \delta \propto E_f(\lambda_f/N)^3 \tag{1.4} \]

Where, \( \lambda_f \) is the wavelength of electron of energy \( E_f \). It is of the order of an interatomic distance. This means that properties such as optical and electronic are size dependent.

Figure 1.2 shows different situations for the separation between the energy levels. The situation for a single molecule, where all the energy levels are separated by definite spacing is as shown in Figure 1.2(c). Figure 1.2(a) shows the typical band structure originated from infinite number of s and d orbital electron. The situation in Figure 1.2(b) is most important when the electronic band structure of the nanosized particles will be discussed. It is the typical situation in case of nanoparticles.

### 1.4 Classification of Nanomaterials:

The nanomaterials can be categorized into three different types based on the quantization or spatial confinement in dimension as shown in Figure 1.4. Fundamental differences exist between these three different quantization regimes, for example the density of states (DOS) as a function of the energy is quite different for each quantum system. For quantum wells or films the DOS is a step function while for
the quantum dots it is a series of discrete values resembling that of a molecule or an atom. Quantum wires have a DOS distribution that is intermediate between the quantum well or quantum films and the quantum dots.

1.4.1 Quantum Well:

When the spatial confinement is in only one dimension i.e. when the size of the material is reduced in only one direction (refer, Figure 1.4), then the nanostructures are called as quantum wells. Both the charge carriers i.e. electrons and holes can be confined in semiconductor quantum wells. A practical example could be in a CD or DVD player. The laser that reads information of the discs is a quantum well laser and confines electrons by sandwiching materials together. The effect of quantum well can also be used to increase the gain and efficiency of the solid state devices such as infrared imaging, and more recently, solar cells.
1.4.2 Quantum Wires:

When the spatial confinement is in two dimensions rather than one as explained for quantum wells, the nanostructures are called as quantum wires or quasi one-dimensional structures. Thus, in quantum wires, the electrons can move freely in only one direction, while they are confined in the other two transverse directions. Carbon nanotubes and nanofibers are the excellent examples of this category. In April 2005, NASA invested $11 million over four years with Rice University to develop quantum wire with 10 times better conductivity than copper at one-sixth the weight. It would be made with carbon nanotubes and would help to reduce the weight of next generation shuttle, and can also have wide range applications.

1.4.3 Quantum Dots:

The term “Quantum Dot” was coined by Mark Reed at Texas Instrument. These are the semiconductor nanostructures whose excitons or charge carriers are spatially confined in all three dimensions reducing the size of materials to a dot in nanometer regime. A dot is a three dimensional object comprising several hundreds or thousands of atoms with finite shape. In quantum dots, the electrons are confined to a point in space. They have no freedom in any dimension and electrons are said to be localized at a point implying that a change in all directions changes the properties. They were discovered and prepared at the beginning of the 1980s by Alexei Ekimov [9] in a glass matrix and by Louis E. Brus [10, 11] in colloidal solutions. Researchers have studied quantum dots in transistors, solar cells, LEDs, and diode lasers. They have also investigated quantum dots as agents for medical imaging and sensing.

In the first approximation, the quantum size effect in quantum dots can be described by a simple “quantum box” model [12], in which the electron motion is restricted in all three dimensions by impenetrable walls. For a spherical QD with radius R, this model predicts that a size dependent contribution to the energy gap is simply proportional to $1/R^2$, implying that the gap increases as the QD size decreases. In addition, quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels. The discrete structure of
energy states leads to a discrete absorption spectrum of QDs, which is in contrast to the continuous absorption spectrum of the semiconductor.

An ideal Q-dot is realizable only when the electronic states within the dot face a discontinuity at the edge of the material. Due to this, the electron within the dot feels an insurmountable barrier at the edge. When a material is truncated at the surface, the surface atoms have unsatisfied valencies. In order to reduce the surface energy, the surface reconstructs, which leads to energy levels in the forbidden gap of the semiconductor. The electrical and optical properties of the material are degraded by these traps.

The following discussion will be focused on the semiconductor quantum dots or nanocrystals that were mainly used for the present thesis work e.g. CdSe, CdTe, CdS and their composites. The Bohr radius for CdSe is \( a_B = 56 \, \text{Å} \). The most easily observable effect is the blue shift of the optical absorption and emission of the semiconductor quantum dot with decreasing size due to the increase in band gap. For example, bulk CdSe has a band gap of 1.74 eV or 714 nm, but for its quantum dots with average diameter of 1, 2 or 3 nm absorption onset will become 400, 480 or 540 nm (3.10, 2.58 or 2.29 eV) respectively, and emission spectra will be similarly shifted. The semiconductor’s band gap widens and its fluorescence shifts towards the blue. Smaller the quantum box, more is the blue shift in the fluorescence. Conversely, lesser the confinement, bigger the quantum box and more will be the red shift in fluorescence. Eventually, one enters the infrared and the invisible. The fluorescence is generated when electron and hole recombine. The restricted confinement requires additional energy and this causes the wavelength shift.

The band gap energy in semiconductor quantum dots can be calculated using an elementary equation of energy and wavelength,

\[
E(eV) = \frac{hc}{\lambda} \tag{1.5}
\]

Where, \( h \) is the Plank’s constant with a value of \( 6.626 \times 10^{-34} \, \text{kg m}^2 / \text{s} \), \( c \) is the speed of the light (\( 2.99 \times 10^8 \, \text{m/s} \)), and \( \lambda \) is the wavelength of the absorbed or emitted light.

Thus, putting the values of all the constants, a relation between energy in eV and
wavelength in nm can be determined as,

\[ E(eV) = \frac{1240}{\lambda(nm)} \] (1.6)

Moreover, interband optical transitions will appear in the absorption spectra, as the valence and conduction bands separates into a number of discrete energy states. This phenomenon is a manifestation of the size quantization effect at these dimensions. It means that the spacing between allowed energy levels becomes sensitive to the size of the nanocrystals (charge carriers start to feel the energy barrier of the walls of the quantum dot).

### 1.5 Synthesis Methods for Colloidal Particles:

A large number of techniques are available for the synthesis of different types of nanostructures in the form of clusters, colloids, quantum wires and well etc. One approach to synthesize the nanostructures, called *top down* method, is to start with a large scale object and gradually reduce its size or dimension to the nanometer regime. These methods are generally called as physical methods. High energy ball milling, melt mixing, physical vapour deposition, Laser ablation, Laser pyrolysis, sputtering, ion beam techniques and lithography are some of the examples of this approach. The apposite approach to the preparation of these nanomaterials, called *bottom up* approach. It includes collecting, consolidating and arranging individual atoms and molecules into different structures, which can be carried out by a sequence of chemical reactions with or without catalysts. Here, we shall discuss particularly the wet chemical methods as we have mainly used these for the synthesis of semiconductor Q-dots that are studied in this thesis work.

#### 1.5.1 Colloidal Particles and Their Stability:

Generally, the nanoparticles synthesized by chemical method are called as ‘colloids’. Colloids are known since ancient time. These are a class of materials, in which two or more phases (solid, liquid and gas) of same or different materials co-exist with at least one dimension being less than micrometer. Several examples of colloids that are around us are liquid in gas (fog), liquid in liquid (fat), solid in liquid
Figure 1.5: A qualitative relationship between the total number of atoms in the solid and the relative percentage of surface atoms.

(Tooth paste), etc. Figure 1.5 shows a qualitative relationship between the total number of atoms in the solid and the relative percentage of surface atoms [13]. The colloids are the particles with large surface to volume ratio having large number of atoms/molecules on the surface of particles. These surface atoms have very less number of neighboring atoms as compared to the bulk or interior. Therefore, the atoms on the surface are highly reactive and interact easily to form bigger clusters, the process is known as coagulation. So, the main concern with the formation of colloids is the stability i.e. how long the colloids can stay as separated particles in the dispersion medium.

There are several interactions and factors involved that determines the stability of the colloids. Interaction of constantly and randomly moving particles with each other and with the dispersion medium could be considered as a result of two type of interactions. The first is repulsion interaction which is effective only at short distances and it arises due to the repulsion between electron clouds in each atom. The second is the van der Waals attraction, effective at long range distances which arises due to interaction between permanent dipoles of atoms or molecules.

In general, the interaction responsible for the stability of colloids can be given as,

$$dG_1 = \frac{A}{R^{12}} - \frac{B}{R^6}$$  \hspace{1cm} (1.7)
where, $dG_1$ is an interaction energy, $A$ and $B$ are the constants and $R$ is the distance between two particles. Colloids in an dispersion medium are mostly charged either negatively or positively but they could be even neutral. So, the ions with apposite charges will try to accumulate around the charged particles. This leads to the formation of electrical double layer. However, due to continuous Brownian motion of counter ions and colloidal particles, it results into formation of dynamic double layer. Therefore, the concentrations of the charges on colloids and the electrolyte would strongly affect the double layer structure and thus the electric potential. The stearic hindrance or repulsion is the another factor that increases the stability of the colloids. This can be generated by adsorbing some kind of material layer on the colloidal particles. Generally, polymers, surfactants and some organic molecules are used for this purpose [14, 15]. These materials are called as capping ligands or capping agents and the particles are called as capped nanoparticles. The ability of the capping ligand to keep the colloidal particles stable depends on type and strength of the bonding between ligands and surface atoms.

Figure 1.6: A general schematic showing experimental setup used for the synthesis of semiconductor Q-dots using wet chemical route.
1.5.2 Synthesis of Colloidal Semiconductor Q-dots:

Synthesis of colloidal particles using chemical route is a very old method. Michel Faraday synthesized very stable gold nanoparticles by this method way back in 19th century that even today are in stable colloidal form. Compound semiconduc-

![Diagram of experimental setup](image)

Figure 1.7: A general schematic showing experimental setup used for the synthesis of semiconductor Q-dots using wet chemical route.

...tor nanoparticles can be synthesized by wet chemical method using appropriate precursor salts. Generally, thiols, amines, phosphines and certain carboxylic acid molecules are used as a capping agents for the synthesis of semiconductor Q-dots. Further, there are different methods for the synthesis of these nanoparticles such as Langmuir-Blodgett method, micro emulsions, and more commonly used sol-gel method. In the present thesis work, sol-gel method has been used extensively for the synthesis of semiconductor Q-dots. As the name suggests sol-gel involved two types of materials ‘sol’ and ‘gel’. Sols are solid particles in a liquid while gels are...
continuous network of particles with pores filled with liquid. A typical schematics of experimental setup used for the synthesis of Q-dots studied in the present thesis is shown in Figure 1.7.

1.6 Applications of Semiconductor Q-dots:

Semiconductor Q-dots finds range of applications in divers fields ranging from drug delivery [16–18], bioimaging [19, 20], light emitting diodes [21–23] to materials for solar cells and photovoltaics [24]. Here, we shall briefly review some of the main fields where quantum dots finds tremendous applications.

1.6.1 Biological Imaging and Disease Detection:

Semiconductor Q-dots finds revolutionary applications in the field of biotechnology and medicines. Few of its aspects can be summarized as below,

Figure 1.8: Bioimaging of rat cells using carbohydrate-encapsulated quantum dots of CdTe@CdS.

1. Quantum dots offer wide broadband absorption spectrum while maintaining a distinct, static emission wavelength. Its emission spectra can be set to allow labeling and observation of detailed biological processes.

2. Quantum dots can be useful tool for monitoring cancerous cells and providing a means to better understand its evolution (refer, Figure 1.8).

3. Q-dots are much more resistant to degradation than other optical imaging probes like organic dyes. It allows them to track cell processes for longer periods of time.
4. Q-dots could also be armed with tumor-fighting toxic therapies to provide the diagnosis and treatment of cancer.

1.6.2 Quantum Dots for LEDs:

Light emitting diodes is the another area where the size and composition tunable optical properties of quantum dots are gaining a lot of attention (refer, Figure 1.9).

![Figure 1.9: Commercially available panel for computer displays made up of quantum dot based light emitting diodes (QDLEDs).](image)

1. Q-dots can be useful to produce inexpensive, industrial quality white light.

2. Q-dot LEDs find marked improvement over traditional LED-phosphor integration by the ability of the dots to absorb and emit at any desired wavelength.

3. Quantum dots with different emission colors such as red, green, and blue can be intermixed homogeneously within the phosphor to produce white light which is very difficult to accomplish with the traditional LED-phosphor setup.

1.6.3 Solar Cells and Photovoltaics:

Semiconductor nanotechnology will play an important role in the field of energy from green sources. The future source of alternate energy will be the sources like solar cells.
1. Traditional solar cells are made of semiconductors and are expensive to produce. Theoretical upper limit of efficiency of conversion of sunlight to electricity is only 33%.

2. Quantum dots allow to reach the upper limit to ca. 60% with lower production and fabrication cost.

3. Quantum dot solar cells are more effective due to their ability to preferentially absorb and emit radiation that generates optimum electric current and voltage.

1.6.4 Other Future Q-dot Applications

1. **Electronics:** Till date, electronics have used only the charge property of electrons and holes and spin has been neglected. Nanotechnology can enable us to use the spin of these charge carriers to produce *spintronics*-spin based electronic devices [25, 26] e.g. spin valves, spin-LED, optical switches etc. Spin valves type devices are already being used in personal computers to ‘read disks’ which have enabled to increase data storage capacity of hard disks.

2. **Defense Applications:** Quantum dots can be integrated into dust that tracks enemies and gives protection against friendly fire events.

3. **Automobiles:** A self cleaning window glass materials made by dissolving small amount of TiO₂ nanoparticles into ingredients of glass are now in use.

4. **Textiles:** Textile industry is also quite excited about the use of nanomaterials to produce clothes with pleasant look and more comfort [27]. These clothes do not require ironing and frequent cleaning.

5. **Cosmetics:** ZnO and TiO₂ nanoparticles with fairly uniform size are able to absorb ultraviolet light and protect the skin [28, 29]. Nanoparticle based colors and dyes are quite harmless to skin and can be used in hair creams and gels.
1.7 Theoretical Encounter:

Different theoretical models have been developed for the determination of band structure parameters and to explain the charge transfer characteristics in semiconductor quantum dots. In this section, we shall consider some of these theories in brief to understand the electronic band structure of semiconductor quantum dots.

1.7.1 Effective Mass Approximation:

Brus et al. [11, 30] laid out the proper framework for understanding the observed effects of size quantization from the view point of molecular quantum chemistry and put forward a theory what is called as **Effective Mass Approximation**. This model gives a correlation between the size of the nanoparticle and its band gap. It says that the electrons in the conduction band and the holes in the valence band are confined by the surface potential. As a result, electron-hole recombination energy, i.e. the lowest energy transition from valence band to conduction band increases in energy. Thus the band gap increases with decrease in particle size.

The effective mass approximation has been used extensively as it gives a good sentiment of the phenomenon [12, 31]. The radiative recombination of photo generated electron-hole pair, before thermalization or trapping leads to the formation of a pair, called as **Wannier exciton**. It is assigned as a single particle in an excited state in which the electron and hole are coupled by attractive Coulomb forces and no net charge is present. Electronic particles diffract off the periodic lattice of the crystal and behave as if they have an inertial mass different from the free-electron mass. This mass is designated as the effective mass \( m^* \). In II-VI and III-V semiconductors, excitons are considered to be similar to a hydrogen atom and can be well described by a hydrogen like model incorporating the effective mass and the screening described by the dielectric constant.

Brus et al. considered that unlike in bulk materials where the electron-hole pair is free to move in small quantum dots they can become physically confined. Strong confinement leads to a rising of the electronic energy in the same way as would be expected from the simple particle-in-a-box model of quantum mechanics.
Based on the effective mass approximation, the energy required for \( S_0 \) to \( S_1 \) transition for such a system is given by the following equation.

\[
E(R) = E_g + \frac{\hbar^2}{8mR^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\epsilon R}
\] (1.8)

where, \( E(R) \) is the band gap energy between valence band edge and conduction band edge of Q-dots, \( E_g \) is the band gap of the bulk semiconductor, \( \hbar \) is Plank’s constant, \( m_e^* \) is the effective mass of electron and \( m_h^* \) is the effective mass of hole, \( R \) is the radius of the nanoparticles with dielectric constant of \( \epsilon \).

The second term of this equation is the kinetic energy and the third term arises due to the Coulombic attraction between the electron and the hole, which is very small as compared to the other two terms and hence is generally neglected. Actually, this equation is the direct solution to the Schrodinger equation for particle in one dimensional box, where a particle is subjected to stepped potential energy function infinite everywhere except for a finite line segment of length \( L \).

\[
\frac{\partial^2 \Psi}{\partial^2 x^2} = \frac{8\pi^2 m}{\hbar^2} (E - \infty) \Psi = 0
\] (1.9)

where, \( \Psi \) outside the box is zero and inside the box \( \Psi = c_1 e^{i\theta} + c_2 e^{i\theta} \) with \( \theta = (2mE)^{1/2}/(2\pi\hbar) \).

Thus, knowing the band gap of semiconductor Q-dots which can be determined by simply recording the UV-vis absorption spectra, we can calculate the average size of the nanocrystallites [11]. Figure 1.10 shows the optical band gap energies for few semiconductor Q-dots as a function of Q-dot size. The results obtained from this model shows good agreement with that of the experimental data for large colloids, however it shows deviation in case of smaller ones overestimating the band gap energy. This could be due to the ignorance of the coulombic interaction energy as effective mass approximation neglects this term. Further, in semiconductors with very small carrier effective masses, the effective mass approximation breaks down even for bulk materials. A rigorous solution to this problem would be to add a correction term to the equation to account for the band nonparabolicity that causes this effect.
1.7.2 Tight Binding Model:

In solid-state physics, the tight binding model (or TB model) is an approach used to calculate the electronic band structure using an approximate set of wave functions based on superposition of wave functions for isolated atoms located at each atomic site. In the tight-binding model, we imagine how the wave functions of atoms or ions will interact as we bring them together [32–35]. This model have several advantages over the effective mass approximation providing substantial improvement in the accuracy of the results. It requires significantly less computational efforts providing a simple physical picture in terms of atomic orbitals and hopping interaction.

Here, the atomic orbitals \( \varphi_m(r) \) are introduced, which are eigenfunctions of the Hamiltonian \( H_{at} \) of a single isolated atom. When the atom is placed in a crystal, this atomic wave function overlaps the adjacent atomic sites and so are not true eigenfunctions of the crystal Hamiltonian. The overlap is less when electrons are tightly bound, which is the source of the descriptor “tight-binding”. Any corrections to the atomic potential \( \Delta U \) required to obtain the true Hamiltonian \( H \) of the system, are assumed small:

\[
H(r) = \sum_{R_n} H_{at}(r - R_n) + \Delta U(r)
\]  \hspace{1cm} (1.10)
We can use this model with the parameter strengths to calculate the electronic structure of corresponding nanocrystals as a function of the size. We build the cluster shell by shell, starting from a central atom. For the tetrahedrally coordinated compounds in the zinc-blende structure, the central atom, say the cation, is surrounded by a shell of four anions. In turn each of these anions is coordinated by four cations, one of them being the central cation. The other three cations form a part of the next shell. The clusters are generated in this manner by successive addition of shells. Assuming a spherical shape of the cluster, the diameter ‘d’ is given by,

\[ d = a \left[ \frac{3N}{4\pi} \right]^{1/3} \]  

(1.11)

where ‘a’ is the lattice constant and N the number of atoms present in the nanocrystal. The Hamiltonian matrix for any given sized cluster is obtained from Equation with the atomic orbital basis and electronic parameter strengths and is diagonalized to obtain the eigenvalue spectra for the nanocrystal. Direct diagonalization methods are practical only for cluster sizes containing less than ca. 1500 atoms. For larger clusters, Lanczos iterative method can be used.

The band gap for a particular sized nanocrystal is then calculated by subtracting the energy of the top of the valence band TVB from that of the bottom of the conduction band BCB. However, the determinations of the TVB and the BCB become ambiguous due to the presence of dangling bonds at the surface of the nanocrystals. These nonbonded states lie in the band-gap region of the nanocrystals. These surface states need to be either selectively disposed off or passivated in order to remove the midgap states. Once the surface states are removed, the band gap can be easily determined.

### 1.7.3 Semi Empirical Pseudopotential (SEPM) Model:

A plane-wave semiempirical pseudopotential method with nonlocal potentials and spin-orbit coupling has been reported by Zunger et al. [2, 3] to calculate the electronic structure of semiconductor Q-dots. In this approach, they used direct
diagonalization to solve the single-particle equation for a quantum dot, namely,

\[
-\frac{1}{2}\Delta^2 + \sum_{n,\alpha} v^\alpha(|r - R_{n,\alpha}|) \psi_i(r) = E_i \psi_i(r)
\]  

(1.12)

where \( v^\alpha(r) \) is the screened pseudopotential of atom of type ‘a’ at position \( R_{n,\alpha} \).

The pseudopotential approach provides an accurate description of the wave function decay outside the Q-dot and of the interband coupling due to quantum confinement, which are critical for a correct evaluation of the polarization and Coulomb energies in small nanocrystals.

Here, the many-particle wave function \( \Psi_N \) of a system of \( N \) electrons in the conduction band of Q-dot is approximated by a single Slater determinant constructed from the wave functions \( \{\psi_n, n = 1, \ldots, N\} \) of the \( N \) single-particle states occupied by \( N \) electrons. The corresponding total energy is,

\[
E_N = E_0 + \sum_i (\epsilon_i^0 + \Sigma_{i}^{pol}) n_i + \sum_{i<j} (J_{i,j} - K_{i,j}) n_i n_j
\]

(1.13)

where \( \epsilon_i^0 \) are the conduction-band single-particle energy levels, \( \Sigma_{i}^{pol} \) are the polarization self-energies, \( J_{i,j} \) and \( K_{i,j} \) are the electron-electron Coulomb and exchange energies, respectively, and \( n_i \) are the occupation numbers of the conduction-band single-particle states (\( \Sigma_i n_i = N \)).

A similar equation holds for the total energy of a system of \( N \) holes in the valence band of the Q-dot:

\[
E_{-N} = E_0 + \sum_i (-\epsilon_i^0 + \Sigma_{i}^{pol}) p_i + \sum_{i<j} (J_{i,j} - K_{i,j}) p_i p_j
\]

(1.14)

Here \( p_i, p_j \) are the hole occupation numbers (\( \Sigma_i p_i = N \)), and the single-particle energies are taken with a minus sign indicating that the corresponding electron is removed from the dot. The ground state \( \Psi_N^0 \) of energy \( E_N^0 \) corresponds to the configuration that minimizes the total energy \( E_N \). It need not coincide with the configuration in which the single-particle levels are occupied in order of increasing energy.

As will be discussed in the following section, the exciton energies obtained from different models with the one obtained experimentally are compared. The SEPM calculations shows better fit to the experimental data as compared to the effective mass approximations, and for SEPM with Coulombic term showing the best [3].
1.8 Theoretical Model for Charge Transfer in Q-dots:

This section will illustrate in brief about the theoretical model for different ways of charge transfer with the Q-dots. It has been realized that the dielectric environment can profoundly affect the optical and transport properties of semiconductor Q-dots. Monodispersed Q-dots capped with organic molecules such as oleic acid or tri-n-octyl phosphine oxide (TOPO), dispersed in an organic electrolyte can be considered as a Q-dot of dielectric constant $\epsilon_{in}$ surrounded by a matrix having dielectric constant $\epsilon_{out}$ [2, 3, 36]. As illustrated in Figure 1.11, the process of charge transfer with Q-dots can be described in three ways, viz. (a) electron addition, (b) creation of non-interacting electron-hole pair, and (c) creation of an interacting electron-hole pair via optical excitation. We shall discuss these types in short as per the following.

1.8.1 Electron Addition:

The process of sequential addition of three electrons to an otherwise neutral Q-dot is depicted in Figure 1.11. At initial i.e. ground state electronic configuration, the system of energy $E_0$ will consists of neutral dot in the ground state and a Fermi reservoir at the reference energy $\epsilon_{ref} \equiv 0$. After addition of one electron to the conduction band edge $\epsilon_1$, the energy of the Q-dot is,

$$E_1[\epsilon_1^1] = E_0 + \epsilon_{c1}. \quad (1.15)$$

where, $\epsilon_{c1} = \epsilon_{c1}^0 + \Sigma_{c1}^{pol}$ is the quasiparticle energy. Here, $\epsilon_{c1}^0$ is single particle energy of the added electron with respect to the reference energy $\epsilon_{ref}$ in the absence of dielectric mismatch. It describes the contribution from the quantum confinement. The $\Sigma_{c1}^{pol}$ is called dielectric confinement, which describes polarization contribution arising due to the dielectric mismatch. It is the self energy of the added electron in electrostatic field generated by its own image charge due to the dielectric constant discontinuity ($\epsilon_{out} \neq \epsilon_{in}$) at the surface of the Q-dot [11, 30].

In the electron addition, the ‘charging energy’, $\mu_1$ required to load the first electron from the reservoir (working electrode in case of voltammetry) to an otherwise
Figure 1.11: A schematic illustrates, (a) loading of electrons into an otherwise neutral Q-dot, (b) the addition of one electron in one Q-dot and simultaneously creation of hole into other Q-dot i.e. creation of non-interacting electron-hole pair with quasi-particle gap ($\varepsilon_{qp}$), and (c) creation of interacting electron-hole pair due to optical transition called exciton in a single Q-dot, resulting into optical band gap. The optical band gap is lower than quasiparticle gap by electron-hole coulombic interaction energy ($J_{e1,h1}$). $\varepsilon_{in}$ and $\varepsilon_{out}$ are the dielectric constants of Q-dot and surrounding medium respectively. $e_1$, $h_1$, $e_2$ and $h_2$ are first and second excited states of electron and hole respectively.

Neutral Q-dot is given as,

$$\mu_1 \equiv E_1[e_1^1] - E_o = \varepsilon_{e1}$$  \hspace{1cm} (1.16)

The energy of Q-dots with two electrons added in the conduction band edge $e_1$ of the Q-dot is given by

$$E_2[e_1^2] = E_0 + 2\varepsilon_{e1} + J_{e1,e1}.$$  \hspace{1cm} (1.17)

And the ‘charging energy’, $\mu_2$ required to add this second electron is,

$$\mu_2 = E_2[e_1^2] - E_1[e_1^1] = \varepsilon_{e1} + J_{e1,e1}$$ \hspace{1cm} (1.18)

where, $J_{e1,e1}$ is total Coulombic interaction between the two electrons which includes contribution from direct electron-electron contribution (screened by the dielectric constant of the Q-dot) and the contribution from the interaction of one electron with the image charge of the other electron across the dielectric discontinuity at the surface [11, 30].

Similarly, the electrons will be added sequentially to the next energy level (i.e $e_2$ and so on) and the energy of the Q-dot will change accordingly.

The electron “addition energy”; the difference between the two charging energies is given as,

$$\Delta^{(e)}_{2,1} \equiv \mu_2 - \mu_1$$ \hspace{1cm} (1.19)
Figure 1.12: Differential conductance spectra of a PbSe-CdSe core-shell QD (top), a 4.3 nm PbSe QD (middle), and a 6.1 nm CdSe QD (bottom).

For the addition of the $N^{th}$ electron, it will be

$$\Delta_{N+1,N}^{(e)} \equiv \mu_{N+1} - \mu_N$$ (1.20)

In the same way, the expression can be derived for the addition of holes to (or removal of electron from) the valence band. The hole “addition energy” for the $N^{th}$ hole to the valence band of the Q-dot will be,

$$\Delta_{N+1,N}^{(h)} \equiv \mu_{N+1} - \mu_N$$ (1.21)

Thus, in an addition spectrum obtained from charging spectroscopies [37, 38] e.g. scanning tunneling spectroscopy, $\mu_N$ corresponds to the peak positions of the charging spectrum, while $\Delta_{N+1,N}$ corresponds to the spacings between these peaks. A typical scanning tunneling spectra recorded on PbSe-CdSe core-shell Q-dot, a 4.3 nm PbSe Q-dot and a 6.1 nm CdSe Q-dot are shown in Figure1.12.

1.8.2 Creation of Non-interacting electron-hole pair:

The formation of noninteracting electron-hole pair is demonstrated in the schematic shown in Figure 1.11(b). Overall, it can be describe as removal of electron from valence band edge $h_1$ of a neutral Q-dot (oxidation at the working electrode) and
placing it indirectly to the conduction band edge $e_1$ of an identical neutral Q-dot separated by an infinite distance (reduction at the counter electrode). The energy required by this process is the difference between ionization potential and the electron affinity and is called as quasiparticle gap ($\varepsilon_{qp}$). It is slightly different than optical band gap, which is the energy required to create an ‘interacting’ electron-hole pair or exciton within a dot as shown in Figure 1.11(c).

In the non-interacting electron-hole pair (refer, Figure 1.11(b)), the initial configuration consist of two neutral dots in the ground state and has total energy, $2E_0$.

The final configuration has energy, $E_1[e_1] + E_{-1}[h_1]$ where $E_1[e_1] = E_o + \varepsilon_{e_1} + \Sigma_{pol}^{e_1}$ and $E_{-1}[h_1] = E_o - \varepsilon_{h_1} + \Sigma_{pol}^{h_1}$. Here, the $E_{-1}[h_1]$ is the energy of the Q-dot with a hole in the highest occupied orbital $h_1$.

Therefore, the quasiparticle gap which is the difference between the energies of the final configuration and the initial configuration is,

$$
\varepsilon_{qp}^{gap} = E_1[e_1] + E_{-1}[h_1] - 2E_o = \varepsilon_{gap}^o + \Sigma_{pol}^{e_1} + \Sigma_{pol}^{h_1}
$$

Where, $\varepsilon_{gap}^o \equiv \varepsilon_{e_1} - \varepsilon_{h_1}$ is the single-particle gap, which can be estimated by the techniques such as tunneling spectroscopy [38], whereas voltammetric measurements give more realistic information as the data is obtained on the ensemble of Q-dots.

### 1.8.3 Optical Excitation

The optical gap as illustrated in Figure 1.11(c) differs from quasiparticle gap by the coulombic electron-hole interaction. It is the process of optically exciting an electron from the highest occupied molecular orbital (HOMO) $h_1$ to the lowest unoccupied molecular (LUMO) orbital $e_1$ of a neutral Q-dot.

The energy required by this process is the optical (or “excitonic” gap) $\varepsilon_{gap}^{opt}$.

$$
\varepsilon_{gap}^{opt} = \varepsilon_{gap}^{qp} - J_{e_1,h_1}
$$

where, $J_{e_1,h_1}$ is the electron-hole Coulombic energy. It consists of a contribution from direct Coulomb term which does not depend on the dielectric constant of the surrounding medium $\epsilon_{out}$ and a polarization contribution $J_{\epsilon_1,h_1}^{pol}$ which strongly depends on dielectric constant of the environment $\epsilon_{out}$ and cancel out self-energy.
Figure 1.13: Comparison of exciton energies determined from effective mass approximation with and without Coulombic term, from SEPM theory with and without Coulombic term and the one obtained experimentally.

contribution $\Sigma^{po}_{e_1} + \Sigma^{po}_{h_1}$ to the quasiparticle gap. As a result, the optical gap depends weakly on the dielectric environment.

This could be the reason for the deviation of band gap determined from effective mass approximation for the small size clusters as for them the dielectric environment will be the determining factor. In Figure 1.13, the band gap values determined from effective mass approximation and semi-empirical pseudopotential calculations with and without Coulombic term are compared with the experimental values. It has been observed that the SEPM model with Coulombic term gives best fit to the experimentally determined values [3, 36]. Therefore, we shall mainly consider the theoretical results from the SEPM with Coulombic term to compare the results obtained from the present study.
1.9 Cyclic Voltammetry as a Tool to Study the Charge Transfer Processes in Q-Dots

Here, we shall discuss in brief the use of cyclic voltammetry (CV) [39] as a tool to study the charge transfer processes in the quantum dots.

1.9.1 A Brief Introduction to Cyclic Voltammetry:

Among all the methods available for studying electrode processes, potential sweep methods are probably most widely used. It consists of applying continuous time varying potential to the working electrode [40] resulting into the occurrence of different processes at the electrode surface. It includes, oxidation and reduction reactions of electroactive species (Faradaic reactions), possible adsorption of species, and a capacitive current due to double layer charging. This method can be used to study the mechanism of electrochemical reactions, for the identification of the species present in solution and for semiquantitative analysis of reaction kinetics.

In cyclic voltammetry, the potential is scanned starting from the initial potential \( E_i \) linearly toward some stopping potential at time \( t = t_1 \). On reaching \( t = t_1 \), the scan direction is swept towards \( E_{min} \), then inverted and swept until \( E_{max} \). The scan direction can be positive or negative and in principle, the sweep rate can have any value. The important parameters to be considered while doing cyclic voltammetry measurements are, the initial potential \( (E_i) \), the initial scan direction, the scan rate \( (\nu) \), the maximum potential \( (E_{max}) \), the minimum potential \( (E_{min}) \) and the final potential \( (E_f) \).

A typical electrode reaction involves the transfer of charge between electrode and electro-analyte species in the electrolyte solution. This involves several steps, typically (i) reactants moves to the interface which is termed as mass transport, (ii) Electron transfer can then occur between electrode and reactant near the electrode surface. (iii) the product can move away from the electrode to allow fresh reactant to the surface. The electrode reaction is driven by the application of a voltage (units of volts) \( V = \text{Joule/Coulomb} \) which is simply the energy required to move the charge. Application of a voltage to an electrode therefore supplies electrical energy. Since electrons possess charge, an applied voltage can alter the ‘energy’ of
the electrons within a metal electrode. The behavior of electrons in a metal can be partly understood by considering the Fermi-level. Metals are comprised of closely packed atoms which have strong overlap between one another. A piece of metal therefore does not possess individual well defined electron energy levels that would be found in a single atom of the same material. Instead a continuum of levels are created with the available electrons filling the states from the bottom upwards. The Fermi-level corresponds to the energy at which the ‘top’ electrons sit. This level is not fixed and can be moved by supplying electrical energy. Therefore we can alter the energy of the Fermi-level by applying a voltage to an electrode.

Figure 1.14 shows a schematic representation of the Fermi level of the electrode at different applied potential and the corresponding charge transfer processes between electrode and analyte species in the solution. In CV, the potential is cycled linearly with time between two potential values. When the Fermi level of the electrode matches (within $\pm kT$) with the energy level of species (e.g. ensemble of Q-dots) in solution (refer, Figure 1.14), the electron transfer will take place, which leads to a
current response.

Faradaic current \(I_f\) will be generated due to the electrode reaction occurring at relevant potential. There is also a contribution of capacitive current which is generated due to the change in the double layer charge with sweeping the potential. Therefore, the total current is,

\[
I = I_c + I_f = C_d \frac{dE}{dt} + I_f = \nu C_d + I_f
\]

where, \(I_c\) is the capacitive current which is proportional to the scan rate (sweep rate), \(C_d\) is the differential capacity of double layer in Farads (F).

Consider a reaction,

\[
O + ne^- \rightarrow R
\]

with only the species ‘O’ initially present with the electrode held initially at potential \(E_i\) where no electrode reaction occurs. The initial scan direction is therefore negative. The observed faradaic current depends on the kinetics and transport by diffusion of the electroactive species. It is thus necessary to solve the equations for diffusion

\[
\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \quad (1.26)
\]

\[
\frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2} \quad (1.27)
\]
with following boundary conditions,

\[ t = 0 \quad x = 0 \quad C_O(x, 0) = C^*_O \quad C_R(x, 0) = 0 \] (1.28)

\[ t > 0 \quad x \to \infty \quad C_O(x, t) \to C^*_O \quad C_R(x, t) = 0 \] (1.29)

The flux balance will be

\[ t > 0 \quad x = 0 \quad D_O \left( \frac{\partial C_O(x, t)}{\partial x} \right)_{x=0} + D_R \left( \frac{\partial C_R(x, t)}{\partial x} \right)_{x=0} = 0 \] (1.30)

The potential will be swept linearly at a rate \( \nu \) (V/s) so that the potential at any time ‘t’ will be, \( E(t) = E_i - \nu t \).

1.9.2 Current Response for Different Systems:

**Reversible System:** If we can assume that the rate of electron transfer is rapid at the electrode surface, so that species O and R in the reaction \( (O + e \rightleftharpoons R) \), immediately adjust the ratio dictated by the Nernst equation,

\[ \frac{C_O(0, t)}{C_R(0, t)} = f(t) = \exp \left[ \frac{nF}{RT} (E_i - \nu t - E^0) \right] \] (1.31)

Solution of the diffusion equations with numerical inversion leads to

\[ I = -nFA[O]_\infty (\pi D_O \sigma)^{1/2} \chi(\sigma t) \] (1.32)

where \( \chi(\sigma t) \) is a pure number constant and

\[ \sigma = \left( \frac{nF}{RT} \right) \nu \] (1.33)

\[ \sigma t = \left( \frac{nF}{RT} \right) \nu t = \frac{nF}{RT} (E_i - E) \] (1.34)

Thus, the current is dependent on the concentration and square root of scan rate. The function \( \pi^{1/2} \chi(\sigma t) \) and hence the current reaches a maximum where \( \pi^{1/2} \chi(\sigma t) = 0.4463 \). So, the peak current, \( i_p \) is

\[ i_p = 0.4463 \left( \frac{F^3}{RT} \right)^{1/2} n^{3/2} A D_O^{1/2} C^*_O \nu^{1/2} \] (1.35)

Where, \( A \) is the surface area of the electrode in cm\(^2\), \( D_O \) is the diffusion coefficient of species O (cm\(^2\)/s), \( \nu \) is the scan rate (V/s). At temperature \( T = 25^\circ C \),

\[ i_p = (2.69 \times 10^5)n^{3/2} A D_O^{1/2} C^*_O \nu^{1/2} \] (1.36)
Then the peak potential at 25°C will be

\[ E_p = E_{1/2} - 1.109 \frac{RT}{nF} = 28.5/n \text{ (in mV)} \quad (1.37) \]

Thus, for reversible wave \( E_p \) is independent of \( \nu \) and \( i_p \) (and current at any point) is proportional to \( \nu^{1/2} \). This proportionality relation indicates the process being diffusion controlled.

**Totally Irreversible System:**

For a totally irreversible one-step, one-electron reaction \((O + e \rightarrow R)\), the Nernstian boundary condition will be replaced by following equation,

\[
\frac{i}{FA} = D_O \left[ \frac{\partial C_O(x,t)}{\partial x} \right]_{x=0} = k_f(t)C_O(0,t) \quad (1.38)
\]

where,

\[
k_f(t) = k^o \exp(-\alpha f \left[E(t) - E^{o'}\right]) \quad (1.39)
\]

After numerical analysis, a solution to the above equation will be,

\[
i = FAC^*_O D^{1/2}_O \nu^{1/2} \left( \frac{\alpha F}{RT} \right)^{1/2} \pi^{1/2} \chi(\alpha f \nu t) \quad (1.40)
\]

Again, the current \( i \) at any point on the wave varies with \( \nu^{1/2} \) and \( C^*_O \).

The function \( \chi(\alpha f \nu t) \) and hence the current reaches a maximum where \( \pi^{1/2} \chi(\alpha f \nu t) = 0.4958 \). So, the peak current, \( i_p \) is given by,

\[
i_p = (2.99 \times 10^5)\alpha^{1/2} A C^*_O D^{1/2}_O \nu^{1/2} \quad (1.41)
\]

and the peak potential is given by,

\[
E_p = E^{o'} - \frac{RT}{\alpha F} \left[ 0.780 + \ln \left( \frac{D^{1/2}_O}{k^o} \right) + \ln \left( \frac{\alpha f \nu}{RT} \right)^{1/2} \right] \quad (1.42)
\]

At 25°C,

\[
|E_p - E_{p/2}| = \frac{1.857RT}{\alpha F} = \frac{47.7}{\alpha} \text{ (in mV at 25°C)} \quad (1.43)
\]

For totally irreversible wave, the peak potential \( E_p \) is a function of scan rate. Thus, the peak position shifts in negative direction (by \( 30/\alpha \text{ mV at 25°C for each tenfold increase in } \nu \)) with the applied negative potential.

An alternate expression for the current can be written as,

\[
i_p = 0.227 FAC^*_O k^o \exp[-\alpha f (E_p - E^{o'})] \quad (1.44)
\]
Thus, a plot of $\ln i_p$ vs $E_p - E^\circ$ determined at different scan rates should be linear with slope of $-\alpha f$ and an intercept proportional to $k^\circ$.

**Quasireversible System:**

Matsuda and Ayabe [41] coined the term ‘quasireversible’ for the reactions where the electron transfer kinetics of the oxidation and reduction reactions have to be considered simultaneously. As a general conclusion, the extent of irreversibility increases with increase in sweep rate, while at the same time there is a decrease in the peak current relative to the reversible case and an increase in separation between anodic and cathodic peaks.

Peak shape and associated parameters are conveniently expressed by a parameter, $\Lambda$, which is a quantitative measure of reversibility, being effectively the ratio kinetics/transport,

$$\Lambda = \frac{k^\circ}{(D_O^{1-\alpha} D_R^\alpha f \nu)^{1/2}}$$

when $D_O = D_R = D$

$$\Lambda = \frac{k^\circ}{(D f \nu)^{1/2}}$$

The current is given by,

$$i = FAD_O^{1/2} C^\circ f^{1/2} \nu^{1/2} \Psi(E)$$

where,

$$\Psi(E) = \frac{i}{FAD_O^{1/2} C^\circ (nF/RT)^{1/2} \nu^{1/2}} ; \text{ for } D_O = D_R = D$$
1.9.3 Determination of Band Structure Parameters of Q-Dots using Cyclic Voltammetry:

As explained in section about CV, when the energy of electrons on the electrode matches with the energy level of the analyte species (Q-dots in our case), a charge transfer takes place. For example, if we apply more negative potential, the Fermi level of the electrode will raise. At particular potential, if the electron from electrode finds more suitable vacant energy level on Q-dots then the electron will get transferred from electrode to the Q-dot. It will results into the generation of cathodic current due to the reduction of Q-dots. On the other hand, if we apply more positive potential, the Fermi level of the electrode will decrease with the applied positive potential and reaches to optimum value. At particular potential, if the electron from the highest filled state of the Q-dot i.e. valence band edge finds more suitable energy level at electrode, the electron will be transferred from Q-dots to the electrode. This will results into the generation of anodic current due to oxidation of the Q-dots. Since the electron transfer processes are mediated through the conduction band edge and valence band edge, it will mark the positions of the respective energy levels. The difference between these two peaks (i.e. reduction and oxidation peak) will corresponds to what is called as electrochemical band gap. Since, the charge transfer is taking place on physically isolated particles, this electrochemical gap in fact coincides with the quasiparticle gap.

With this brief background, we shall now discuss and review some of the examples of voltammetric determination of band structure parameters in semiconductor Q-dots systems. The first report related to this particular topic was by Haram et al. [42] where they have carried out voltammetric measurements on various sized thiol capped CdS Q-dots dispersion in DMF. The separation between reduction (C1) and oxidation (A1) peaks was found to be comparable to the optical band gap calculated from absorption spectra. Thus, a good correlation between the optical band gap obtained from UV-vis absorption spectroscopy and electrochemical band gap determined from voltammetric measurements has been observed. On a qualitative level, a decrease in A1-C1 peak separations with increasing particle size was observed, as predicted. The nature of charge transfer to Q-CdS particles was
observed to follow electron transfer followed by chemical reaction (EC) mechanism. Thus, the simple electrochemical methods can provide useful information concerning the stability of Q-dots upon charge transfer.

This study was followed and supported with extensive work related to the band structure parameters in different Q-dots by using voltammetry. Thomas Nann and co-workers [43] carried out CV measurements on Q-CdSe to determine its ionization potentials, electron affinities and quantum confinement. The results were compared to values obtained from spectroscopic measurements, especially UV-vis absorption and photoluminescence spectra. The results were in good agreement with the theoretical expectations and spectroscopic data. This method was found to be comparatively easier than, e.g., the ultraviolet photoelectron spectroscopy and includes the additional advantage of compatibility to analogous measurements with conducting polymers. This is of special interest for nanocrystal/conducting polymer composite materials used for novel light-emitting or photovoltaic devices and polymer microelectronics.

In order to study the charge transfer mechanism, similar measurements have been reported on several conducting polymers and polymer/CdSe nanocrystal composites [44]. It was found that most of the composites, used so far, undergoes charge transfer processes but with relatively slow kinetics. The resulting data give an overview over the potential qualification of these hybrid bulk heterojunction composites for the use in electroluminescence devices and solar cells.

Bard and co-workers reported differential pulse voltammetry (DPV) measurements on TOPO-capped CdTe Q-dots in dichloromethane and benzene-acetonitrile mixture [45]. It showed two anodic and one cathodic peaks of the NPs themselves and an additional anodic peak resulting from the oxidation of reduced Q-dots. The electrochemical band gap (ca. 2.1 eV) between the first anodic and cathodic DPV peaks was close to the value (2.0 eV) obtained from the absorption spectrum. They also carried out electrogenerated chemiluminescence measurements on CdSe and CdTe Q-dots.

Adam Pron and co-workers have studied electrochemical properties of CdSe Q-dots with electrochemically inactive surface ligands (TOPO) in comparison with the analogous nanocrystals containing electrochemically active oligoaniline ligands.
The obtained HOMO and LUMO levels have been found in good agreement with the one determined from photoluminescence studies and those predicted theoretically. Ligand exchange with aniline tetramer significantly influence the voltammetric peaks associated with the oxidation (HOMO) and the reduction (LUMO) of the Q-dots, which are shifted to higher and lower potentials, respectively. These shifts are interpreted in terms of the positive ligand charging which precedes the oxidation of the nanocrystals and the insulating nature of the ligand in case of the Q-dot reduction.

The influence of grafting is manifested by a shift in the onset of ligand oxidation as compared to the case of “free” model compound. Since both components (ligands and nanocrystals) mutually influence their electrochemical and spectroelectrochemical properties, the newly developed system can be considered as a true molecular hybrid. Such hybrids are of interest because the potential zone of ligand electroactivity is well separated from that of the nanocrystals and, as a result, the organic part can be electrochemically switched between the semiconducting and conducting states with no change in oxidation state of the Q-dots. The newly developed system offers therefore the possibility of an electrical addressing of individual Q-dots via the conducting ligands.

The use of ionic liquid (IL) as an electrolyte has also been made for CV measurements pertaining to study the charge transfer kinetics in Q-dots. Kucur et al. [47] has developed a method to phase transfer the Q-dots from nonpolar solvents to IL. CV measurements with this novel dispersion were used to estimate the potentials of differently sized colloidal CdSe Q-dots as well as the rate of electron transfer processes. These experiments are not only an intriguing combination of two exciting fields of science, but also enable future experiments, such as the charge-transfer rates of surface defects in semiconductor Q-dots, to be measured by CV.

Colloidal, monodisperse CdSe Q-dots were homogeneously dispersed in an ionic liquid and investigated by means of CV. Almost all known defect states in semiconductor Q-dots were quantitatively measured with this nonoptical method (including nonradiative defect states). Variation of the illumination and temperature resulted in excitation of defect-trapped electrons into the conduction band. Thus for the first time, defect states in Q-dots were correlated with those in the corresponding
Figure 1.16: The values of conduction band edge (*) and valence band edge (*) of CdSe Q-dots as a function of size, obtained from CVs. For comparison, the SEPM results of Wang and Zunger and the experimental results of Kucur et al. and Querner et al. are also plotted.

Recently, we have reported the determination of band structure parameters viz. valence band edge, conduction band edge and quasiparticle gap in CdSe Q-dots as a function of size using CV [36]. The results obtained from voltammetry were in good accordance with the spectroscopic data and the theoretical predictions. To our knowledge, the fit obtained to the reported calculations based on semi-empirical pseudopotential (SEPM) method especially in the strong size-confinement region is the best reported, so far. For the smallest CdSe Q-dots, the difference between the quasi-particle gap and the optical band gap gives the electron-hole Coulombic interaction energy \( J_{e1,h1} \). The interband states seen in the photoluminescence spectra were verified with the CV measurements.

Overall, the voltammetric measurements have shown great potential as a tool to determine the band structure parameters and size quantization effect in semiconductor Q-dots.
1.10 Objectives of the Present Thesis:

From the above discussion, it is clear that determination of band structure parameters in semiconductor Q-dots plays the pivotal role for the development of semiconductor based nanotechnology. Researchers are attempting to engineer the band structure of semiconductor nanomaterials through the manipulation of different parameters such as size, shape and stoichiometric and non-stoichiometric composition variation, etc. Many attempts have been devoted towards the determination of these parameters in different nanomaterials including Q-dots. Yet, several lacunae still plague for the complete understanding about many physico-chemical phenomena related to semiconductor nanomaterials.

Based on the present wisdom and challenges from the reported studies related to the determination of band structure parameters in semiconductor Q-dots, we through this thesis work have tried to surmount some of the problems in this field. The following objectives have been set for the present thesis work.

- Till date most of the studies have been carried out related to the determination of band structure parameters of n-type semiconductor Q-dots e.g. CdS and CdSe. However, less attention has been paid towards the determination of band structure parameters of p-type semiconductor Q-dots. Therefore, to overcome this, the band structure parameters of p-type semiconductor Q-dots as a function of size have been determined using cyclic voltammetry measurements. CdTe quantum dots (Q-CdTe) have been chosen as a model system for this purpose.

- The effect of size quantization on the band structure parameters of semiconductor Q-dots are well studied and reported in the literature. On the other hand, the studies related to the effect of composition on these parameters are comparatively less studied. Therefore, the effect of alloying while keeping the size constant on the band structure parameters of the semiconductor Q-dots have been studied. Voltammetric measurements on CdS$_x$Se$_{1-x}$ alloy Q-dots model system would reveal the band structure parameters and band gap bowing effect in this system.
• In addition to the determination of band structure parameters, the effect of electrochemical charge injection on the opto-electronic properties of semiconductor Q-dots have been studied. For this purpose, Q-CdSe monolayer on ITO electrode have been used and potential was applied to it in both the direction i.e. positive as well as negative potential direction and the effect of charge injection on photoluminescence of Q-CdSe monolayer have been studied.

• Similarly, the effect of chemical charge injection on the photoluminescence of semiconductor Q-dots have been studied. Ten different metal ions including physiologically important ones have been used for this purpose. Among these, Ag ions have found to quench the emission very effectively. Based on this, a selective photometric detection of Ag ions using luminescence quenching of citrate capped CdSe have been proposed.

We will try to address these objectives throughout the present thesis work. Based on the data procured in these studies, the work has been organized and presented in the form of different chapters.
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