Chapter 1

Review of Literature
1.1 Quantum confinement effect

1.1.1 Quantum Confined Atom (QCA)

The phenomenon of quantum confinement is defined as the influence of electronic wave functions by size restriction. In a semiconductor quantum dot (QD), the confinement of the electron or hole orbit (Bohr diameter) influences the excitonic energy levels in a significant manner [1.1-4]. The band gap of the semiconductor increases rapidly when the size of the quantum dot (nanocrystal) approaches the Bohr diameter [1.3]. Properties such as the band gap and characteristic emission of isolated semiconductor nanocrystals are greatly influenced by the size in the 2-10nm range.

A novel approach where by incorporating a localized impurity within the quantum dot so as to replace the excitonic emission of the quantum dot by the impurity emission has been reported by Bhargava et al. [1.5-6]. This concept has shown that one can improve the efficiency of the system significantly by caging an atom in a nanocrystal referred as ‘Quantum Confined Atom (QCA)’. In these doped nanocrystals the characteristic emission is associated with the caged atomic ion and is separated in energy from the excitation, i.e. there is very little self-absorption as in the QD system. Since the properties of the activators, particularly the luminescent efficiency critically depends on the size of the cage; they prefer to refer these doped nanocrystals as quantum confined atom-based nanophosphors (QCA-NP).

In QCA, a single atomic-ion is caged in a host-nanoparticle of 2-5 nm as shown in figure 1.1. Under the influence of the confinement provided by the host-nanoparticle, the properties of a single atom are modified without hardly any change in the property of the host. The size of the ‘cage’ is critical in modifying the properties of the quantum-confined atom. The recent results on high quantum efficiency in QCA based nanophosphors, gives us the confidence of producing the nanophosphors for LEDs and display successfully within the scope of this undertaking.
The schematic representation in figure 1.1 shows atomic ion as charged cloud that would be affected by the quantum confinement. The emission wavelength of these localized impurities does not depend on the size of the quantum dot (host). The host is also chosen so as to reduce the non-radiative contribution of the surfaces, but yield efficient transfer of carriers from the host to the impurity (transition or rare-earth dopants) without changing internal electronic levels. [1.7-9].

The emission characteristics of quantum dots (QD) are:

i. The size of the quantum dot singularly determines the wavelength of its emission.

ii. The smaller the size of the QD, higher is the energy of emission. For example, the wavelength of emission shifts toward blue as the size of the QD decreases.

iii. The efficiency of emission is high but its value depends critically on size and the surface-preparation of the QD. In order to have high efficiency, the QD must be coated with a passivation layer.

iv. The QD-emission is due to recombination of electron and hole of the exciton that is self-absorbed reducing the external quantum efficiency.

v. The color which is due exciton-recombination, changes with size. i.e. one can tune the wavelength of emission by varying the size of the QD-particle, an advantage.

vi. However, if the size of the QD increases due to possible agglomeration, the color of emission will change. Hence, reliability over time becomes an issue. This is a serious deterrent for many applications where QDs are used as emitter. To prevent the agglomeration, a passivating coating as a shell around QD has to be developed and used. The coating can never be fully efficient.
vii. The quantum dot is not a classical phosphor system since in true phosphors; the light emission is due to electron-hole recombination that occurs at an external impurity (activator) rather than from exciton.

1.1.2 Finite size effect in semiconductor nanocrystals: Energy Gap Tunability

A semiconductor nanocrystal is a crystalline arrangement of hundreds to thousands of atoms, with a bulk structure similar to the macrocrystalline compound. Starting from the macrocrystalline semiconductor, as the particle size is reduced to the nanosize regime, there is an increase in the ratio between the number of surface atoms and the total number of atoms. This increase in the surface area originates an increasing number of disrupted chemical bonds at the surface, therefore creating an excess of energy when compared to the bulk structure. This increase in the surface energy is thermodynamically unfavorable. Nanocrystals form a metastable phase, in which surface reconstruction occurs. This leads to chemical and structural environments distinct from those of the bulk. Unless nanocrystals are properly stabilized, with time they will grow to yield the stable metacrystalline phase, although the kinetics involved may be slow. In a compound semiconductor, the surface in the nanocrystal is different from the macroscopic material surface.

In the simplest treatment, electrons and holes in an isolated semiconductor nanoparticle can be modeled as independent particles (neglecting coulombic interactions) in an infinite spherical well. Under this assumption, the energy eigenvalues $E_{nl}$ are given by:

$$E_{nl} = \frac{\hbar^2 \eta_{nl}^2}{2ma^2}$$  \hspace{1cm} (1.1)

where $\eta_{nl}$ are the roots of spherical Bessel functions with $n$ being the number and $l$ the order of the root, $a$ is the particle radius, and $m$ the effective mass of the charge carrier (electron or hole). Each state with a particular orbital quantum number $l$, is $2l+1$ times degenerate, as the magnetic quantum number takes values from $-l$ to $l$. An important difference between the energy levels of a particle in a quantum well (such as an electron in a nanoparticle) and in a coulombic well (such as an electron in a hydrogen atom) is that in the former case the spacing between the levels increases with an
increase in the quantum number, while in the latter case it decreases and eventually leads to a continuum. So far we have considered electrons and holes to be non-interacting, but in reality they do interact through coulombic attraction, which may lead to the formation of a bound two-particle system, known as an exciton. The energy levels of an unconfined exciton are similar to those of the hydrogen atom and are given by:

\[ E_n(k) = E_g - \frac{R_y^*}{n^2} + \frac{\hbar^2 k^2}{2\mu} \]  

(1.2)

where \( E_g \) is the band gap energy, \( R_y^* \) is the exciton Rydberg energy (for a hydrogen atom, \( = 13.6\text{eV} \)), \( k \) is the wave vector of the center of mass of the exciton, and \( \mu \) is the reduced mass of the exciton. The Rydberg energy \( R_y^* \) for an exciton is given by:

\[ R_y^* = \frac{e^2}{2\varepsilon a_B} = \frac{e^2}{2\varepsilon} \times \frac{\mu e^2}{\varepsilon \hbar^2} = \frac{\mu e^4}{2\varepsilon^2 \hbar^2} \]  

(1.3)

where \( \varepsilon \) is the dielectric constant of the crystal, \( a_B \) is the excitonic Bohr radius, and \( \mu \) is the reduced mass of the exciton.

The extent to which quantum confinement affects the energy levels depends on the ratio of the nanoparticle radius and excitonic Bohr radius in the ground state, \( a/a_B \). Two confinement limits are defined on the basis of this ratio. When \( a \geq a_B \), we have the “weak confinement” limit, while \( a \ll a_B \) corresponds to the “strong confinement” limit [1.10].

**i. Weak confinement:** The electrons and holes inside a semiconductor nanoparticle are said to be weakly confined when the radius of the particle is quite small but still a few times larger than the Bohr radius \( a_B \) and there is a confinement of the center-of-mass motion. In this case, the energy levels of an exciton, \( E_{nlm} \), are given by,

\[ E_{nlm} = E_g - \frac{R_y^*}{n^2} + \frac{\hbar^2 \eta_{nlm}^2}{2\mu a^2} \]  

(1.4)
However, the blue shift in the energy of the ground state of the exciton is small compared to the binding energy $R_y^*$, which is why the term ‘weak confinement’ is used.

**ii. Strong confinement:** Particle size which becomes comparable to De-broglie wavelength of electrons in a semiconductor. When the particle radius is small compared to the Bohr radius, the exciton is said to be strongly confined. In this case, even though the electron and hole are confined within a nanoparticle, they do not form a bound state because of the large zero-point energy. The ground state energy (with both the electron and hole in their 1s states) in this case can be expressed as Brus equation [1.11]

$$E_{1s1s} - E_g = \frac{\hbar^2 \pi^2}{2\mu a^2} - \frac{1.786e^2}{\varepsilon a} - 0.248R_y^* \quad (1.5)$$

In the above Brus equation the first term is the kinetic energy of both the electron and the hole ($1/a^2$ dependence). The second term represents the coulomb energy ($1/a$ dependence). For semiconductors with small dielectric constants, the spatial correlation between the charge carriers can be significant, hence a third term corresponding to effective Rydberg energy ($R_y^*$) has to be taken in account. Here the shift in the band gap energy is quite significant compared to weak confinement limit.

A comprehensive treatment of the theory of semiconductor QDs can be found in the book of Banyai and Koch [1.12]. An increasing sophistication of theoretical concepts such as effective mass approximation (EMA) and linear combination of atomic orbitals (LCAO) has resulted in a steadily improving understanding of the band structure of semiconductor QDs and their optical properties [1.13-15]. Along with the blue shift in the band gap and excitonic levels, a reduction in particle size also causes an enhancement in the oscillator strengths ($f$) of the optical transitions. This can be understood as follows. The probability of an optical transition in a bulk semiconductor is proportional to the probability of finding the electron and hole in the same unit cell of the crystal. Hence the oscillator strength ($f_{QD}$) is inversely proportional to $a_h^3$. The transition probability is therefore proportional to the spatial
restriction of carrier motion in its volume due to quantum confinement and we obtain [1.10]

$$\frac{f_{\text{QD}}}{f} \sim \frac{a^3}{a^2}$$  \hspace{1cm} (1.6)

which implies that an enhancement in oscillator strength is evident only when the size of the QD decreases below the Bohr radius.

In the energy level diagram the difference between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) increases with decreasing particle dimension as shown in figure 1.2. This has been experimentally confirmed and has been observed as blue shift in the band edge of the optical spectrum.

**Figure 1.2:** Left, schematic evolution of the electron structure between macroscopic solids and nanocrystals of decreasing size (the filling of electron levels and energy bands are not indicated). HOMO and LUMO represent respectively the topmost occupied level and the bottommost empty level. Right, Theoretical calculation of the gap calculated from the equation for the nanocrystals of different semiconductors ZnO, ZnSe, CdS, CdSe and GaAs.

### 1.1.3 Quantum dots

Quantum dots are small devices that contain a tiny droplet of free electrons. They are fabricated in semiconductor materials and have typical dimensions is of few nanometers. The size and shape of these structures and therefore the number of
electrons that contain can be precisely controlled; a quantum dot can have anything from a single electron to a collection of several thousands. The physics of quantum dots shows parallels with the behavior of naturally occurring quantum systems in atomic and nuclear physics. As in an atom, the energy levels in a quantum dot become quantized due to the confinement of electrons. Unlike atoms however, quantum dots can be easily connected to electrodes and are therefore excellent tools to study atomic-like properties. There is a wealth of interesting phenomenon that has been measured in quantum dot structures over the past decade.

1.1.3.1 Artificial atoms

The three-dimensional (3D) spherically symmetric potential around atoms yields degeneracies known as shells, 1s, 2s, 3s, 3p,…….Each shell can hold a specific number of electrons. The electronic configuration is particularly stable when these shells are completely filled with electrons, occurring at ‘magic’ atomic numbers 2, 10, 18, 36,….In a similar way, the symmetry of two dimensional (2D), disk-shaped dots leads to a shell structure with magic numbers 2, 6, 12, 20….The lower degree of symmetry in 2D results in a different sequence of magic numbers than in 3D.

By measuring electron transport through quantum dots, a periodic table of artificial 2D elements can be obtained. For this purpose, dots are connected via potential barriers to source and drain contacts. If the barriers are thick enough, the number of electrons on the dot, N, is a well defined integer. This number changes when the electron tunnels to and from the dot. However, due to Coulomb repulsion between electrons, the energy of a dot containing N+ 1 electron is larger than when it contains N electrons. Extra energy is therefore needed to add an electron to the dot. Consequently, no current can flow which is known as the Coulomb blockade (figure 1.3). The blockade can be lifted by means of a third electron close by, known as the gate contact. A negative voltage applied to this gate is used to supply the extra energy and thereby, change the number of free electrons on the dot. This makes it possible to record the current flow between source and drain as the number of electrons on the dot, and hence its energy, is varied. Quantum dots are 2D analogies for real atoms. But since they have much larger dimensions they are suitable for experiments that can not be carried out in atomic physics. It is especially interesting to observe the effect of a magnetic field, B, on the atom-like properties. A magnetic flux quantum in an atom
requires typically a B-field as high as $10^6$ T whereas for dots this is of the order of 1 T, which is experimentally accessible.

**Figure 1.3:** Coulomb blockade in electron transport

### 1.1.3.2 Magic number or full shell clusters

Clusters with full shell atomic lattices are known as 'magic number' clusters, they have an extra stability due to this packing nature [1.16]. The number of surface atoms $S_n$ in `$n^{th}$ shell for different crystal system (table 1.1) is as follows,

<table>
<thead>
<tr>
<th>Polyhedron</th>
<th>Formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Truncated tetrahedron</td>
<td>$S_n = 14 n^2 + 2$</td>
</tr>
<tr>
<td>Cuboctahedron or twinned cuboctahedron</td>
<td>$S_n = 10 n^2 + 2$</td>
</tr>
<tr>
<td>Truncated octahedron</td>
<td>$S_n = 30 n^2 + 2$</td>
</tr>
<tr>
<td>Truncated cube</td>
<td>$S_n = 46 n^2 + 2$</td>
</tr>
<tr>
<td>Triangular prism</td>
<td>$S_n = 4 n^2 + 2$</td>
</tr>
</tbody>
</table>

The atomic arrangement in magic number crystals is more compact and symmetrical which is favored to non-compact and unsymmetrical arrangements. This compactness gives more stability for a crystalline solid. For example, the atomic arrangement of three, four, six or eight spheres of equal or nearly equal sizes are more compact and symmetrical than five, seven or nine spheres.
1.2 Electronic and optical properties of microcrystallites (zero-dimensional systems): Theoretical models

With 0D systems there is confinement in all three dimensions, and these systems include microcrystallites, nanocrystals, clusters, colloids and quantum dots. Reducing the radius of the cluster (assumed to be spherical) results in the blue shift of the characteristic transition energies such as excitons, and several examples are given in figure 1.4 taken from Ekimov et al. [1.17]. He also makes several general points concerning such quantum confinement effects.

i. As the radius $R$ becomes very small, the energy levels for carriers change from continuous bands to a ladder of discrete levels.

ii. There is enhanced volume-normalized oscillator strength of exciton features as $R$ is reduced. This arises because the oscillator strength becomes concentrated over sharp electron-hole transitions, rather than being distributed over a continuum of states as for the case of bulk semiconductors.

iii. There is enhanced exciton nonlinearity and a reduction in optical power required for optical saturation relative to the bulk semiconductor. Cooperation between quantum dots for optical nonlinear effects is also an important practical factor (for example Takagahara (1992)) [1.18].

iv. Most theoretical treatments assume spherical shapes for the crystallite, and this is a reasonable approximation in many cases (Goldstein et al. 1992) [1.19].
Figure 1.4: Exciton spectra at 4.2K for CuCl and CuBr microcrystallites, and excitons and electron-hole pair spectra for CdS. For CuCl, \( k = 31 \text{ nm} \) (curve 1), 2.9 nm (curve 2) and 2.0 nm (curve 3); for CuBr, \( k = 24 \text{ nm} \) (curve 1), 3.6 nm (curve 2) and 2.3 nm (curve 3); for CdS, \( k = 33 \text{ nm} \) (curve 1), 2.3 nm (curve 2), 1.5 nm (curve 3) and 1.2 (curve 4). (After Ekimov 1991)

1.2.1 Tight binding model (TBM) and Effective mass approximation (EMA)-A review

On a quantitative footing, various different theoretical approaches have been employed to account for the variation in the electronic structure of nanocrystallites as a function of its size. The first explanation for the size dependence of electronic properties in nanocrystals was given by Efros and Efros [1.28] It is based on the effective masses of the electron \( (m_e^*) \) and the hole \( (m_h^*) \). Known as the effective mass approximation (EMA), it is solved by taking various choices for the electron and hole wave functions and solving the effective mass equation variationally. In most
EMA calculations, the confining potentials for the electron and the hole have been assumed infinite [1.20-25]. Therefore, the electron and the hole wave functions vanish at and beyond the surface of the nanocrystal, without the possibility of any tunneling. In the strong confinement regime, where \( R \), the nanocrystals radius, is much smaller than \( a_B \), the Bohr exciton radius, Brus proposed [1.22] the following expression [equation 1.5] for the band gap of the finite-sized system:

\[
E(a) = E_g + \frac{\hbar^2}{2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \frac{\pi^2}{a^2} - 1.786 \frac{e^2}{\varepsilon a} - 0.248 R^* \tag{1.5}
\]

where \( E_g \) is the bulk band gap. The second term is the kinetic-energy term containing the effective masses, \( m_e^* \) and \( m_h^* \), of the electron and the hole, respectively. The third term arises due to the Coulomb attraction between the electron and the hole, and the fourth term due to the spatial correlation between the electron and the hole which is generally small compared to the other two terms.

EMA calculations have also been reported where a finite confining potential was used to account for the passivating agents that coat the surface of the nanocrystals in order to arrest their growth. Finite potential calculations are shown to improve the description for CdS nanocrystals to a large extent [1.26]. Another improvement to the single band EMA is the inclusion of multiple bands for describing the hole effective mass. This is prompted by the fact that the top of the valence band for II-VI semiconductors comprised of triply degenerate bands at the \( \Gamma \) point and thus is better defined using a multiband theory. To account for this degeneracy, Einevoll [1.27] and Nair et al. [1.28] have used the effective bond-orbital model for the hole wave function, while the electron is described by a single-band EMA. Finite barrier heights and the electron-hole Coloumb attraction are included in the calculation and exciton energies are obtained variationally in an iterative Hartree scheme. The multiband and finite potential EMA methods explain the experimental results reasonably well, but lack the predictive capabilities desirable of a theoretical model, since the finite potentials need to be adjusted to match the experimental results in each specific case. Pseudo potential calculations have also been carried out to study the variation of electronic structure with the nanocrystals size [1.29-31]. Recently, the semi empirical pseudo potential method has been employed to calculate the electronic structure of Si, CdSe [1.30] and InP [1.31] nanocrystals. The atomic pseudo potentials are extracted
from first-principles local density approximation (LDA) calculations on bulk solids. Thus, the wave functions are LDA-like while the band structures, effective masses, and deformation potentials are made to match experimental results. This method provides a reasonable description of the electronic structure of the nanocrystals. However, major computational efforts and difficulties do not allow one to calculate the properties of large sized nanocrystals.

The tight-binding (TB) scheme has been employed by a number of researchers over the past decade [1.32-39]. This method enjoys several advantages over the other methods discussed above, explaining its popularity. Compared to EMA, both pseudo potential method and the tight-binding approach provide a substantial improvement in the accuracy of the results. The tight-binding method has the further advantage of being significantly less demanding in terms of computational efforts, besides providing a simple physical picture in terms of the atomic orbitals and hopping interactions defined over a predetermined range. A detailed analysis of the first-principle electronic structure calculations can lead to a judicious tight-binding scheme that is minimal in terms of the dimension of the Hamiltonian matrix and yet is highly accurate due to the use of a physical and realistic basis [1.40]. The earliest such TB parametrization was provided by Vogl et al. [1.41] who used a TB model with the $sp^3s^*$ orbital basis in order to describe the electronic structure of bulk semiconductors. The $s^*$ orbital was employed in an ad hoc manner in addition to the $sp^3$ orbital basis in order to improve the TB fit to the ab initio band dispersions. Subsequently, this TB model was used by Lippens and Lannoo [1.32] to calculate the variations in the band gap for the corresponding semiconducting nanocrystals as a function of the size. Though their results are in better agreement compared to the infinite potential EMA, the $sp^3s^*$ TB model tends to underestimate the band gap. The main problem with the $sp^3s^*$ model appears to be a failure to reproduce even the lowest lying conduction band within that scheme [1.32]. Improvements in the nearest neighbor $sp^3s^*$ model have been carried out by including the spin-orbit coupling and the electron-hole interaction [1.33-34]. However, to account for the conduction bands, the inclusion of $d$ orbitals becomes necessary [1.35, 39]. This has been shown in the case of InP [1.39] nanocrystals, a III-V semiconductor, that TB model with the $sp^3d^5$ orbital basis for the anion and the $sp^3$ basis for the cation with next-nearest-neighbor interactions, for both the anion and the cation, gives excellent agreement with the experimental data. In a
recent work, we have shown that the $sp^3d^5$ orbital basis for both the cation and the anion and the inclusion of the next-nearest-neighbor interactions for the anions provide a very good description of the electronic structure of bulk II-VI semiconductors [1.40]. This model is shown to describe accurately the band gap and the band dispersions for both the valence and the conduction bands over the energy range of interest. Therefore, this improved model and the parametrization should provide a good starting point for calculating the electronic properties of corresponding nanocrystals, provided the model and parameters are transferable from the bulk to the cluster limit. 

*Ab initio* calculations for a CdS cluster of about 16 Å diameter as well as reported results suggest that the present scheme is of sufficient accuracy down to about 16 Å, though the applicability of this approach may be limited for still smaller sized clusters. In order to explore the possibility of utilizing it effectively, we have used this model for calculating the band-gap variation over a wide range of sizes for $A^{II}B^{VI}$ semiconductor nanocrystals, with $A=$Cd or Zn and $B=$S, or O, comparing the calculated results with our experimental data. The present results show a good agreement with experimental results.

### 1.2.2 Experimental constraints for theoretical models

A. D. Yoffe [1.42] collected here the conditions which need to be imposed on theoretical models if realistic calculations are to have any quantitative value, and some of these have already been touched on by Brus [1.43] and Bawendi *et al.* [1.44].

i. Semiconductor microcrystallites in a matrix such as glass which are of interest have dimensions in the region of 2-10 nm, and this size should be compared with the corresponding bulk exciton Bohr radius.

ii. In general, crystallites will retain their bulk structure, but there may be departures; see (v-vii).

iii. Experimental spectra can show the presence of discrete features which can be related to 3D confinement of the carriers.

iv. When $\tilde{R}$ very small, shifts to higher photon energies are can be as large as 1 eV.
v. Optical properties show a change from bulk-semiconductor-type behaviour to that appropriate to molecular system as $\bar{R}$ decreases.

vi. Semiconductors which have open-type structures, for example tetrahedral, appear to divide into two broad categories. For elemental semiconductors such as Si, clusters such as Si$_n$ with $n < 50$ can deviate from tetrahedral bonding (Raghavachari and Logovinsky) [1.45]. Chelikowsky [1.46] assumes metallic-type f.c.c. structures in his calculations, but the $n > 50$ a change to the open covalent diamond structure may take place. Furthermore even for these clusters, the proportion of surface atoms relative to the bulk will be high, and there can also be problems related to surface reconstruction.

vii. For the binary II-VI semiconductors such as CdS, and a major proportion of experimental work involves these materials, Brus [1.47] and his colleagues consider that clusters with about 200 atoms already possess the same unit cell and bond lengths as bulk material. This means that, for the larger clusters, excited states can be described by confinement models analogous to those used in simple quantum wells. This is illustrated in a very simple way in the scheme shown in figure 1.5.

![Figure 1.5: Schematic energy level scheme diagram for the bulk semiconductor and for the microcrystallite. (From Chestnoy et al.) [1.48-49]](image)
1.3 Background and motivation

In principal, the QDs can down-convert the UV/blue LEDs to white light when a combination of different color-emitting QDs is used. The sub wavelength dimensions of quantum dots eliminate the light scattering and the associated optical losses that reduce the package efficiency of conventional phosphors by as much as 50%. For quantum dots to be used for lighting, however, they need to be removed from the solution in which they are fabricated and encapsulated (usually in an epoxy or silicone film layer) dense enough to provide bright illumination. Demands on the encapsulation process include that it is not alter the surface chemistry of the quantum dots and not allow them to clump up or agglomerates, either of which would alter the optical characteristics.

Nevertheless, nanoparticles tend to have negligible Stokes shift (difference between the peak positions of absorption and the emission spectra) in comparison with conventional phosphors. The lack of Stokes shift leads to low quantum efficiencies in quantum dots. For efficient down-conversion from UV/blue to white light absorption in a thin layer and high density of quantum dots is needed. However QDs interact at high densities leading to a cascading effect, because there is almost no Stokes effect. Essentially, the larger dots absorb photons from the smaller ones. So even with 90 % quantum efficiency, if the absorption process casecades 10 times, the ‘external’ quantum efficiency effectively drops to about 10 %. “The quantum dots exhibit nice properties in aqueous solutions but not in silicon and epoxies”. They are also strongly affected by temperature in a negative way.

In order to develop reliable and efficient nanophosphors and overcome the shortcomings people faced in QDs we have followed the approach of Bhargava et al. [1.50]. Here we incorporated a single impurity atom within the quantum dot so as to replace the exciton related emission within the quantum dot by the impurity related emission. In these ‘doped nanocrystals’ the characteristic emission is associated with the caged impurity atom or ion (also referred to as activator/dopant). The efficiency critically depends on the choice of the impurity atom and the size of the quantum dots cage. By embedding a single atomic impurity in the quantum dot, we have eliminated;

i. The dependence of light output on the size of the quantum dot, a critical step needed for reliable use of Nanophosphors especially since it is impossible to
avoid agglomeration of the nanophosphors and size variations. On the other hand, the impurity related emission is phenomenon related to each individual atom, and hence agglomeration plays an insignificant role in the wavelength of emission.

ii. The impurity based emission now provides a large Stokes shift. This eliminates any deleterious cascade effect observed in conventional QDs.

1.3.1. Quantum efficiency dependence on nano-size

In conventional usage, phosphors comprise of a host and a small amount of impurity that is referred as activator. The absorption of the excited emission occurs within the manifold of energy-states that are either from host or a combination of the host and activator. The emission is the characteristic radiative transition associated with the activator. By incorporating a single atomic ion (activator) in a nanosize (2 to 10 nm) host it has been reported that the created nanophosphors yield luminescent efficiencies comparable to the best bulk-phosphors (size 1 to 10 μm). As the size decreases below 1μm, the efficiency begins to drop rapidly, primarily due to the enhanced non-radiative contribution of the surface states. R.N. Bhargava et al. [1.50] showed in figure 1.6 that this trend reverses when the particle size reaches approximately 10 nm. In particular, in the size range of 2 to 5 nm they observe luminescent efficiency comparable to that of the best commercially used phosphor [1.51].

![Figure 1.6: Quantum Efficiency of Nanophosphors increases non-linearly as the size decreases below 10 nm.](image)

**Figure 1.6:** Quantum Efficiency of Nanophosphors increases non-linearly as the size decreases below 10 nm.
1.3.2 Efficient lighting: Choice of materials

The size dependent efficiency of individually separated nanocrystals has already been measured by combining atomic force microscopy (AFM) and high N.A. fluorescence optical microscopy at Oak Ridge National Laboratory [1.52-54]. The size of individual nano-phosphor particle was measured utilizing AFM technique while their brightness was assessed at the same time by collecting the photo-excited light using far field optical microscopy [1.54]. The data in figure 1.7 shows the dependence of light output as the sizes of nanocrystals vary. The confirmation that the efficiency increases rapidly with decreasing size in the range of 2 to 10 nm in nanophosphors has enabled us to develop several efficient QCA-NP systems such as ZnS:Mn\(^{2+}\), CdS/CdS:Mn\(^{2+}\), ZnO/ZnO:Mn\(^{2+}\), Li, Na, Cu etc. and other systems like YAG:Ce\(^{3+}\), TAG:Ce\(^{3+}\) (broad-band emitters), Y\(_2\)O\(_3\):Tb\(^{3+}\) [1.54], Gd\(_2\)O\(_3\):Tb\(^{3+}\) and Y\(_2\)O\(_3\):Eu\(^{3+}\) (line-emitters). The Quantum efficiency in 2-7 nm size QCA-NP of Y\(_2\)O\(_3\):Tb\(^{3+}\) was reported to be over 80%.

![Figure 1.7: Dependence of light output as the sizes of nanocrystals vary](image)

The objective of the present work is to develop QCA-nanophosphors and the nanophosphors having sizes in the quantum confinement regime that can be used for wide range of applications ranging from opto-electronic devices to biomedical engineering. One of the major goals is to develop nanophosphors by artificially designing new materials using energy band-gap engineering. This is expected to lead
to nanophosphors that are tuned for specific application such as white LEDs but
would help in improving the color rendition index (quality of the color) and better
color control and biomedical applications.

The confinement of the atomic impurity achieved in a nanocrystalline size
host allows efficient transfer of the energy to the atom. The caged atom derives the
oscillator strength from the host in a very different manner than known heretofore.
The QCA model is developed on the basis of the changes observed in the optical
properties as a function of the size of the nanocrystalline host. The modulation of the
Mn$^{2+}$ atomic-states was responsible for shortening the decay time in ZnS: Mn$^{2+}$
nanocrystals. It is observed that the changes in the efficiency are strongly dependent
on the size and particle size distribution [1.55].

In the original work on ZnS:Mn$^{2+}$ NC, which is considered to be the main
system in our study, the changes observed were initially explained on the basis of
hybridization of the d-electrons of Mn$^{2+}$ with the s-p electrons of NC [1.56]. This now
can be explained more clearly on the basis of QCA as developed for Y$_2$O$_3$: Tb$^{3+}$ NC.
The Mn atom ($3d^54s^2$) replaces Zn in the lattice and results in Mn$^{2+}$ ion ($3d^5$) in the
bulk crystal. In the QCA system, the $3d^5$-electron can appear at 4s or higher excited
levels under quantum confinement imposed by the ZnS nanocrystals. These s-like
electrons upon recombining with the hole in the ground state (either directly or via d-
states), yield parity-allowed, ultra-fast and efficient radiative recombination. The
atomic manifold of Mn$^{2+}$ particularly excited states is modulated by quantum
confinement when Mn is incorporated in 2-3 nm size range ZnS-NC. Indeed, the
shortening of decay time occurs only in this range [1.56] and has very little to do with
the excitonic radius of the host semiconductor. The charge transfer of electrons from
ZnS-NC to the Mn$^{2+}$ manifold is critically dependent on the overlap of Mn$^{2+}$ excited
states with ZnS-NC as also in the case of Tb$^{3+}$ in Y$_2$O$_3$-NC. This transfer which
critically depends on the size of NC allows efficient mixing of s-p states of ZnS and
d-like excited states of Mn$^{2+}$ via excited states of Mn. The recombination kinetics of
internal transitions such as d-d transition in these impurities can drastically vary with
the size of NC due to quantum confinement. The confinement of the atomic impurity
achieved in a nanocrystalline size host allows transferring the energy efficiently to the
atom via its excited states.
In conclusion, quantum-confined atom in nanocrystals can lead to materials where properties of atoms are only modulated without changing its signature. In fact, the properties of the atoms are retained, protected and significantly amplified via their interaction with the host. Such a quantum confined atomic-system offers numerous possibilities for the next generation devices in the field of lighting, displays, sensors, bio-tags and lasers.

1.3.3. Engineering of Nanophosphors

The fundamental question of incorporating a dopant (or an activator) in a nanosize particle is very different to incorporating the same impurity in the bulk. Since in case of nanoparticles most of the experiments are carried at room temperature, incorporation of the impurity is more statistical rather than driven by process of diffusion.

It has been reported that, incorporating a single impurity in a host-nanoparticle is best achieved when the concentration of dopant salt is comparable to the host ion it is replacing. In case of nanophosphors, since there is only a single dopant-ion is present in QCA based nanophosphors, concentration quenching is prevented. To achieve the best quantum efficiency we need to get only one dopant per nanoparticle. All our preparative efforts have been conducted keeping this in mind.

Besides selecting the atomic ion that emits the proper color, we have to also engineer the energy band gap that absorbs the exciting radiation. This has been successfully achieved for all semiconductor lasers, LEDs and optoelectronic devices. Our task is to achieve this for nanophosphors i.e. engineer the energy band gap in nanosize where only a single activator-ion is acting as the radiative center.

1.3.4. Advantages of QCA-Nanophosphors for LED and Display applications

i. In QCA-Nanophosphors the caged atom (activator) is responsible for the light emission and its spectral characteristics remain invariant with respect to the size of the nanoparticle.

ii. Inherently more robust with respect to the stability of the emission color/wavelength with operating temperature in an application.

iii. No parasitic re-absorption of complementary phosphor emission.
iv. When incorporating Nanophosphors in polymers/matrices for integration in devices, the conversion efficiency of QCA-Nanophosphor is not adversely affected by the surface modifications that are required in order to embed them in polymers.

1.4 Biological labelling

The use of labelling or staining agents has greatly assisted the study of complex biological interactions in the field of biology. In particular, fluorescent labelling of biomolecules has been demonstrated as an indispensable tool in many biological studies. Types of fluorescent labeling agents that are commonly used include conventional classes of organic fluorophores such as fluorescein and cyanine dyes, as well as newer types of inorganic nanoparticles such as QDs, and novel fluorescent latex/silica nanobeads. The newer classes of fluorescent labels are gaining increasing popularity in place of their predecessors due to their better optical properties such as possessing an enhanced photostability and a larger Stokes shift over conventional organic fluorophores, for example.

Semiconductor nanoparticles have attractive photoluminescence properties that have stimulated interest in their use as a new class of biological labels with properties and applications that are not available with traditional organic dyes and fluorescent proteins [1.58-61]. Figure 1.14 a and b show the normalized absorption and the emission spectra of fluorescein (an organic dye [1.62]) and CdSe nanoparticles of the kind described figure 1.15. The semiconductor nanoparticles have a huge absorption spectrum compared to the organic dye. This allows them to be excited by wavelengths from 500 nm down into the ultraviolet, i.e. spectrally far from their emission wavelength. This property turns to be extremely advantageous for practical applications because it allows efficient filtering of exciting radiation, without affecting emission detection.

Multicolour analysis with different dyes requires multiple excitation sources and multiplexed channels recorded simultaneously; this greatly increases the complexity of the detection systems [1.63]. To simplify microarray systems and analysis, multiple labeling applications need an alternative technology to organic fluorophores. Quantum dots could potentially be this technology. The quantum dot
emission spectrum is narrower than that of the fluorescein molecules (figure 1.9) and its central wavelength can be tuned with the nanoparticles size (figure 1.10b). Nanocrystals with different sizes can be excited with a single radiation wavelength, resulting in many emission colors that can be detected simultaneously [1.64].

Figure 1.9: Absorption and emission spectra of (a) Fluorescein organic molecules [46] and (b) CdSe nanoparticles of 2.5 nm in diameter.

Figure 1.10: (a) Schematic of CdSe nanoparticles and of the TOPO ligand shell. (b) Absorption and emission spectra of CdSe nanoparticles of different size. In the inset a picture of the different nanoparticles dispersed in toluene is shown (the size increase from left to right).

Another important property of nanoparticles is their low photo-degradation compared to organic dyes, which makes them particularly suitable for in vivo experiments [1.64-65]. Synthetic fluorophores or fluorescent proteins are currently used as tracers for in vivo imaging, but these approaches are restricted by photo-bleaching and the limited availability of different colours. Dubertret et al. [1.66] demonstrated that CdSe
nanocrystals encapsulated in phospholipid block copolymer micelles could be used in lineage-tracing experiments in embryogenesis. Moreover the nanoparticles were found to be stable, non-toxic and slow to photo-bleach when injected into early-stage embryos. Similarly, Dahan et al. [1.67] observed the lateral dynamics of individual glycin receptors tracked with quantum dots in the neuronal membranes of living cells for periods ranging from milliseconds to minutes. Moreover, the quantum dots, being suitable for TEM imaging, provided information on the precise localization of diffusing glycin and demonstrated access into the core of the synapse.

One of the main questions that have to be solved for future developments of cell-labelling techniques based on semiconductor quantum dots is that of their toxicity. CdSe nanoparticles, for example, were found to be toxic under certain condition due to the release of free Cd ions during surface oxidation [1.68]. However, surface coatings such as ZnS and BSA were shown to significantly reduce their cytotoxicity. In general, the use of quantum dots in in vivo experiments must be critically examined because they could induce cell death because of their inherent chemical composition, although novel mechanisms of toxicity due to their size.

The biological application of quantum dots is also limited by problems in surface chemistry. Semiconductor nanocrystals can be grown directly in aqueous solutions [1.69-70], but their size distribution and quantum yield are in general poorer than those of particles grown in organic surfactants. To make organically synthesized particles water-soluble, the surface species are generally exchanged with monolayers made of bifunctional molecules [1.65, 71]. Alternatively, a glass shell may be grown around the nanoparticle. Modification of silica surface with different groups has been used to control the interaction of the nanoparticles with the biological sample [1.64, 72]. However, these capping techniques generally produced quantum dots which tended to aggregate and adsorb non-specifically. Many efforts have been made during last years to face these problems [1.73]. Recently Bäumle et al. [1.74] demonstrated the synthesis of CdSe nanoparticles with high fluorescence quantum yield directly in water; glutathione was used as a stabilizing agent while the quantum dots were coated with streptavidin for application as fluorescent probes. A further peculiarity of semiconductor nanoparticles with respect to common fluorophores is their long fluorescence lifetime.
Quantum dots are mostly synthesized in organic solvents, they are insoluble in water, often non-biocompatible, and do not have any reactive functional groups for conjugation with biomolecules. Until recently, the research on QDs was primarily focused on the traditional applications in optoelectronic devices, quantum-dot lasers, and high density memory [1.75-77]. It was not until 1998 when Alivisatos [1.78] and Nie [1.79] simultaneously demonstrated that QDs could be made water soluble and conjugated with biological molecules that the applications of QDs were extended to the biological field. The advantages of using QDs as fluorescent labels are numerous. Firstly, they permit great assay sensitivity and stability over conventional organic fluorophores. For example, Chan and Nie reported that QDs are 20 times as bright, 100 times as stable against photobleaching, and one third as wide in spectral line width compared to conventional organic dyes such as rhodamine [1.79]. Secondly, it has also been observed that the onset of absorbance and emission maxima of the QDs shift with a change in the size of the QDs or chemical composition [1.76, 80]. Furthermore, since QDs’ emission could be size-tuned to improve spectral overlap with a particular acceptor dye, they are also considered as efficient fluorescence resonance energy transfer (FRET) donors [1.81]. Thirdly, QDs also emit light at a rate slow enough to eliminate most of the auto fluorescence in the background but fast enough to maintain a high photon turnover rate. Therefore, they are ideal probes for time gated detection with enhanced selectivity and sensitivity [1.82]. Fourthly, it is possible to obtain polarized fluorescence by using shape-controlled QDs, which can be exploited to study conformational change and energy transfer in biological systems [1.83].

The unique optical properties of QDs make them appealing as fluorescent labels in biological investigations. A range of biomolecules, including deoxyribonucleic acid (DNA) and proteins, have been conjugated to QDs and used in diverse biomedical studies such as in vitro detection assays [1.84-85], deep tissue imaging [1.86-88], and most recently in the selective and generalized imaging of live cells and organisms [1.89-94] For example, Nie [1.92] has developed a multifunctional QD probe linked with tumor targeting antibodies for cancer targeting and imaging. In his in vivo studies on mice expressing human cancer, it was shown that these QD probes accumulated specifically at the tumor sites. At the same time, he
also demonstrated multicolour visualization of the cancer cells under in vivo conditions by spectral imaging. In addition, imaging tissue with QDs under NIR excitation has achieved much better results than using available dyes. By synthesizing NIR emitting QDs (840–860 nm) and using only 5 mW cm\(^{-2}\) excitation, Kim [1.87] demonstrated the imaging of lymph nodes 1 cm deep in the tissue, where lymphatic vessels were clearly visualized draining QD solutions into the sentinel nodes. More interestingly, green-emitting QDs have been excited in the NIR region at low intensity via a two-photon excitation technique, which allowed the imaging of mouse capillaries hundreds of micro meters deep at sub-cellular resolution in a mouse brain [1.88, 95]. In addition to the extensive studies on their biological application as fluorescent labels, the emerging importance of QDs has been documented in a number of recent reviews [1.96–102]. For example, Nie and coworkers [1.96] presented an excellent overview of the synthesis, optical properties and surface chemistry of QDs and provided some examples of QD-bioconjugation; Niemeyer [1.97] gave a comprehensive review covering the biomolecular interactions of all nanoparticles; while Medintz [1.101] looked at the current methods for preparing QD bioconjugates and presented an overview of their applications as well.

1.5 Implications for the miniaturization of electronic devices

The development of electronics demands a continuous decrease of the element sizes. The aim of this trend is not only to increase the integration level, but mainly, to increase the operation speed. Commercial requirements for miniaturized microelectronic devices provide strong motivation for exploring the synthesis of nanoscale systems using bottom-up techniques. II-VI nanocrystals (NCs) are receiving considerable attention for fundamental studies, as an example of zero-dimensional quantum confined material and for their exploitation in appealing applications in opto-electronics and photonics [1.77]. The NC based emitters can be used for many purposes such as optical switches, sensors, electro-luminescent devices [1.103], lasers [1.104] and biomedical tags [1.105]. Nanometer size quantum dots exhibit a wide range of electrical and optical properties that depends sensitively on the size of the nanocrystals and are of both fundamental and technological interest. It is, therefore, possible in principal to manipulate the properties of the nanomaterials for
specific application of interests by designing and controlling the parameters that affect their properties.

If on the one hand we are developing a technology able to product nano-devices, on the other it is necessary to face the conceptual problems that arise when the dimension of the electronic components reaches some nanometers: quantum phenomena will increasingly start to dominate the overall behaviour of such structures and the large surface to volume ratio is deadly for conventional semiconductor devices. The electrical conductivity in metals is based on their band structure. As the discrete energy level structure dominates in nanostructures, Ohm’s law will be no longer valid; we will be dealing with a very few numbers of charge carriers, if at all, and control of charge and electrical current on a single electron level will be required. It appears clear therefore that the miniaturization process towards nano-electronics will not be as natural as it has been for micro-electronic, but that new concepts need to be developed.

1.5.1 Flash back

The constituent components of conventional devices are carved out of larger materials relying on physical methods. This top-down approach to engineered building blocks becomes increasingly challenging as the dimensions of the target structures approach the nanoscale. Nature, on the other hand, relies on chemical strategies to assemble nanoscaled biomolecules. Small molecular building blocks are joined to produce nanostructures with defined geometries and specific functions. It is becoming apparent that nature’s bottom-up approach to functional nanostructures can be mimicked to produce artificial molecules with nanoscaled dimensions and engineered properties. Indeed, examples of artificial nanohelices, nanotubes, and molecular motors are starting to be developed. Some of these fascinating chemical systems have intriguing electrochemical and photochemical properties that can be exploited to manipulate chemical, electrical, and optical signals at the molecular level. This tremendous opportunity has lead to the development of the molecular equivalent of conventional logic gates. Simple logic operations, for example, can be reproduced with collections of molecules operating in solution. Most of these chemical systems, however, rely on bulk addressing to execute combinational and sequential logic operations. It is essential to devise methods to reproduce these useful functions in
solid-state configurations and, eventually, with single molecules. These challenging objectives are stimulating the design of clever devices that interface small assemblies of organic molecules with macroscaled and nanoscaled electrodes. These strategies have already produced rudimentary examples of diodes, switches, and transistors based on functional molecular components. The rapid and continuous progress of this exploratory research will, we hope, lead to an entire generation of molecule-based devices that might ultimately find useful applications in a variety of fields, ranging from biomedical research to information technology.

1.6 Energy gap in semiconductors

The suitability of a semiconductor material for optical applications is determined by its energy band structure. There are two important features of the band structure upon which the material can be judged: the nature of the energy gap and its magnitude. There are two types of semiconductor band gaps, direct and indirect, which are shown schematically in figure 1.11. A direct gap semiconductor is one in which the maximum of the valence band and the minimum of the conduction band occur at the same value of \( k \), the momentum vector of the wave function representing the carriers. An indirect gap semiconductor is one in which the valence band maximum and conduction band minimum occur at different values of \( k \). For transitions in which carriers move from one band into the other, it is a fundamental law that momentum must be conserved. In the event of photo excitation of carriers, in which light (which has very little momentum) is the promoting agent, it is easy to transfer electrons up into the conduction band for a direct gap material. In fact, if the light is of sufficient energy above the band gap, there may be states available in the conduction band at the same momentum in an indirect gap material, which means absorption transitions can be easy as well. When the time comes for the excited electron to recombine, however, there are significant differences between the two types of semiconductors. Generally, the electron will make its way to the minimum of the conduction band before the transition, no matter how much energy it was originally given, and the hole it is destined to recombine with will float to the top of the valence band. In a direct gap material, these two actors will have the same value of \( k \), and so their recombination can be made with only a change in energy required, but no change in momentum. This can be achieved by the emission of a photon only, which is a very efficient
process. For an indirect gap material, things are not so simple. The electron and hole will have different values of momentum, which means that recombination will require a change of energy, which can be handled with a photon, and also a change of momentum, which requires the presence of a phonon. This added degree of complexity makes the process far less likely, making light emission very inefficient from indirect gap semiconductors.

**Figure 1.11:** Schematic representation of both direct and indirect energy gap band structures in semiconductors. A phonon is required for transitions across the gap in the indirect gap material

1.7 Semiconductor nanostructures: II-VI Group

1.7.1 Structure determining properties

In traditional semiconductor technology, the properties of bulk semiconductors are precisely tailored for particular application through the introduction of impurities (doping) or external fields (charging). The unique properties of semiconductor quantum dots indicate different structures in them. Compared with bulk semiconductors, the quantum dot counterparts have more complicated defect structures. *On one hand*, for instance, due to the large surface-to-volume ratio, more atoms will locate on the surface with dangling bonds, which usually act as nonradiative traps [1.106] and/or may incorporate foreign atoms to form a core-shell structure [1.107-109]. *On the other hand*, the conventional doping by introducing impurity atoms is difficult, especially in colloidal nanocrystals. The main challenge is
to introduce the impurity in the core of the particle. Since the impurity is always only a few lattice constants from the surface of the nanocrystal, it may tend to diffuse to the surface or into the surrounding matrix due to the thermodynamic driving forces. In addition, the electronically active doping with extra carriers remains another challenge. To date, most efforts have focused on equivalent valence charge doping, for example, transition metals Mn [1.110-111], Cu [1.112], or rare earth elements such as Tb [1.113-114] or Eu [1.115] in II-VI chalcogenide semiconductor nanocrystals. Typically, these impurities do not affect the band-to-band absorption spectrum, but strongly modify the luminescence properties because they do not introduce extra carriers, but rather provide impurity centers that interact with the quantum confined electron hole pair. Since these impurities can be paramagnetic, they also introduce a localized spin into the nanocrystal, and form the so called diluted magnetic semiconductors (DMS). In this work, we intend to explore the structure behind II-VI semiconductor quantum dots, illustrated mainly by ZnO, ZnS and CdS as representative examples. The doping with Mn, Cu, Na, Li is also studied. Bulk zinc oxide has received much attention due to its many technological applications, particularly in optical devices. The green photoluminescence behavior of ZnO has been of interest for building flat panel displays [1.116]. Other applications include gas sensors [1.117], solar cells [1.118], catalysts [1.119], substrates or buffer layers [1.120-121] for growth of GaN. In the recent years, great interest in ZnO has been stimulated by the increasing demand in developing short-wavelength lasers and room temperature green-blue diode lasers from wide band gap semiconductors. The unique features that ZnO has, both, a wide band gap (3.37 eV) and a large exciton binding energy (~ 60 meV), makes it the most promising candidate for room temperature ultraviolet (UV) laser [1.122-123]. Furthermore, theory predicts [1.124] that Mn-doped ZnO may form a ferromagnet with a very high Curie temperature (> 300K). Questions, whether ZnO quantum dots maintain similar optical and/or electrical properties or behave differently, rise up as our starting points of the present work. It has been widely reported that UV emission is rather weak in ZnO quantum dots, while a few groups claim the observation of strong UV transition [1.125-126]. In the past years, the debate whether Mn doped II-VI chalcogenide semiconductor nanocrystals form new luminescence materials [1.111] or not [1.127-128] has been in heated disputation. In the Results and discussions section, we also present our understanding of the luminescence properties of Mn in ZnS and CdS quantum dots.
Both the local structure of Mn impurities in ZnS quantum dots and the luminescence are intensively studied.

1.8 Doped semiconductor nanocrystals

Doping is the intentional introduction of impurities into a material is fundamental to controlling the properties of bulk semiconductors. This has stimulated similar efforts to dope semiconductor nanocrystals [1.129-132]. Incorporation of impurities or defects into semiconductor lattices (dopants) can be used to control electrical conductivity, optical, luminescent, magnetic and other physical properties of the semiconductor depending on the type of impurity. It will be immensely important to understand doping in nanoscale semiconductors as this class of materials is going to evolve into practical applications in electronics and photonics applications. Despite some successes [1.133-139], many of these efforts have failed, for reasons that remain unclear. For example, Mn can be incorporated into nanocrystals of CdS and ZnSe [1.135-137], but not into CdSe [1.140]-despite comparable bulk solubilities of near 50 per cent. These difficulties, which have hindered development of new nanocrystalline materials [1.141-143], are often attributed to ‘self-purification’, an allegedly intrinsic mechanism whereby impurities are expelled.

When a macroscopic semiconductor crystal is grown under conditions of thermal equilibrium, impurity atoms can be incorporated up to their solid solubility limit as much as 50% or more for Mn in II–VI semiconductors [1.144]. This thermodynamic limit is completely determined by the Gibbs free energy (approximately equal to the impurity formation energy) and the growth temperature. For semiconductor nanocrystals—which is typically grown using colloidal synthesis—the impurity concentrations attained in experiments are much lower than expected from this limit [1.135-136], and for some materials are even zero [1.140]. The likely reason is that thermal equilibrium, which requires facile diffusion, may be far from realized. Indeed, at the temperatures used in colloidal growth, typically around 300 C, diffusion of Mn in II–VI semiconductors is negligible; for example, the diffusion length of Mn in CdTe after 1 h at this temperature is only 1–3Å° [1.145]. This suggests that thermal equilibrium is an inappropriate starting point for describing doping in nanocrystals.
1.9 Absorption: Optical properties of QDs

Excitons

i. Excitons are combined electron-hole states: A free electron and a free hole (empty electronic state in the valence band) exert Coulomb force on each other.


iii. Wave functions of electron and hole look similar to free electron and free hole.

iv. Exciton can move through crystal, i.e. not bound to specific atom.
Excitonic absorption

i. Light can excite an electron from the valence band and generate an exciton at energies slightly below the bandgap.

ii. See absorption at $E_{\text{phot}} = E_{\text{gap}} - E_b$ (absorption slightly below $E_{\text{gap}}$).

iii. Exciton binding energy on the order of a few meV

iv. Thermal energy at room temperature: $kT \sim 25$ meV

v. Exciton rapidly dissociates at room temperature.

vi. Absorption lines broaden / disappear for higher temperatures.

Figure 1.14: Creation of electron-hole pair into the semiconductors

$E_b$ is the exciton binding energy = energy released upon exciton formation, or energy required for exciton breakup

Life and death of an exciton

Figure 1.15: Life and death of an exciton
1.9.1 Implications for Optical Properties

The increase in emission efficiency for quantum confined structures means that not only will the emission be shifted in energy, but there will also be more of it, making it possible to fabricate useful devices since the luminescence will be bright enough to be seen by the human eye [1.147]. The finite density of states has ramifications for both the absorption behavior and the photoluminescence emission of quantum confined materials. As is evident in the absorption spectra shown in figure 1.16, the discrete levels lead to narrow absorption peaks of finite height. This means that it is possible to saturate the absorption of the quantum dots, since any light intensity above that represented by the height of the absorption peak cannot be absorbed and will simply be transmitted. The absorption saturation also affects the photoluminescence spectra of quantum confined materials. Typically, this luminescence is excited by high energy photons, such as ultraviolet light. These photons excite carriers into higher energy states which subsequently find their way to the lowest state that is unoccupied in the ground state of the quantum dot. In the bulk, these carriers would be making their way to the conduction band edge via thermalization (figure 1.17). From this lowest level, the electrons undergo a radiative recombination event. Under sufficiently high excitation intensity, it is possible to promote more electrons than can be accommodated in the lowest unoccupied ground level of the quantum dot. These carriers will take up residence in higher levels, from which they can de-excite via radiative recombination events. Since the carriers are recombining from higher energy levels, the light they emit is of higher energy, or shifted to the blue. As a consequence of the filling of this discrete density of states, under high intensity photoexcitation quantum confined materials will exhibit a blue shifting of the photoluminescence emission spectrum [1.148].
1.10 Luminescence

Luminescence is the general term applied to all forms of cool light, i.e., light emitted by sources other than a hot, incandescent body, such as a black body radiator. It is caused by applying an external source of energy to an atomic or molecular system which undergoes a transition to higher energy levels. In the course of decaying to a lower energy the system subsequently emits optical radiation. Luminescence radiators are classified according to the source of excitation energy, as indicated by the following examples.
i. **Cathodoluminescence** is caused by accelerated electrons colliding with the atoms of a target.

ii. **Photoluminescence** is caused by energetic optical photons.

iii. **Chemiluminescence** provides energy through a chemical reaction.

iv. **Electroluminescence** results from energy provided by an applied electric field.

v. **Sonoluminescence** is caused by energy acquired from a sound wave.

![Figure 1.18: Types of luminescence.](image)

**1.10.1 Concepts of Fluorescence**

Fluorescence is a member of the ubiquitous luminescence family of processes in which susceptible molecules emit light from electronically excited states created by either a physical (for example, absorption of light), mechanical (friction), or chemical mechanism. Generation of luminescence through excitation of a molecule by ultraviolet or visible light photons is a phenomenon termed photoluminescence, which is formally divided into two categories, fluorescence and phosphorescence, depending upon the electronic configuration of the excited state and the emission pathway. Fluorescence is the property of some atoms and molecules to absorb light at a particular wavelength and to subsequently emit light of longer wavelength after a brief interval, termed the fluorescence lifetime. The process of phosphorescence occurs in a manner similar to fluorescence, but with a much longer excited state lifetime.
Figure 1.19: Fluorescence and phosphorescence mechanism

The fluorescence process is governed by three important events, all of which occur on timescales that are separated by several orders of magnitude (see table 1.2). Excitation of a susceptible molecule by an incoming photon happens in femtoseconds (10E-15 seconds), while vibrational relaxation of excited state electrons to the lowest energy level is much slower and can be measured in picoseconds (10E-12 seconds). The final process, emission of a longer wavelength photon and return of the molecule to the ground state, occurs in the relatively long time period of nanoseconds (10E-9 seconds). Although the entire molecular fluorescence lifetime, from excitation to emission, is measured in only billionths of a second, the phenomenon is a stunning manifestation of the interaction between light and matter that forms the basis for the expansive fields of steady state and time-resolved fluorescence spectroscopy and microscopy. Because of the tremendously sensitive emission profiles, spatial resolution, and high specificity of fluorescence investigations, the technique is rapidly becoming an important tool in genetics and cell biology.

Timescale Range for Fluorescence Processes

Table 1.2: Timescale Range for Fluorescence Processes
Fluorescence is generally studied with highly conjugated polycyclic aromatic molecules that exist at any one of several energy levels in the ground state, each associated with a specific arrangement of electronic molecular orbitals. The electronic state of a molecule determines the distribution of negative charge and the overall molecular geometry. For any particular molecule, several different electronic states exist (illustrated as \( S(0) \), \( S(1) \), and \( S(2) \) in figure 1.19), depending on the total electron energy and the symmetry of various electron spin states. Each electronic state is further subdivided into a number of vibrational and rotational energy levels associated with the atomic nuclei and bonding orbitals. The ground state for most organic molecules is an electronic singlet in which all electrons are spin-paired (have opposite spins). At room temperature, very few molecules have enough internal energy to exist in any state other than the lowest vibrational level of the ground state, and thus, excitation processes usually originate from this energy level.

With ultraviolet or visible light, common fluorophores are usually excited to higher vibrational levels of the first (\( S(1) \)) or second (\( S(2) \)) singlet energy state. One of the absorption (or excitation) transitions presented in figure 1.19 (left-hand green arrow) occurs from the lowest vibrational energy level of the ground state to a higher vibrational level in the second excited state (a transition denoted as \( S(0) = 0 \) to \( S(2) = 3 \)). A second excitation transition is depicted from the second vibrational level of the ground state to the highest vibrational level in the first excited state (denoted as \( S(0) = 1 \) to \( S(1) = 5 \)). In a typical fluorophore, irradiation with a wide spectrum of wavelengths will generate an entire range of allowed transitions that populate the
various vibrational energy levels of the excited states. Some of these transitions will have a much higher degree of probability than others, and when combined, will constitute the absorption spectrum of the molecule. Note that for most fluorophores, the absorption and excitation spectra are distinct, but often overlap and can sometimes become indistinguishable. In other cases (fluorescein, for example) the absorption and excitation spectra are clearly separated.

Immediately following absorption of a photon, several processes will occur with varying probabilities, but the most likely will be relaxation to the lowest vibrational energy level of the first excited state \((S(1) = 0; \text{figure 1.19})\). This process is known as internal conversion or vibrational relaxation (loss of energy in the absence of light emission) and generally occurs in a picosecond or less. Because a significant number of vibration cycles transpire during the lifetime of excited states, molecules virtually always undergo complete vibrational relaxation during their excited lifetimes. The excess vibrational energy is converted into heat, which is absorbed by neighboring solvent molecules upon colliding with the excited state fluorophore.

An excited molecule exists in the lowest excited singlet state \((S(1))\) for periods on the order of nanoseconds (the longest time period in the fluorescence process by several orders of magnitude) before finally relaxing to the ground state. If relaxation from this long-lived state is accompanied by emission of a photon, the process is formally known as fluorescence. The closely spaced vibrational energy levels of the ground state, when coupled with normal thermal motion, produce a wide range of photon energies during emission. As a result, fluorescence is normally observed as emission intensity over a band of wavelengths rather than a sharp line. Most fluorophores can repeat the excitation and emission cycle many hundreds to thousands of times before the highly reactive excited state molecule is photobleached, resulting in the destruction of fluorescence. For example, the well-studied probe fluorescein isothiocyanate (FITC) can undergo excitation and relaxation for approximately 30,000 cycles before the molecule no longer responds to incident illumination.

Several other relaxation pathways that have varying degrees of probability compete with the fluorescence emission process. The excited state energy can be
dissipated non-radiatively as heat (illustrated by the cyan wavy arrow in figure 1.19),
the excited fluorophore can collide with another molecule to transfer energy in a
second type of non-radiative process (for example, quenching, as indicated by the
purple wavy arrow in figure 1.19), or a phenomenon known as intersystem crossing to
the lowest excited triplet state can occur (the blue wavy arrow in figure 1.19). The
latter event is relatively rare, but ultimately results either in emission of a photon
through phosphorescence or a transition back to the excited singlet state that yields
delayed fluorescence. Transitions from the triplet excited state to the singlet ground
state are forbidden, which results in rate constants for triplet emission that are several
orders of magnitude lower than those for fluorescence.

Both of the triplet state transitions are diagrammed on the right-hand side of
the Jablonski energy profile illustrated in figure 1.19. The low probability of
intersystem crossing arises from the fact that molecules must first undergo spin
conversion to produce unpaired electrons, an unfavorable process. The primary
importance of the triplet state is the high degree of chemical reactivity exhibited by
molecules in this state, which often results in photobleaching and the production of
damaging free radicals.

The probability of a transition occurring from the ground state (S(0)) to the
excited singlet state (S(1)) depends on the degree of similarity between the vibrational
and rotational energy states when an electron resides in the ground state versus those
present in the excited state, as outlined in figure 1.20. The Franck-Condon energy
diagram illustrated in figure 1.20 presents the vibrational energy probability
distribution among the various levels in the ground (S(0)) and first excited (S(1))
states for a hypothetical molecule. Excitation transitions (red lines) from the ground to
the excited state occur in such a short timeframe (femtoseconds) that the internuclear
distance associated with the bonding orbitals does not have sufficient time to change,
and thus the transitions are represented as vertical lines. This concept is referred to as
the Franck-Condon Principle. The wavelength of maximum absorption (red line in
the center) represents the most probable internuclear separation in the ground state to
an allowed vibrational level in the excited state.
At room temperature, thermal energy is not adequate to significantly populate excited energy states and the most likely state for an electron is the ground state ($S(0)$), which contains a number of distinct vibrational energy states, each with differing energy levels. The most favored transitions will be the ones where the rotational and vibrational electron density probabilities maximally overlap in both the ground and excited states (see Figure 1.20). However, incident photons of varying wavelength (and quanta) may have sufficient energy to be absorbed and often produce transitions...
from other inter-nuclear separation distances and vibrational energy levels. This effect gives rise to an absorption spectrum containing multiple peaks (figure 1.21). The wide range of photon energies associated with absorption transitions in fluorophores causes the resulting spectra to appear as broad bands rather than discrete lines.

The hypothetical absorption spectrum illustrated in figure 1.21 (blue band) results from several favored electronic transitions from the ground state to the lowest excited energy state (labeled S(0) and S(1), respectively). Superimposed over the absorption spectrum are vertical lines (yellow) representing the transitions from the lowest vibrational level in the ground state to higher vibrational energy levels in the excited state. Note that transitions to the highest excited vibrational levels are those occurring at higher photon energies (lower wavelength or higher wave number). The approximate energies associated with the transitions are denoted in electron-volts (eV) along the upper abscissa of figure 1.21. Vibrational levels associated with the ground and excited states are also included along the right-hand ordinate.

**Stokes Shift**

**Figure 1.22:** Schematic representation of Stokes Shifts

Because the energy associated with fluorescence emission transitions (see figures 1.19-22) is typically less than that of absorption, the resulting emitted photons have less energy and are shifted to longer wavelengths. This phenomenon is generally known as Stokes Shift and occurs for virtually all fluorophores commonly employed
in solution investigations. The primary origin of the Stokes shift is the rapid decay of excited electrons to the lowest vibrational energy level of the S(1) excited state. In addition, fluorescence emission is usually accompanied by transitions to higher vibrational energy levels of the ground state, resulting in further loss of excitation energy to thermal equilibration of the excess vibrational energy. Other events, such as solvent orientation effects, excited-state reactions, complex formation, and resonance energy transfer can also contribute to longer emission wavelengths. In practice, the Stokes shift is measured as the difference between the maximum wavelengths in the excitation and emission spectra of a particular fluorochrome or fluorophore. The size of the shift varies with molecular structure, but can range from just a few nanometers to over several hundred nanometers.

1.10.2 Fluorescence Lifetimes and Quantum Yields

The fluorescence lifetimes and quantum yields of fluorescent substances are frequently measured. The meaning of these parameters is best illustrated by reference to a modified Jablonski diagram (figure 1.19). In this diagram the individual relaxation processes leading to the relaxed S1 state are not explicitly illustrated. Instead attention to those processes responsible for return to the ground state is increased. Of special interest is the emissive rate of the fluorophore ($\Gamma$) and its rate of radiationless decay to $S_0$ ($k$).

The fluorescence quantum yield is the ratio of the number of photons emitted to the number absorbed. The rate constants $\Gamma$ and $k$ both depopulate the excited state. The fraction of fluorophores that decays through emission, and hence the quantum yield, is given by

$$\phi = \frac{\Gamma}{\Gamma + k}$$  \hspace{1cm} (1.7)

The quantum yield can be close to unity if the radiation less rate of deactivation is much smaller than the rate of radiative decay, that is $k \sim \Gamma$. The lifetime $\tau$ of the excited state is defined by the average time the molecule spends in the excited state prior to return to the ground state.

$$\tau = \frac{1}{\Gamma + k}$$  \hspace{1cm} (1.8)
The lifetime of the fluorophore in the absence of nonradiative processes is called intrinsic lifetime $\tau_0$, and is given by

$$\tau_0 = \frac{1}{\Gamma} \quad (1.9)$$

This leads to the familiar relationship between the quantum yield and the lifetime

$$\phi = \frac{\tau}{\tau_0} \quad (1.10)$$

The quantum yield and lifetime can be modified by any factors which affect either of the rate constants. For example, a molecule may be nonfluorescent as a result of a large rate of internal conversion or a slow rate of emission [1.149]. Because it is difficult to determine absolute quantum yields, relative methods are often used which compare the sample with a compound of known quantum yield. The determination of quantum yields using optically dilute solutions is the most common method currently employed. These measurements rest on Beer’s law and a spectrofluorimeter is used as the detector. Absorbance of sample and reference must be similar and it is preferable that they are in the same solvent. If this is not possible, then correction for the differences in the refractive indices of the solvents must be made. The need for the refractive index correction arises from two sources. As radiation passes from the solution to air (i.e., from high to low index region), its intensity changes because of the refraction. Second, internal reflection within the measure cell can occur [1.150]. When this is taken into account the sample quantum yield $\Phi_S$ can be calculated with equation 1.11 [1.151], where $A$ is the absorbance, $E$ the integral over the emission peak and $n$ the refractive index. The indices S and R always indicating sample and reference.

$$\phi_S = \frac{A_S E_S n_S^2}{A_S E_R n_R^2} \phi_R \quad (1.11)$$

### 1.10.3 Fluorescence quenching

Fluorescence quenching refers to any process which decreases the fluorescence intensity of a given substance. A variety of processes can result in quenching. This includes excited state reactions, energy transfer, complex formation (static quenching) or collisional quenching (dynamic quenching). In the following we will only consider dynamic and static quenching. For static quenching the fluorophore and its quencher
form a nonfluorescent complex, for dynamic quenching the fluorophore returns to the
ground state without emission of a photon on contact with the quencher.

1.10.4 Quenching and lifetimes

Lifetime measurements can give additional information that help to distinguish
between collisional and static quenching. Collisional quenching is a additional
process which depopulates the excited state of the fluorophore and influences
therefore the lifetimes as described in section 1.10.2. The lifetimes in absence (τ₀)
given by equation 1.9 and presence (τ) of quencher are given by

\[ \tau = \frac{1}{\Gamma + k_q \tau_0} \]  

(1.12)

and therefore

\[ \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] \]  

(1.13)

This latter deviation corresponds to equation 1.12 and illustrates an important
characteristic of collisional quenching, which is an equivalent decrease in
fluorescence intensity and lifetime.

\[ \frac{F_0}{F} = \frac{\tau_0}{\tau} \]  

(1.14)

The decrease in lifetime occurs because quenching is an additional process which
depopulates the excited state. The decrease in yield occurs because the quenching
depopulates the excited state without fluorescence emission. Static quenching
removes a fraction of the fluorophores from observation. The complexed fluorophores
are nonfluorescent and the only observed fluorescence is from the uncomplexed
fluorophore. The uncomplexed fraction is unperturbed, and hence the lifetime is τ₀.
Therefore, for static quenching \( \tau_0/\tau = 1 \).

1.11 Carrier Recombination Mechanisms

Electrons which are excited into the conduction band of a material can lose their
energy in two manners. The electron can either recombine radiatively with its
corresponding hole in the valence band and give off photons of energy equivalent to the energy of the recombination transition, or nonradiatively, where the energy is dissipated in the system without a photon emission event. The recombination implies that the system is already in a nonequilibrium state. The path that the excited electron uses to relax back down to its ground state is a function of the band structure of the material and therefore is dependent on the structure, defect concentration, surface properties, and carrier concentrations in the system.

1.11.1 Radiative Recombination

All materials emit light. If this emission is the result of an optical excitation, it is called photoluminescence. If the emission is due to electrical excitation, it is known as electroluminescence. Other forms of luminescence include cathodoluminescence from excitation by an electron beam or triboluminescence due to mechanical excitation. The types of radiative recombination can be differentiated by the location and origin of the initial and final transition levels for the emission event. Examples of these mechanisms are shown in figure 1.23 Light emission in semiconductors is typically characterized by photoluminescence (PL). This technique will be described in detail elsewhere. In it, photoexcited carriers give back energy in the form of emitted photons. This emission is typically characterized by its energy or wavelength, intensity as a function of wavelength, spectral width, and lifetime or duration of emission. These characterizations give insight into the nature of the emitting species and the recombination mechanism.
1.11.1.1 Excitonic Recombination

A free hole and a free electron in a system can feel a Coulombic attraction. Thus, the electron can be thought of as orbiting around the hole. This pairing is called an exciton. The electron and hole can be thought of as wandering as a pair throughout the crystal, a free exciton, or as being localized near an impurity or defect in the system, a bound exciton. When a free exciton recombines in a direct gap system, the energy of the transition is given by

$$\Delta E = E_g - E_x$$  \hspace{1cm} (1.15)
where $E_g$ is the energy gap of the material and $E_x$ is the ionization or binding energy of the exciton. This ionization energy is a measure of the Coulombic attraction between the charged particles. This energy is given by,

$$E_x = \frac{-m_e e^4}{2\hbar^2 \epsilon^2}$$

(1.16)

Thus the energy emitted by the exciton is slightly lower than that from a strict band to band recombination event. In an indirect gap material, the presence of the momentum conserving phonon changes the transition energy of the exciton to

$$\Delta E = E_g - E_x - E_p$$

(1.17)

where $E_p$ is the phonon energy. Excitons may also be bound to an impurity in the lattice. The ionization energy for a bound exciton is given by

$$E_i = E_x + E_b$$

(1.18)

where $E_b$ is the additional energy binding the free exciton to the impurity center. The luminescence emission from an exciton is very narrow spectrally, and shows up as a sharp, intense line in an emission spectrum. Excitons represent the lowest energy state for electron-hole pairs, however excitonic effects are only seen in the purest materials, and at very low temperatures. Excitons tend to break up in the presence of electric fields caused by defects in the lattice, and thermalize when the thermal energy is greater than the exciton's binding energy,

$$kT > E_x$$

where $k$ is Boltzmann's constant and $T$ is the system temperature. In nanocrystalline materials, the exciton binding energy has been predicted to be greater than in bulk systems [1.152]. Roughly, as nanostructure size decreases, localization increases the energy gap and reduces the dielectric constant, leading to an increase in binding energy. This means that for a given semiconductor, excitons can survive thermalization longer in a quantum confined system than in its bulk counterpart. This opens up the possibility for nonlinear optical effects, such as the saturable absorption. These intense, narrow bandwidth nonlinearities may also be exploitable in the development of photonic applications [1.153].
1.11.1.2 Band to Band Transitions

Although most electrons and holes will remain in excitons before recombination, a number are thermalized into the conduction and valence bands and can undergo band to band recombination. Direct gap band to band recombination results in the emission of energy equivalent to the band gap of the material. In an indirect transition, this is modified by the energy of the momentum conserving phonon absorption or emission event. For a direct gap material this recombination occurs very quickly, resulting in a nanosecond luminescence lifetime. In an indirect gap material this lifetime can be longer, extending into the microsecond or millisecond regimes. In these band to band type events, the density of states of the material will control the line shape of the luminescence, through the control of how many carriers can be at specific energies, and where those energies lie with respect to each other. Therefore, in a monodisperse nanocrystalline semiconductor system, like chemically synthesized CdS, one would expect to see narrow emission line widths reflecting recombination from discrete energy levels [1.154].

1.11.1.3 Impurity Level Transitions

Radiative transitions can also occur through energy states created within the band gap of a material by the presence of impurities, defects, or surfaces. Electrons or holes can become trapped within these defects and recombine radiatively with their oppositely charged counterparts in bands or at other mid gap states. For example, it is possible to get emission through shallow donor or acceptor states, involving low energy transitions to a nearby band. These radiative transitions have been found to be much less likely to occur than carrier relaxation to the band through a number of very small energy, nonradiative, phonon events. Deep transitions involve larger energy relaxations between donor levels and the valence band, or acceptor levels and the conduction band. Recombination can also occur between impurity or defect states that lie at different levels in the band gap. These transitions can also be relatively sharp, as the levels are fixed in energy. The transition energy is a measure of the Coulombic attraction of the impurity centers and so is strongly dependent on their spatial separation. The lifetime of the emission is a function of this energy, where higher energy transitions represent impurities in close proximity and therefore shorter
lifetimes, while lower energy transitions represent spatially distant impurities and result in longer lifetimes. In general, radiative transitions that are coupled through a defect state are slower than band to band or excitonic recombination, because of the extra time required for a carrier to move into the impurity level, for example by tunneling processes.

1.11.1.4 Intraband Transitions

Intraband recombination is another type of transition present in semiconductor materials. Here a carrier relaxes to another level within its own band and this result in the emission of a photon. This transition is much more common in the reverse direction, intraband absorption, but has been observed in emission on occasion [1.155]. It is more likely that an excited carrier deep within a band relaxes via a thermalization process accompanied by the absorption or emission of phonons.

1.11.2 Nonradiative Recombination

An electron and hole can also recombine nonradiatively, giving off their excess energy in forms other than the emission of light. In many systems, this is the dominant form of recombination and so results in very poor emission efficiencies. For example, in germanium the radiative lifetime is predicted to be on the order of one second, however, the minority carrier lifetime in these systems is measured to be in the millisecond range. This means that many carriers are losing their energy quickly to nonradiative transitions that are much faster and more probable than typical radiative emission. In general, nonradiative transitions between two energy levels will occur if the energy difference between the excited state and the adjacent level is small, that is on the order of phonon emission. Once the difference becomes larger, it becomes more likely that a radiative recombination event will occur, and a photon of equivalent energy will be emitted. The presence of specific defects in a material creates a continuum of closely spaced states which act as a complete nonradiative bridge between the excited and ground levels. There are a number of physical phenomenon which do not result in photon emission, but serve as relaxation pathways for excited carriers. These nonradiative recombination processes include: phonon emission, Auger recombination, and surface or defect recombination. These processes
are often difficult to study since they only manifest themselves as a decrease in radiative emission, and there is often no clear way to isolate the specific mechanism of nonradiative recombination in a system.

1.11.2.1 Phonon Emission

Electrons excited into the conduction band can give back their energy through the emission of phonons or lattice vibrations. The typical energy for an individual phonon is on the order of millielectronvolts (meV) and so a number of these transitions must occur for the carrier to return to its ground state. These phonon emission events are similar in effect to the thermalization process that carriers excited deep into a band undergo while they relax back down to the band edge.

1.11.2.2 Auger Recombination

The Auger effect results when the emitted radiation from a carrier recombination event is used to excite another excited carrier, which then dissipates the energy nonradiatively. This dissipation typically occurs through a cascade emission of phonons. Since the effect requires carrier interaction, the effect becomes more intense with larger carrier concentrations. This has been seen in luminescence excitation studies, where the emission intensity scales with the excitation intensity until a point where the excitation process creates too many carriers and induces Auger nonradiative recombination. It has also been shown that porous silicon luminescence can be quenched through an application of voltage, due an injection of extra carriers into the system [1.156]. Auger recombination also results in processes that utilize the energetic or "hot" carrier created during the event. These carriers can recombine radiatively to emit a high energy photon, or even have enough energy to be ejected from the semiconductor entirely.

1.11.2.3 Surface and Defect Recombination

The presence of perturbations, such as structural defects or surfaces, can disrupt the periodicity of the crystalline lattice and cause disturbances in the energy band structure of the material. These can act as sites for the nonradiative relaxation of
excited carriers. Figure 1.24 is a model of a defect's effect on the density of states of a semiconductor. At the defect or surface, a continuum of localized states is created, linking the conduction band to the valence band. An excited carrier that is spatially within a diffusion length of the defect will be drawn to it and lose its energy nonradiatively through the continuum of states. For example, this effect has been observed in light emitting device structures that lose efficiency due to the presence of dislocations [1.157].

In the case of surface states, the continuum of nonradiative transition states in the gap is thought to be the result of unsatisfied dangling bonds on the semiconductor surface. These missing bonds trap carriers and prevent them from recombining radiatively, thereby reducing the emission efficiency in the system. In nanocrystalline systems, it is expected that even one dangling bond will be enough to trap carriers and prevent photon emission [1.158]. In addition, the fast relaxation caused by these trap sites and continuum of states prevents a buildup of excess carriers in the energy levels of the quantum dot material. This prevents the development of any nonlinear optical effects in the semiconductor nanocrystallite. Therefore, it becomes vitally important to remove these nonradiative centers from the system in order to promote novel optical behaviors. The nonradiative recombination centers present due to dangling bonds on the semiconductor surface can be eliminated by chemically passivating the bonds.

**Figure 1.24:** Model for effect of defect state on energy band and density of states of semiconductor. Defects create a continuum of states in gap which act as a nonradiative pathway for the relaxation of excited carriers. $L$ represents the carrier diffusion length and $r$ the defect radius [1.155].
This is the end of the chapter 1 that concluded with review of literatures discussing structural, electronic, and optical and luminescence properties of the materials with reference to II-VI semiconductor nanocrystals which provide basis of our research. Our experimental works are started from the next chapter. Chapter 2 introduces principles and pre-requisites for nucleation and growth of the nanoparticles. It then provides an overview on general synthesis strategies and the synthesis of monodispersed nanoparticles they form, in particular, quantum dots that form from their dilute solutions. Basic parameters that affect the growth and kinetics of nanoparticles are then discussed. All the particles synthesis strategies studied in this thesis are further elaborated and also discussed in more detail.