Chapter 1

Introduction

The central theme of materials physics is to predict the properties of materials, based on the knowledge of only its constituent elements. Over the past two decades, *ab initio* or first principles electronic structure calculation methods, based on density functional theory (DFT) [1, 2], have emerged as a forefront simulation tool. Different physical properties of materials, viz., bulk lattice constant, phase transition pressures and temperatures, heat of formation for alloys, magnetic, and optical properties etc, can be explained with reasonable accuracy employing these techniques [3]. Further, the availability of ever-increasing computational power, coupled with efficient and novel algorithms, have made this field very exciting.

Pseudopotentials based DFT methods [3, 4] are, perhaps, the most widely used techniques. The popularity of these methods lies in the ease of their usage, scalability across large numbers of processors as well as with problem size, and the availability of many user friendly, free as well as commercial packages [5–7]. With the advent of massively parallel supercomputers, it is possible to simulate the properties of materials and compare them with those obtained from experiments. Such possibilities are leading to exciting developments in the design of materials. Recently Hasegawa *et al.*, [8] showed that with a real space DFT implementation, one self-consistent field (SCF) iteration of 1,07,292 atoms of Si nanowires was possible on K computer, which is world’s second fastest supercomputer as on date.

1.1 Semiconductor quantum dots

Semiconductor Quantum dots (QD) are zero dimensional (0-D) objects whose excitons are confined in all the three spatial dimensions. These man-made particles could be considered as objects whose properties lie between two extreme ends: (i) bulk systems which are characterised by the

*Latin word which means from the beginning [Source: Oxford English Dictionary].
number of atoms that is at least of the order of Avogadro’s number ($\sim 6 \times 10^{23}$) and (ii) naturally occurring molecules which are composed of few atoms. The credit for the discovery of these exciting QD structures goes independently to Ekimov and Brus, by employing optical characterisation techniques. Ekimov et al., [9], in early 1980’s, had embedded CuCl semiconductor crystals with average radius ranging from 31 to 2.5 nm, in a transparent matrix. The absorption spectra of the largest crystal, matched well with the spectra of the CuCl film. However, for smaller crystals, the spectra was shifted to lower wavelengths (i.e. higher energy gap), with the corresponding broadening of the absorption line. This unusual phenomenon, demonstrated the size effects on the electronic structure of semiconducting materials, for the first time. A couple of years later, Brus and co-workers [10], synthesised self-standing CdS nanocrystals (NC) in a colloidal solution with an average particle diameter of $\sim 35$ Å. Raman spectroscopy of these colloidal NCs showed a blue shift in their spectra as compared to their bulk counterparts, indicating quantum confinement effect.

Reed et al., [11] observed discrete density of states, a typical characteristic of an electron-hole gas confined in all the three spatial dimensions. As opposed to the optical probe, electronic transportation was achieved in a heterogeneous semiconductors of zero dimensions. Apparently, it was Reed who gave the nomenclature quantum dot to these exotic objects.

Soon Bawendi’s group [12] demonstrated a single synthesis method to produce high quality CdE (E = S, Se, Te) NC of sizes ranging from 12 to 115 Å. These NC had a uniform size, shape, surface passivation, and consistent crystal structure. Even for small NC of 20 Å, a bulk like crystal

![Image](image.png)

Figure 1.1: Experimentally observed variation in HOMO-LUMO gap of CdSe QD w.r.t. size (shown in diamonds) is compared with the behavior obtained from effective mass approximation (solid line) [12]
structure was observed. Fig. 1.1 compares experimentally observed variation in the gap between
the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals
(LUMO) of CdSe NC plotted as a function of increasing size, with those obtained from calculations
based on effective mass approximation. Parameters of this crude approximation were derived from
bulk crystal structure. Though the experimental values matched well with those obtained from
theory for larger sized NC, there was a clear disagreement between the two methods for smaller
sizes.

In 2002, Peng’s group [13] developed a synthesis technique by which certain sizes of CdSe
clusters were formed in abundance and showed a distinct, sharp peak in the absorption spectra.
Moreover, these unique sized clusters formed a monomer which served as a nuclei for the growth
of larger sized NC with different shapes and sizes. In recent years, with the improvement in
synthesis method, ultranarrow CdSe clusters were produced, and again these clusters showed
distinct blue shifted absorption peak: a characteristic of this particular size. Transmission electron
microscopy (TEM) study revealed the size of such spherical clusters to be ∼ 16 Å [14]. Thus,
with the combination of tools like blue shifted absorption spectra combined with TEM data,
the approximate size of these clusters could be estimated. However, a clear identification of the
number of atoms in a particular sized stable cluster with atomic precision is possible only through
study of mass spectra analysis of vapours of NC.

1.2 Mass spectra experiments

When a bulk sample is laser ablated, locally high temperature is created and the material evap-
orates in the form of clusters. At equilibrium, clusters with certain sizes are produced in high
probability. Such cluster sizes are very stable and are said to be magic in nature due to their
exceptional stability and high abundance. To find out their mass, they are ionized and passed
through time-of-flight mass spectrometer which records the intensity of the counts w.r.t. the
atomic mass of the clusters [15]. The peaks in the mass spectrum indicate the magic number in
a given sample. Fig. 1.2 shows the mass spectra of different II-VI compound semiconductors like
ZnS, ZnSe, ZnO, CdSe and CdS. From the mass spectra, it is evident that the closed shell clusters
with \( n = 13 \) and 34 are very stable in most of the II-VI compounds. However in certain cases
such as in ZnSe, cluster with \( n = 33 \) are more stable.

In 2004, Kasuya et al., [16] revealed the existence of magic CdSe QD with \( n = 13, 33, \) &
34, employing mass spectrometry analysis (Fig. 1.2d). They further confirmed their findings by
measuring the optical absorption spectra of these clusters in a colloidal solution. The spectra was
similar to the one obtained earlier [12], indicating the presence of extremely stable clusters, whose
size was $\sim 15 \, \text{Å}$. These results indicate that, irrespective of the preparation method, certain magic
sized cluster grow preferentially due to their stability. Extended X-ray absorption fine structure
measurements of $(\text{CdSe})_{33,34}$ showed the coordination number of Se atoms as $3.2$. Note that
bulk CdSe is tetrahedrally coordinated, while a hollow cage is triply coordinated. This finding
indicated that the structure of these magic cluster is different from bulk and not exactly hollow.
First principles calculations predicted a novel $(\text{CdSe})_{28}$ cage encapsulating a $(\text{CdSe})_{6}$ core for $n$
$= 34$. The average coordination in such structure which was totally different from bulk, was $3.18,$
very close to the experimental value.

1.3 Magnetic doping in quantum dots

Intentional addition of magnetic impurities in a bulk semiconductor is a well known technique to
change their properties. However, similar doping in NC is a complex process. With doping, one
gets an additional degree of freedom, apart from controlling the shape, size, and composition, to
tune the properties of QD. For example, magnetism can be induced in semiconductors by doping
impurities like $3d$ transition metals. The optical spectra of doped NC show high luminescent
efficiencies and faster luminescent decay, as compared to the corresponding bulk doped system [19].
Studies on Mn doped II-VI NC has been an active area of research. Due to the similar chemical
nature of Mn$^{2+}$ as that of Cd$^{2+}$ & Zn$^{2+}$, it is much easier to incorporate Mn impurities in II-VI
host materials [20]. There is a growing interest in spintronic materials, where the spin of an
electron is used as a information carrier. The prediction of room temperature ferromagnetism in
Mn:ZnO [21], has triggered enormous interest in this material due to its possible usage as a dilute
magnetic semiconductor for spintronic applications [22]. We have explored in this thesis, doping
of Mn in QDs.

1.4 Applications of quantum dots

QDs are materials with potential applications in various fields, from solid state lighting to bio-
logical marker. Light emitting diodes (LED) which emit pure white light can be fabricated from
magic sized CdSe QD [23]. Self assembeled QDs introduced into the active layer of a quantum
well laser, improves its lasing charasteristics [24]. Large optical gain with wavelengths tunable
with the size of the nanocrystal in colloidal CdSe and CdS QDs were observed, demonstrating
the feasibility of a quantum dot laser [25]. Self standing QDs can be used as a medium for optical
storage. An optically generated exciton can be separated and preserved as an electron-hole pair, for an extended period of storage time in a coupled QD pairs, thus making them a candidate for optical storage [26].

One of the most exciting applications of QDs is its usage as a fluorescent marker in imaging living cells, where the unique opto-magnetic properties of QDs are harnessed. In the present (established) imaging technique, organic dyes are widely used as a biomarker. However, this

Figure 1.2: Mass spectrum of ions of different II-VI compound semiconductors indicating their abundance and the magic numbers. (a) ZnS [15] (b) ZnSe [17] (c) ZnO [18] & (d) CdSe, CdS, & ZnS [16].
traditional method suffers from major shortcomings, with a growing requirement for a more accurate, sensitive and cost-effective imaging technique. In a multicolour experiment, problems associated with relative intensity of the signal, short lifetimes, narrow excitation ranges, and broad emission spectra, impose serious limitations on the usage of organic dyes [27].

On the other hand, semiconductor QDs have emerged as a promising alternative for in vivo imaging, due to several attractive features [28–30]. The optical properties of QDs can be tuned in a controlled manner, by varying its size, shape, composition and by doping impurities. QDs have a broadband absorption spectrum. But the emission peaks in a narrow and symmetric band, which is a desirable feature for accurate and sensitive imaging. Doping of magnetic impurities further alters the QD emission spectra, apart from inducing magnetic moments, which can be detected by magnetic resonance imaging (MRI) technique. However, QDs made from Cd are inherently toxic and lead to the death of cells [27]. Hence, there are serious efforts to find a viable alternative to Cd based QD in II-VI semiconductor family.

1.5 Aim and scope of the thesis

The structure of II-VI compound semiconductor clusters below 20 Å diameter are totally different from their bulk counterpart. Further, with the data available from mass spectrometry, the exact numbers of atoms in a magic clusters are known. This gives us a unique opportunity to undertake a systematic study, aimed at finding the geometries and hence the electronic structure of these clusters. For example, the structures of (ZnS)$_n$ $(n = 13 & 34)$ given in Fig. 1.2a by Martin [15] are fragment of bulk. However, in an attempt to obtain the desired number of atoms $n$ in a cluster, the bulk is cut in such a way that the terminating ions are doubly bonded, while all other ions are triply bonded. This situation is not favourable and hence there could be structures lower in energy than plain bulk fragments.

Doping magnetic impurities like Mn in II-VI NC is a well studied problem. The isovalent Mn$^{2+}$ impurity substitutes the equivalent Zn$^{2+}$ or Cd$^{2+}$ site, inducing a net magnetic moment of 5 $\mu_B$ due to the presence of five unpaired 3$d$ electrons of the doped Mn atom. However, simple calculations show that, even the unpaired 3$d$ electrons in Mn can bind strongly with additional anions, thereby further lowering the magnetic moment of the clusters. Recent experimental results on Mn:ZnO thin films have shown mixed and higher oxidation state of Mn, viz., Mn$^{3+}$ and Mn$^{4+}$ [31, 32]. Further, as seen earlier, Cd based II-VI semiconductors have major ill effects of toxicity and hence are not environment friendly.

In view of these experimental developments in II-VI semiconductor nanoclusters, we focus on
the following aspects in this thesis:

- To understand the evolution of atomic structures of II-VI compound semiconductor clusters with size for clusters smaller than 20 Å, as their structures are very different from a bulk fragment. The emphasis is on biocompatible compounds like ZnSe and ZnO. We employ, state-of-the-art, first principles methods based on density functional theory (DFT) to obtain the electronic structure of these clusters.

- To investigate structures of small, bare as well as surface passivated ZnSe clusters with partially charged hydrogen atoms that are taken as models for ligation and compare their optical absorption spectra with experiments.

- To study the effects of doping magnetic impurities like Mn on the electronic structure, geometry, magic nature and magnetic moment of \((\text{ZnSe})_n\) & \((\text{ZnO})_n\) clusters, with a focus on sizes \(n = 12, 13, & 34\), that are most interesting from the point of view of growth and abundance.

1.6 Organisation of the thesis

The rest of the thesis is organised as follows:

- Chapter 2, summarises the theoretical formulation which are required to carry out first principles calculations. We start with explaining the Thomas-Fermi-Dirac (TFD) model, its drawbacks and then introduce the modern DFT by stating the Hohenberg-Kohn and the Kohn-Sham theorems. Hartree-Fock method is briefly described followed by pseudopotential based plane wave formulation to solve the Kohn-Sham equations. A real space method is also explained and compared with the plane wave method. The time dependent DFT (TD-DFT) approach to calculate the optical absorption spectra based on the real space formulation is described at the end.

- In chapter 3, the optical properties of small, bare and surface passivated ZnSe clusters are calculated. Initially, DFT based geometry optimisation is carried out to obtain the electronic structure of the clusters with increasing size. The charge density and the corresponding electronic eigen values of the Kohn-Sham equations serve as an input to the TD-DFT method, for calculating the optical absorption spectra. The optical gaps, thus obtained, are then compared with the experimental data.
• The doping of Mn in (ZnSe)$_n$ ($n = 12, 13, \& 34$) clusters and the discovery of a magnetic, magic, non-stoichiometric cluster with a configuration of $\text{Zn}_{11}\text{MnSe}_{13}$ is explained in chapter 4.

• Chapter 5 describes the doping of Mn in (ZnO)$_n$ ($n = 12, 13, 34 \& 35$) clusters. With Mn doping, \textit{ab initio} calculations show that O rich, non-stoichiometric $\text{Zn}_{12}\text{MnO}_{15}$ and $\text{Zn}_{34}\text{MnO}_{37}$ clusters become magic with 1 $\mu_B$ magnetic moment. The Mn doped clusters can be also viewed as nanocomposites where a $\text{MnO}_x$ molecule ($x = 1$ to 4) is attached to (ZnO)$_n$ ($n = 12$ and 34) cages.

• The summary and the possible extensions to the current work presented in the thesis are described in chapter 6.

Conclusion of the research work is written at the end of each chapter. An updated bibliography is appended at the end.