STUDY OF ELECTRONIC STRUCTURE OF DISORDERED SYSTEMS

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To my parents and my fianćee......

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"The first principle is that you must not fool yourself and you are the easiest person to fool."-Richard P. Feynman

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Publications

1. **A new approach to determine accurate band gaps within density functional formalism**

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3. **Magnetic behaviour of AuFe and NiMo alloys**

   Prashant Singh, Rudra Banerjee, Moshiour Rahman, A.V. Ruban, Biplab Sanyal and Abhijit Mookerjee

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4. **Magnetic transitions in $Ni_{(1-x)}Mo_x$ and $Ni_{1-x}W_x$ disordered alloys**

   Prashant Singh, Moshiour Rahman and Abhijit Mookerjee

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5. **Effect of donor (acceptor) impurities on Cr doped $(ZnTe)_{12}$ clusters**

   Prashant Singh and Abhijit Mookerjee

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Chapter 1

Introduction

In this thesis we have addressed three classes of problems : (a) the basic density functional theory. We have modified the underlying exchange-correlation potential such that the new formulation describes semi-conductors and insulators accurately. (b) study of magnetism and electronic structure of bulk disordered alloys and (c) doped and co-doped clusters.

1.1 Density Functional Theory

First principles description of the electronic structure and related properties of disordered solids has been a challenging problem. The Bloch theorem, which allows us to use lattice translation symmetry of the Hamiltonian to simplify the problem to a large extent, is no longer valid in the presence of disorder. This puts constraints in formulating a new quantitative calculational technique with the same degree of accuracy and efficiency as that for crystalline solids. In our research group considerable volume of work has been done on disordered metallic solids but semiconductor and insulators have not been touched much. The density functional theory (DFT) [3] and its local density approximation (LDA) upon which majority of our work has been based underestimates the band gaps in such solids considerably.

The first part of our work will be to propose and apply a modified version of DFT, going beyond the standard LDA, which will yield accurate band gaps and also a better picture of the excited states.

As we shall see subsequently, the part of the total energy contributed by the electron-electron repulsion is a functional of the two particle reduced density matrix. The exact functional relationship between the correlation function arising out of such a pair density and the density is not, in general, known. This leads to approximations which could be one of the causes of the failure to predict the band-gap with any degree of accuracy. The challenge of DFT lies in determining the unknown form of the exchange-correlation functional. The simple formulae for exchange-correlation derived for the homogeneous free electron gas were used with the Thomas-Fermi ideas as an approximation for the exact interacting electron cloud. This procedure was justified by the Hohenberg-Kohn theorem [4]. This theorem proves that

(i) The ground state density uniquely determines all the terms in the many-body Hamiltonian; consequently leads to evaluation of all properties of the system, which includes many-body wave function [5].

(ii) The correct determination of ground-state density for which true density functional leads to the electronic energy minimum of the system.

Subsequently, using above propositions the many-body Schrödinger equation effectively maps onto a single particle Kohn-Sham equation. In spite of making huge progress in electronic structure calculations, obtaining the exchange-correlation potential and energy still remains unsatisfactory. This is the only major approximation involved in solving the Kohn-Sham equation. Many different functionals have been introduced since the very first functional proposed by Kohn-Sham [6] based on the homogeneous electron gas (HEG) model. Without considering the atomic lattice and structure which constitute a real material, HEG model allows one to understand the effects of quantum nature of electrons and mutual electronic repulsions in solids. LDA successfully predicts many ground state property quite accurately e.g. structural, elastic and vibrational properties. In the LDA binding energy estimations are too negative, activation energies are not reliable, as also is the relative stability of crystal bulk phases. While LDA provides a better insight into the density of states and band structure, it fails to resolve the problem of the band gap. Drastic underestimation of band gap and wrong band positions in semiconductors and insulators turn out to be one of the classic failures of the LDA. The motivation of our work was to develop a method which we can apply for semiconductors and insulators. Since our electronic structure methods all depend upon the LDA, they too suffer from its drawbacks. The LDA exchange potential does not have the derivative discontinuities that are present in other functionals. It is a well-behaved function of density which is not sensitive to the particle number. No correct treatment of self-interaction for electrons is present as in the Hartree-Fock and the exchange functionals. The success of any density functional method depends on a good choice of the exchange-correlation functional, our task was to decide upon how to replace the LDA exchange potential. The criteria that the new potential must meet are : (a) the derivative discontinuity should be there and (b) the functional should be self-interaction free.

1.2 Dealing with disorder

Disorder in solids falls in two main classes : substitutional disorder, where the underlying lattice remains unchanged, only the lattice sites are randomly occupied by different species of atoms ; and topological disorder where the underlying lattice is itself randomly distorted. In several situations both types of disorder may become relevant. In this thesis we shall address only substitutional disorder : a canonical example of this is a random alloy.

Configuration averaging of physical quantities is a central idea in the study of disordered systems. Several techniques have been proposed to evaluate such configuration averages. Among them coherent potential approximation (CPA) [10] turned out to be the most successful. The idea was proposed by Soven (1967) to tackle electronic motion in the background of a random potential. This was motivated by an idea proposed by Landau and Lifshitz (1975) to study randomly dispersed spherical globules of one dielectric in another. The problem with the CPA was that it was a single-site, mean field approximation. It cannot accurately take into account of local correlations leading to clustering or short-ranged order. Neither can it deal with disorder in the off-diagonal part of the Hamiltonians that arise, for example, when there is a large difference in the band widths of the constituents. Later many attempts have been made to generalize CPA to include multi-site correlations. One of the first novel approaches to this problem was based on the augmented space theorem introduced by Mookerjee [2, 11]. The augmented space formalism (ASF) is very powerful tool. It has been shown that the CPA is a special approximation within the ASF. The ASF, therefore, is a generalization of the CPA. We can introduce such approximations that short-ranged correlations are included and the essential properties like positive definite spectral densities and, in cases of homogeneous disorder,lattice translation symmetry of averaged quantities are all preserved. ASF is one of alternatives suggested for CPA due to some difficulties pointed above. In this thesis we have projected both ASF and CPA in our calculations.

To study the ordering effects in disordered alloys, we shall use the generalized perturbation method (GPM) [12, 13]. The expansion coefficients are small energy differences of large energies. We have chosen the Lichtenstein formula [14, 15] to accurately obtain such small energy differences. The GPM mapped our problem on the Ising model for doing magnetic phase analysis of disordered systems under consideration.

1.3 Transition Metal Clusters

By clusters we mean systems with a finite number of bonded atoms.The number of atoms can vary from a few to millions. Clusters lie somewhere between an atom and the bulk, forming a bridge between the two. Studying physical and chemical properties of clusters with increasing size from a few atoms to bulk leads us to an understanding of how they evolve with increasing size of cluster. Clusters of varying sizes can be generated using a variety of techniques such as sputtering, chemical vapor deposition, laser vaporization, supersonic molecular beam etc. Semiconductors with dilute magnetic impurities (DMS) [16] have opened up a possibility of manipulating the spin degree of freedom of electrons through interaction between the local moments of the doping magnetic ions and the spins of the charge carriers of the host semiconductors. Magnetic clusters and nano-particles are interesting not only because of their possible technological applications, but also because in these systems we can systematically study the effect on magnetism with diminishing size and dimension. As clusters are interesting because finite size effect can lead to quite different structural, electronic, magnetic and other properties different from molecule and bulk.

In transition metal clusters have incomplete d-shells and localized d-shell electrons which make them interesting in comparison to clusters with sp-shells whose properties are largely affected by delocalized sp-orbitals. The studies done on clusters and solids to calculate different properties shows intrinsic difference between atomic and bulk nature. Magnetism in transition metal (TM) clusters is one of fundamental issues to be addressed at the atomic level. The magnetic properties of nano particles depending on size, composition and local atomic environment show variety of intriguing phenomena. The deflection experiment of Stern-Gerlach (SG) type is commonly used by experimentalist to study magnetism of free transition-metal clusters in molecular beams [17]-[22].

We shall address a different class of problem, namely finite clusters of atoms with dopants (alloyed clusters). S. Kuroda et.al. [23] has shown that the effect of additional doping of charge impurities in ferromagnetic semiconductor $\mathrm{Zn}_{1-x}\mathrm{Cr}_x\mathrm{Te}$ e.g. iodine or nitrogen, (which is expected to act as an n-type or p-type) dopant in ZnTe, brought about a drastic enhancement or reduction of the ferromagnetism in $Zn_{1-x}Cr_xTe$, while the grown films remained electrically insulating. Furthermore we have explored, how the energetics and magnetism will change if we look at clusters instead of $Zn_{1-x}Cr_xTe$ bulk or films. So we choose a particular type of $(\mathrm{ZnTe})_{12}$ clusters [24] doped with transition metal Cr, at either of Zn or Te site cites and then co-doped with donor type impurities from group VII e.g. Iodine(I) or acceptor type of impurities from group V e.g. Nitrogen(N) respectively. Donor or acceptor type of impurities has been doped either at Zn or Te sites or outside(or inside) of the $(\mathrm{ZnTe})_{12}$ cage to see it's effect on energetics, magnetic properties etc. of the cluster.

1.4 Outline of the thesis

The thesis has been outlined as follows:

(I) In **chapter 2**, we shall introduce the detailed theoretical framework of electronic structure calculations carried out in this thesis.

(II) Our aim in **chapter 3** is to develop a non-variational approach, the exchange-correlation functional introduced by Harbola-Sahni [7] to calculate excited state properties e.g. band gap. We shall also show that Harbola-Sahni exchange-correlation potential gives good ground state properties in agreement with experiments e.g. mechanical properties viz bulk moduli.

(III) Why does NiMo alloy not show spin glass nature unlike AuFe ?. In **chapter 4**, we look at very small concentration range of Mo from 0-18 at.%, using augmented space formalism [2] within mean field approximation.

(IV) A comparative study of NiMo and NiW alloys at low concentration range of Mo and W ($\approx$ 0-18 at.%). In **chapter 5** coherent potential approximation [10] is been employed to look into the properties of above mentioned alloys.

(VI) Transition metal clusters are of special interest, as the transition metal atom in free state posses an incomplete d-shell in the ground state and many ground state properties are governed by these localized d-electrons. In **Chapter 6** we studied, what happens to structural stability, magnetism etc. of $\mathrm{Zn}_{1-x}\mathrm{Cr}_x\mathrm{Te}$ cluster doped with donor (I) or acceptor (I) impurity at diminishing size.

Chapter 2

A brief review on Electronic Structure Theory

In this chapter, we shall present an overview of the density functional theory (DFT) and linearized muffin-tin orbital (LMTO) method which describes the ground state properties of a many electron system in terms of the density of the system. All calculations has been done within DFT.

2.1 The many-body Schrödinger equation

The Schrödinger equation is the conventional point to begin description of many-electron systems. For stationary state problems :

$$\hat{H}\psi = i\bar{h}\frac{\partial\psi}{\partial t} = E\psi \tag{2.1}$$

where $\hat{H}$ represents the Hamiltonian of an N-electron system and can be written as (atomic units are used throughout)

$$H = \sum_{I=1}^{N_c} \frac{-\nabla_I^2}{2M_I} + \sum_{i=1}^{N} \frac{-\nabla_i^2}{2m} + \frac{1}{2}\sum_{i,j} \frac{1}{r_{ij}} + v_{eI}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) + V_{II}(\{\mathbf{R}_I\}) \tag{2.2}$$

where we have considered a system consisting of N_c ion-cores (the I^{th} ion core having a mass M_I) bonded in a solid by N valence electrons (the i^{th} valence electron having a mass m). V_{II} and v_{eI} are the Coulomb interactions between the ions themselves and between the electrons and ions. r_{ij} is the distance between the i^{th} and the j^{th} electron.

The mass of the ion is much larger than that of an electron (M $\gg$ m), so that the characteristic time scale over which an electron changes its state is much smaller than that associated with the motion of the ions. Hence, the ion-cores can be treated as stationary during the short time the electron state evolves. This makes it possible to solve the Schrödinger equation for the wave function of electrons alone. This is the Born-Oppenheimer approximation. The wave function may then be written in a separable form $\chi(\{\mathbf{R}_I\})\psi(\{\mathbf{r}_i\}|\{\mathbf{R}_I\})$. Thus, the Schrödinger equation for the electrons (for a given position of the ion cores $\mathbf{R_I}$) can be written as:

$$\left[-\sum_{i=1}^{N} \frac{\nabla_i^2}{2m} + v_{eI}(\{\mathbf{r}_i\}|\{\mathbf{R}_I\}) + \frac{1}{2}\sum_{i,j} \frac{1}{r_{ij}})\right] \psi(\{\mathbf{r}_i\}|\{\mathbf{R}_I\}) = E_e(\{\mathbf{R}_I\})\psi(\{\mathbf{r}_i\}|\{\mathbf{R}_I\}) \tag{2.3}$$

The total energy of the system is a sum of electron and ion-core energies. The problem in trying to solve this equation is the number of variables involved. Which shows the difficulty of the problem. We quote Feynman "The trouble with quantum mechanics is not only in solving the equations, but in understanding what the solutions mean."

Attempts to solve these problems due to the immensely large number of variables and lack of easy interpretation has led to the development of newer approaches. An important class of methods has been based on the variational principle where one minimizes the quantity

$$\tilde{E} = \langle \tilde{\Psi} | H | \tilde{\Psi} \rangle \tag{2.4}$$

using suitable forms of the trial function $\tilde{\Psi}$ mainly guided by the one-particle orbital picture leading to single particle self-consistent field schemes like Hartree, Hartree-Fock and multi-configuration methods. However, due to the computational expense the routine application of such methods to realistic models of systems of interest is not practical and not likely to become so despite rapid advances in computer technology. So, the question that arises is - *Is it necessary to solve the Schrödinger equation and determine the 3N dimensional wave function in order to compute the ground state energy?*

2.2 Avoiding the solution of the Schrödinger equation

An alternative approach has been based on the reduction to lower dimensions based on the density functional theory. For more than past three decades density functional theory has been the dominant method for the quantum mechanical simulation of periodic systems. It has been adopted by quantum chemists and is now very widely used for the simulation of energy surfaces in molecules.

Although the electronic wave function for the N electron system is a function of 3N variables, the expectation value $\langle\Psi|\hat{A}|\Psi\rangle$ can be calculated through other derived quantities that depend on less number of variables, if $\hat{A}$ is a sum of one- or two-particle operators, as is the case for the Hamiltonian. Thus, for the ion-core - electron potential energy consisting of one-particle terms, one has :

$$\begin{aligned}&\int \Psi^*(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)\sum_i v_{eI}(\mathbf{r}_i|\{\mathbf{R}_I\})\Psi(\mathbf{r}_1,\mathbf{r}_2,...\mathbf{r}_N)d\mathbf{r}_1d\mathbf{r}_2...d\mathbf{r}_N\\ &= N\int d\mathbf{r}\ v_{eI}(\mathbf{r}|\{\mathbf{R}_I\})\int \Psi^*(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,...\mathbf{r}_N)d\mathbf{r}d\mathbf{r}_2...d\mathbf{r}_N \qquad (2.5)\end{aligned}$$

All electrons are identical, so we choose any of the variables and rename it $\mathbf{r}$ and renumber the rest $\mathbf{r}_2, \mathbf{r}_3 \ldots \mathbf{r}_N$. Hence the result

$$V_{eI} = \langle\Psi|\sum_i v_{eI}(\mathbf{r}_i|\{\mathbf{R}_I\})|\Psi\rangle = \int d\mathbf{r}\ v_{eI}(\mathbf{r}|\{\mathbf{R}_I\})\rho(\mathbf{r}) \qquad (2.6)$$

valid for any single-particle multiplicative operator, where the single-particle density is defined as

$$\rho(\mathbf{r}) = N\int \Psi^*(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,...\mathbf{r}_N)\ d\mathbf{r}_2d\mathbf{r}_3...d\mathbf{r}_N \qquad (2.7)$$

Similarly, for two-particle multiplicative operators such as the electron-electron repulsion, one can write

$$V_{ee} = \langle\Psi|\frac{1}{2}\sum_{i,j}\frac{1}{\mathbf{r}_{ij}}|\Psi\rangle = \frac{1}{2}\int d\mathbf{r}_1d\mathbf{r}_2\ \Gamma_2(\mathbf{r}_1,\mathbf{r}_2)/\mathbf{r}_{12} \qquad (2.8)$$

where the two-particle density, which gives the joint probability of finding an electron at $\mathbf{r}_1$ and an electron at $\mathbf{r}_2$, is defined as

$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)d\mathbf{r}_3...d\mathbf{r}_N \tag{2.9}$$

The functional Γ_2 is often referred to as the pair density.

The reduced density functions can also be expressed as the expectation values of the corresponding density operators, viz.

$$\rho(\mathbf{r}) = \langle\Psi|\sum_i \delta(\mathbf{r} - \mathbf{r}_i)|\Psi\rangle \tag{2.10}$$

Thus we can write

$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \langle\Psi|\sum_{i\neq j}\sum \delta(\mathbf{r}_1 - \mathbf{r}_i)\delta(\mathbf{r}_2 - \mathbf{r}_j)|\Psi\rangle \tag{2.11}$$

For the kinetic energy term which involves differential operators, one can write

$$\begin{aligned} T &= -\langle\Psi|\sum_i \frac{\nabla_i^2}{2m_i})|\Psi\rangle \\ &= -\frac{1}{2}N\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \nabla_1^2 \Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)\ d\mathbf{r}_1 d\mathbf{r}_2...d\mathbf{r}_N \\ &= -\frac{1}{2}N\int \left[\frac{\nabla_1^2}{2m_1}\Psi^*(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)\right]_{r_1=r_1^{'}} d\mathbf{r}_1 d\mathbf{r}_2...d\mathbf{r}_N \\ &= -\frac{1}{2}\int d\mathbf{r}_1 \left[\frac{\nabla_1^2}{2m_1}\gamma(\mathbf{r}_1;\mathbf{r}_1^{'})\right]_{r_1=r_1^{'}} \end{aligned} \tag{2.12}$$

with the first-order reduced density matrix defined as

$$\gamma(\mathbf{r}_1;\mathbf{r}_1^{'}) = N\int \Psi^*(\mathbf{r}_1^{'}, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)d\mathbf{r}_2 d\mathbf{r}_3...d\mathbf{r}_N \tag{2.13}$$

Clearly, the following relationships among the reduced density functions and matrices hold good.

$$\begin{gathered}
\rho(\mathbf{r}_1) = \gamma(\mathbf{r}_1, \mathbf{r}_1) \quad ; \quad \Gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \\
\int \rho(\mathbf{r}_1) d\mathbf{r}_1 = N \quad ; \quad \int \Gamma_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = N(N-1) \\
\gamma(\mathbf{r}_1; \mathbf{r}_1^{'}) = \gamma^*(\mathbf{r}_1^{'}; \mathbf{r}_1) \quad ; \quad \rho(\mathbf{r}_1) = \frac{1}{N-1} \int \Gamma_2(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2
\end{gathered} \tag{2.14}$$

For spin-polarized situation one has to include the spin dependence, such that,

$$\begin{gathered}
\rho(x) \equiv \rho(\mathbf{r}\ s) \quad ; \quad \int dx \rightarrow \sum_s \int d\mathbf{r} \quad ; \quad \rho(\mathbf{r}) = \sum_s \rho(x) ds \\
\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}) \qquad s(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})
\end{gathered} \tag{2.15}$$

The total energy can thus be expressed in terms of the reduced density matrices (RDM) as

$$E[\rho, \gamma, \Gamma_2] = T[\gamma(\mathbf{r}_1; \mathbf{r}_1^{'})] + V_{eI}[\rho(\mathbf{r})] + V_{ee}[\Gamma_2(\mathbf{r}_1, \mathbf{r}_2)] + V_{II} \tag{2.16}$$

where V_{II} is the ion-core - ion-core interaction energy. This leads to the possibility of developing the quantum mechanics of many-electron systems in reduced space in terms of the RDM's bypassing the wave function. One of the important requirements is the possibility of direct determination of RDM by minimizing the energy with respect to the RDM's for which the effect of the Pauli exclusion principle has to be built-in into the RDM's. The existence of an antisymmetric ψ from which the RDM's can be obtained has to be guaranteed.

This is the so called N-representability problem which has to be solved by imposing necessary and sufficient conditions on $\gamma_1(\mathbf{r}_1;\mathbf{r}_1^{'})$ and $\Gamma_2(\mathbf{r}_1,\mathbf{r}_2)$, which are unfortunately not yet known. The N-representability conditions on $\rho(\mathbf{r})$ are however known and are very simple, viz.

$$\int \rho(\mathbf{r})d\mathbf{r} = N; \qquad \rho(\mathbf{r}) \geq 0. \tag{2.17}$$

This makes the single-particle density (simplest reduced quantity) a promising candidate for the formulation of quantum mechanics in reduced space. Some of the many advantages for the electron density $\rho(\mathbf{r})$ to be the basic variable are :

(a) it is a function in 3D space in which we live and perceive,

(b) it is simpler to tabulate and plot,

(c) it provides a better visualization and

(d) it is an experimental observable, thus enabling one to compare the results of theoretical calculations directly with experiments.

The question now is whether it is possible to develop a quantum theory in terms of density alone bypassing the wave function, for which one has to ensure if (a) the density contains sufficient information (b) calculation of the properties and the energy is possible from the density alone (c) it is possible to develop a method for the direct calculation of density.

The possibility of a density description of many-electron systems has been explored by many people leading to the so called density functional theory (DFT). Although the first DFT, viz. The Thomas Fermi method has existed since 1927, the birth of modern DFT has been through the formal proof of a theorem by Hohenberg and Kohn (1964).

2.3 Hohenberg-Kohn Theorem

The Hohenberg-Kohn Theorem [4] establishes the density as the basic variable. This theorem states that the ground-state density $\rho(\mathbf{r})$ of a bound system of interacting electrons in an external potential $v(\mathbf{r})$ determines this potential uniquely (up to an uninteresting additive term).

Consider the ground states of two N-electron systems characterized by the two external potentials (differing by more than an additive constants) $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ with corresponding Hamiltonian:

$$H_1 = T + U + \sum_i v_1(r_i) \quad ; \quad H_2 = T + U + \sum_i v_2(r_i)$$

where

$$T = -\frac{1}{2}\sum_{i}^{N} \nabla_i^2 \quad \text{and} \quad U = \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

with the corresponding Schrödinger equation, $H_1\psi_1 = E_1\psi_1; H_2\psi_2 = E_2\psi_2$ and we assume that the two wave functions ψ_1 and ψ_2 yield the same density as,

$$\rho(\mathbf{r}) = N \int \psi^*_{1|2}(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N)\psi_{1|2}(\mathbf{r}, \mathbf{r}_2, ...\mathbf{r}_N)\ d\mathbf{r}_2 d\mathbf{r}_3 ... d\mathbf{r}_N \tag{2.18}$$

Now,

$$\begin{aligned} E_1 &= \langle \Psi_1 | H_1 | \Psi_1 \rangle \ \leq \ \langle \Psi_2 | H_1 | \Psi_2 \rangle \\ &\leq \langle \Psi_2 | H_2 | \Psi_2 \rangle + \langle \Psi_2 | H_1 - H_2 | \Psi_2 \rangle \\ &\leq E_2 + \int dr \rho(r)[v_1(\mathbf{r}) - v_2(\mathbf{r})]. \end{aligned} \tag{2.19}$$

Now, similarly one could show that,

$$E_2 \leq E_1 + \int dr \rho(r)[v_2(\mathbf{r}) - v_1(\mathbf{r})]. \tag{2.20}$$

Summation of the above two inequalities leads to the contradiction

$$E_1 + E_2 \leq E_2 + E_1 \tag{2.21}$$

Hence the assumption of identical density arising from the two different external potentials is wrong. Thus a given $\rho(r)$ can only correspond to only one $v(\mathbf{r})$ and since $v(\mathbf{r})$ is fixed, the Hamiltonian and hence the wave functions are also fixed by density

$\rho(\mathbf{r})$. Since the wave function is a functional of density, the energy functional $E_v[\rho]$ for a given ion-core - electron potential $v_{eI}(\mathbf{r})$ is a unique functional of density. It can also be directly proved that this energy functional assumes a minimum value for the true density.

The minimization of $E_v[\rho]$ subject to the constraint of normalized density, as given by eqn. (2.17), leads to the Euler equation for the direct calculation of density, viz.

$$\begin{aligned} \delta[E_v[\rho] - \mu \int \rho(\mathbf{r}) d\mathbf{r} - N] = 0 \\ \frac{\partial E}{\partial \rho} - \mu = 0 \Rightarrow \mu = \frac{\partial E}{\partial \rho} = v(\mathbf{r}) + \frac{\partial F}{\partial \rho}. \end{aligned} \tag{2.22}$$

The essence of the problem now is to obtain an expression for the energy functional in terms of density which has the general form

$$E_v[\rho] = \textstyle\int v_{eI}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + F[\rho]$$

where $F[\rho]$ is a universal functional of density. Comparing with the energy functional in terms of the RDM's, i.e.,

$$E_v[\rho, \gamma, \Gamma_2] = T[\gamma] + \int v_{eI}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\Gamma_2(\mathbf{r}_1, \mathbf{r}_2)}{\mathbf{r_{12}}} d\mathbf{r}_1 d\mathbf{r}_2 \tag{2.23}$$

and using the decomposition

$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)[1 - f(\mathbf{r}_1, \mathbf{r}_2)] \tag{2.24}$$

where $f(\mathbf{r}_1, \mathbf{r}_2)$ is the correlation function, one can separate out from the electron-electron repulsion term, the classical electrostatic contribution

$$E_{coul}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \tag{2.25}$$

The exact kinetic energy functional $T[\rho]$ is usually replaced by the kinetic energy of a system of non-interacting particles $T_s[\rho]$ and the contribution from the electron-electron interaction energy other than the classical electrostatic contribution and the difference $T[\rho] - T_s[\rho]$ constitute what is known as the exchange-correlation (xc) energy functional $E_{xc}[\rho]$. Thus, one can write

$$E_v[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})d(\mathbf{r}) + E_{coul}[\rho] + T_s[\rho] + E_{xc}[\rho]. \tag{2.26}$$

Thus E_{xc} is simply the sum of the error made in treating the electrons classically and in the error made in using a non-interacting kinetic energy. We note at this point that the nomenclature in general use and also used in the present context, exchange-correlation (xc) energy functional is quite misleading for as stated above the E_{xc} contains an element of the kinetic energy and is not the sum of the exchange and correlation energies.

The scheme for obtaining the non-interacting kinetic energy functional $T_s[\rho]$ for a certain $\rho(\mathbf{r})$ is through the solution of the one-particle Schrödinger equations

$$\left[-\frac{1}{2}\bigtriangledown^2 + \lambda(\mathbf{r})\right] \psi_i = \epsilon_i \psi_i \tag{2.27}$$

for a suitably chosen $\lambda(\mathbf{r})$ such that the resulting orbitals yield the density as

$$\rho(\mathbf{r}) = \sum_i |\psi_i|^2 \tag{2.28}$$

and then evaluating the functional as

$$T_s[\rho] = \sum_i \epsilon_i - \int dr \lambda(\mathbf{r})\rho(\mathbf{r}). \tag{2.29}$$

The energy functional that is to be minimized for determining the correct equilibrium density is then given by

$$E_v[\rho] = \sum_i \epsilon_i - \int dr \lambda(\mathbf{r})\rho(\mathbf{r}) + \int v_{eI}(\mathbf{r})\rho(\mathbf{r})d(\mathbf{r}) + E_{coul}[\rho] + E_{xc}[\rho] \tag{2.30}$$

which leads to the variational condition

$$\partial E_v[\rho] = 0 = \sum_i \delta\epsilon_i - \int d\mathbf{r}\delta\lambda(\mathbf{r})\rho(\mathbf{r}) + \int \delta\rho(\mathbf{r})[-\lambda(\mathbf{r}) + v_{eI}(\mathbf{r}) + \tag{2.31}$$

$$\frac{\partial E_{coul}}{\partial\rho(\mathbf{r})} + \frac{\partial E_{xc}}{\partial\rho(\mathbf{r})} \tag{2.32}$$

Considering the expression for ϵ_i,

$$\epsilon_i = -\langle\Psi_i|\frac{1}{2}\bigtriangledown_i^2|\Psi_i\rangle + \langle\Psi_i|\lambda(\mathbf{r})|\Psi_i\rangle \tag{2.33}$$

we get,

$$\begin{aligned}\delta\epsilon_i &= \langle\delta\Psi_i|\frac{1}{2}\bigtriangledown_i^2|\Psi_i\rangle + \langle\delta\Psi_i|\lambda(\mathbf{r})|\Psi_i\rangle + c.c. + c.c. + \langle\Psi_i|\delta\lambda(\mathbf{r})|\Psi_i\rangle \\ &= \epsilon_i\delta\langle\Psi_i|\Psi_i\rangle(=0) + \langle\Psi_i|\delta\lambda(\mathbf{r})|\Psi_i\rangle \qquad (2.34)\end{aligned}$$

and hence the result:

$$\sum\delta\epsilon_i = \int dr\rho(\mathbf{r})\delta\lambda(\mathbf{r}) \qquad (2.35)$$

which in combination with the variational condition leads to the result

$$\delta E_v[\rho] = 0 = \int dr\delta\rho(\mathbf{r})[-\lambda(\mathbf{r}) + v_{eI}(\mathbf{r}) + \frac{\partial E_{coul}}{\partial\rho(\mathbf{r})} + \frac{\partial E_{xc}}{\partial\rho(\mathbf{r})}] \qquad (2.36)$$

Since the variation of $\delta\rho(\mathbf{r})$ is arbitrary, the bracketed quantity must be zero and hence one has

$$\lambda(\mathbf{r}) = v_{eI}(\mathbf{r}) + \frac{\partial E_{coul}}{\partial\rho(\mathbf{r})} + \frac{\partial E_{xc}}{\partial\rho(\mathbf{r})} \qquad (2.37)$$

This clearly shows that if one chooses $\lambda(\mathbf{r})$ given by this expression, the single particle Schrödinger equation leads to the correct density for the system.

This provides the basis for the Kohn-Sham (K-S) density functional scheme which involves solution of a set of N nonlinear integro-differential equations:

$$[-\tfrac{1}{2}\bigtriangledown^2 + v_{eff}(\mathbf{r};\rho)]\psi_i = \epsilon_i\psi_i$$

with the effective potential given by

$$v_{eff}(\mathbf{r}) = v_{eI}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} = \phi(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \tag{2.38}$$

where, $\bigtriangledown^2 \phi = 4\pi\rho(\mathbf{r})$ and the density is calculated as

$$E_v[\rho] = \sum_i \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} dr dr' + E_{xc}[\rho] - \int d\mathbf{r} \rho(\mathbf{r}) \frac{\partial E_{xc}}{\partial \rho(\mathbf{r})} \tag{2.39}$$

for spin-polarized situations, incorporating the spin-components of the density as well we have,

$$E_v[\rho_\alpha, \rho_\beta] = T_s + \int v(\mathbf{r})\rho(\mathbf{r}) d(\mathbf{r}) + E_{coul}[\rho] + T_s[\rho] + E_{xc}[\rho_\alpha, \rho_\beta]. \tag{2.40}$$

and the Kohn-Sham equation under the spin-polarized situation becomes

$$[-\frac{1}{2} \bigtriangledown^2 + v_{eff}(\mathbf{r}; \rho_\sigma)] \psi_{k\sigma} = \epsilon_{k\sigma} \psi_{k\sigma} \tag{2.41}$$

with an effective potential given by

$$v_{eff,\sigma}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}^{'})}{|\mathbf{r}-\mathbf{r}^{'}|} d\mathbf{r}^{'} + \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma(\mathbf{r})} \tag{2.42}$$

The corresponding density is given by

$$\rho(\mathbf{r}) = \textstyle\sum_i |\psi_{k\sigma}|^2$$

This set of non-linear equations (the Kohn-Sham equations) describes the behaviour of non-interacting “electrons” in an effective local potential. For the exact functional, and thus exact local potential, the “orbitals” yield the exact ground state density and corresponding energy. The Kohn-Sham approach gives an exact correspondence of the density and ground state energy of a system consisting of non-interacting Fermions and the “real” many body system described by the Schrödinger equation. The correspondence of the charge density and energy of the many-body and the non-interacting system is only exact if the exact functional is known. In this sense Kohn-Sham density functional theory is an empirical methodology - we do not know (and have no way of systematically approaching) the exact functional. However the functional is universal - it does not depend on the materials being studied. For any particular system we could, in principle, solve the Schrödinger equation exactly and determine the energy functional and its associated potential. This, of course, involves a greater effort than a direct solution for the energy. Nevertheless, the ability to determine the exact properties of the universal functional in a number of systems allows excellent approximations to the functional to be developed and used in unbiased and thus predictive studies of a wide range of materials -a property usually associated with an *ab initio* theory. In practice, the utility of the theory rests on the approximation used for $E_{xc}[\rho]$.

2.4 The Local density approximation for $E_{xc}[\rho]$

The generation of approximations for E_{xc} has lead to a large and still rapidly expanding field of research. There are now many different flavours of functional available which are more or less appropriate for any particular study. In the early days practical implementations of density functional theory was dominated by one particular system for which near exact results could be obtained - the homogeneous electron gas. In this system the electronic charge density (ρ) is uniform due to a constant external potential faced by the electrons.

Thomas and Fermi studied the homogeneous electron gas in the early twentieth century [25]. The orbitals of the system are, by symmetry, plane waves.

If the electron-electron interaction is approximated by the classical Hartree potential (that is exchange and correlation effects are neglected) then the total energy functional can be readily computed. Under these conditions the dependence of the kinetic and exchange energy on the density of the electrons can be extracted and expressed in terms of a local functions of density. This suggests that in the inhomogeneous system we might approximate the functional as an integral over a local function of the charge density. Using the kinetic and exchange energy densities of the non-interacting homogeneous electron gas this leads to;

$$T[\rho] = 2.87 \int \rho^{\frac{5}{3}}(\mathbf{r}) d\mathbf{r} \tag{2.43}$$

and

$$E_x[\rho] = 0.74 \int \rho^{\frac{4}{3}}(\mathbf{r})d\mathbf{r} \tag{2.44}$$

These results are highly suggestive of a representation for E_{xc} in an inhomogeneous system. The local exchange correlation energy per electron might be approximated as a simple function of the local charge density (say, $\epsilon_{xc}^{LDA}(\rho)$). That is, an approximation of the form;

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r})\epsilon_{xc}^{LDA}(\rho(\mathbf{r}))d\mathbf{r} \tag{2.45}$$

An obvious choice is then to take $\epsilon_{xc}^{LDA}(\rho)$ to be the exchange and correlation energy density of the uniform electron gas of density ρ - this is the *local density approximation (LDA)*. Within the LDA $\epsilon_{xc}^{LDA}(\rho)$ is a function of only the local value of the density. It can be separated into exchange and correlation contributions;

$$\epsilon_{xc}^{LDA}(\rho) = \epsilon_{x}^{LDA}(\rho) + \epsilon_{c}^{LDA}(\rho) \tag{2.46}$$

The Dirac form can be used for E_x^{LDA};

$$\epsilon_{x}^{LDA}(\rho) = -C\rho^{\frac{1}{3}} \tag{2.47}$$

Where for generality an arbitrary free constant, C, has been introduced rather than that determined for the homogeneous electron gas. This functional form is much more widely applicable. The functional form for the correlation energy density, ϵ_c^{LDA}, is unknown and has been simulated for the homogeneous electron gas in numerical quantum Monte Carlo calculations which yield essentially exact results [26]. It is a remarkably noteworthy fact that the LDA works as well as it does given the reduction of the energy functional to a simple local function of the density. One of the reasons could be that in LDA there are very significant errors in the exchange and correlation energies but, as the exchange energy is generally underestimated and the correlation energy overestimated, these errors tend to cancel. The success of the LDA is in part due to this cancellation of errors.

Further insight into the behaviour of functionals can be obtained by examining how well they approximate Γ_2 - the probability of finding an electron at $\mathbf{r}_1$ and an electron at $\mathbf{r}_2$. LDA seems to make a very poor approximation of Γ_2. So, we are faced with the question - how can the LDA produce such reasonable energetics if the functional Γ_2 is so poorly described by it? The answer is based on the structure of the Coulomb operator. We remember from eqn. 2.8 that the electron-electron interaction can be written as;

$$V_{ee} = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \Gamma_2(\mathbf{r}_1, \mathbf{r}_2)/\mathbf{r}_{12} \tag{2.48}$$

From this it seems a poor approximation to Γ_2 leads to a poor estimate of the electron-electron interaction. However, the Coulomb operator depends only on the magnitude of the separation of $\mathbf{r}_1$ and $\mathbf{r}_2$, $\mathbf{r}_{12}$. We can re-write V_{ee} as ::

$$\begin{aligned} V_{ee} &= \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_{12} \Gamma_2(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{r}_{12})/\mathbf{r}_{12} \\ & \frac{1}{2}\int_0^\infty 4\pi|\mathbf{r}_{12}|^2 [\frac{\int \Gamma_2(\mathbf{r_1}, \mathbf{r_1} + \mathbf{r_{12}})}{\mathbf{r}_{12}} \frac{d\Omega_{r_{12}}}{4\pi}] dr_{12} \end{aligned} \tag{2.49}$$

Thus the electron-electron interaction depends only on the spherical average of the pair density - $P(\mathbf{r}_{12})$;

$$P(\mathbf{r_{12}}) = \int \mathbf{\Gamma_2}(\mathbf{r_1}, \mathbf{r_1} + \mathbf{r_{12}})\mathbf{dr_1}\frac{\mathbf{d\Omega_{r_{12}}}}{\mathbf{4\pi}} \tag{2.50}$$

The LDA makes a reasonable approximation to this spherically averaged pair density. This explains in part the success of the LDA.

Thus, we can conclude that the remarkable performance of the LDA is a consequence of its reasonable description of the spherically averaged pair density along with the tendency for errors in the exchange energy density to be canceled by errors in the correlation energy density.

2.5 The Generalized Gradient Approximation for E_{xc}

In the generalized gradient approximation (GGA) the exchange-correlation functional E_{xc} depends on the density and its derivative,

$$E_{xc}^{GGA}[\rho] = \int \rho(\mathbf{r})\epsilon_{xc}^{GGA}(\rho(\mathbf{r}), | \bigtriangledown \rho(\mathbf{r})|)d\mathbf{r} \tag{2.51}$$

Now one can use the GGA functionals by Perdew and Wang [27], by Perdew, Burke and Ernzerhof (PBE) [28] and Becke's formula [9] for the exchange part combined with Perdew's 1986 formula for correlation [29]. The GGA improves significantly on the LDA's description of the binding energy of molecules - it was this feature which lead to the very wide spread acceptance of DFT in the chemistry community during the early 1990's. We use the PBE functional mostly for DFT-based calculations in this thesis.

2.6 Orbital-dependent functionals: An overview

The first question comes into mind is : Why would one even think about using orbital-dependent functionals, given the tremendous success of the LDA and GGA in evaluating different properties? There are many considerable points related to this question in which LDA and GGA fails.

Failure of LDA/GGA

Failure of LDA/GGA leads physicist to move farther from density based functionals to orbital-dependent functionals. Few of important issues where density based functional does not perform:

I -Heavy Elements.

II -Negative Ions.

III -Dispersion Forces.

IV -Strongly Correlated Systems.

It is very important to understand about orbital-dependent functional (ODF) and why ODF's are so important. So exact-exchange term E_x from DFT is the obvious starting point for whole discussion which is the suppose to be most simple functional of this type. Definition of the exact exchange term E_x comes from the Fock expression and can be written in terms of KS orbitals:

$$E_x = -\frac{e^2}{2}\sum_{kl}\partial_k\partial_l \int\int d^3\mathbf{r}d^3\mathbf{r}\frac{\phi_k^\dagger(\mathbf{r})\phi_l\mathbf{r})\phi_l^\dagger(\mathbf{r}')\phi_k^(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{2.52}$$

Expression given above is very conclusive which shows that for $k = l$ self-interaction of orbital is completely canceled present in Hartree term E_H, which has been the origin of the problem of the LDA/GGA with ionic system (negative ions). Last equation automatically induces a correlation functional of DFT,

$$E_c = E_{xc} - E_x. \tag{2.53}$$

It is necessary to mention that E_x and E_c are not same as the exchange and correlation energies defined in conventional many-body theory. Although in the Fock-term of Hartree-Fock (HF) approach and the functional form of E_x agrees with the exchange, difference lies with orbitals inserted into the Fock-term: the KS orbitals in eqn. 2.52 has been used, evaluated using solutions of the KS equations with their effective potential v_{eff} which comprised of ion-electron, electron-electron and exchange-correlation potential. The ϕ_k does not agree with the HF orbitals which satisfy the non-local HF equations. The difference between the resulting exchange energies as well as the difference between T_0 and the full kinetic energy are absorbed into E_c. The right-hand side of eqn. 2.52 is a density functional in the same sense as the kinetic energy T_0: The KS orbitals ϕ_k are unique solution of KS equations evaluated with the help of density n, also density n uniquely determines v_{eff} (which is guaranteed by the HK theorem [4] for non-interacting systems), which then allows the unique calculation of the ϕ_k. Thus, E_x represents an implicit density functional dependence, whereas LDA/GGA shows explicit density dependence. To study the complete spectrum of KS we extended the class of functional which includes unoccupied part of KS-states and eigenvalues along with the occupied part which is uniquely determined by v_{eff}.

This approach is more like a transit from variational type Thomas-Fermi equation to the KS equation. Here we step-out from explicitly density-dependence to orbital-dependent xc-functionals. In the latter we recast kinetic energy functional in orbital-dependent form which is very important part of $E_{tot}[n]$. We can use concept same as above to E_{xc}. Much celebrated orbital based functionals enjoys now a status of third generation of density functionals.

From the above term we can see that This is the most appropriate definition as it guarantees the exact cancellation of the self-interaction energy contained in E_H, which has been identified as the origin of the problem of the LDA/GGA with negative ions (and also seems to be relevant for the description of Mott insulators). It automatically induces a corresponding definition of the correlation functional of DFT.

2.6.1 Optimized Potential Method (OPM)

The question to be emphasized is how to calculate the potential which corresponds to xc-functionals of the type eqn. 2.52. There are three distinct ways for the derivation of the basic equation which yields this potential [42].

I -Direct Functional Derivative

II -Total Energy Minimization

III -Invariance of the Density

2.6.2 Harbola-Sahni Potential (HSP)

Harbola-Sahni provided an approach alternate OPM to evaluate the exchange correlation potential in KS-DFT in his paper titled "*Quantum-Mechanical Interpretation of the Exchange-Correlation Potential of Kohn-Sham Density-Functional Theory*" [7] and applied for atoms and in this thesis, we adopted HSP within DFT to evaluate various structural properties (e.g. bulk moduli) as well as electronic properties (e.g. band gap) of solids. HS provided a distinct interpretation of the exchange-correlation potential of KS-DFT from the general concept of electrostatics as the work done against the electric field of the Fermi-Coulomb hole charge distribution by an electron. This interpretation also provides insights into the exact Slater exchange potentials. Correct evaluation of the Fermi-Coulomb hole will provide the exchange-correlation potential as the work done (this has been discussed in chapter 3 of this thesis).

2.7 Linear Muffin-Tin Orbital Method

The tight binding linear muffin-tin orbital (TB-LMTO) method is a specific implementation of density functional theory within the local density approximation (LDA) and discussion of this part has been taken from the book *The LMTO method: muffin-tin orbitals and electronic structure* by H.L. Skriver [31]. In this method there is no shape approximation to the crystal potential, unlike methods based on the atomic-spheres approximation (ASA) where the potential is assumed to be spherically symmetric around each atom. For mathematical convenience the crystal is divided up into regions inside muffin-tin spheres, where Schrödinger equation is solved numerically, and an interstitial region. In all LMTO methods the wavefunctions in the interstitial region are Hankel functions. Each basis function consists of a numerical solution inside a muffin-tin sphere matched with value and slope to a Hankel function tail at the sphere boundary. The so-called multiple-kappa basis is composed of two or three sets of s, p, d, etc. LMTOs per atom. The extra variational degrees of freedom provided by this larger basis allow for an accurate treatment of the potential in the interstitial region. The first approximation in using atomic sphere method, is that the potential in the crystal has a local spherical symmetry and extremely at potential in interstitial space. This approximation is called atomic sphere approximation(ASA) as shown schematically. The wave function at energy E can be written as

$$\psi_j(\mathbf{k},\mathbf{r}) = \sum_{lm} b^{jk}_{Rlm} \psi_{Rl}(E, |\mathbf{r}-\mathbf{R}|) i^l Y_l^m(\widehat{\mathbf{r}-\mathbf{R}}) \tag{2.54}$$

where b^{jk}_{Rlm} is the expansion coefficient of the partial wave, Y_l^m is a spherical harmonics, i^l is a phase factor and ψ_{Rl} a solution of radial Schrödinger equation

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+v(\mathbf{r})-E\right] r\psi_l(E,\mathbf{r})=0 \tag{2.55}$$

Phase conventions of[32] is used for spherical harmonics. Wigner and Seitz [33, 34] suggested the spherically symmetric potential to extend until the boundary of atomic polyhedron. The wave functions in solid is then expressed as Bloch sum of eqn. 2.54

$$\psi_j(\mathbf{k},\mathbf{r})=\sum_R \exp^{i\mathbf{k}\dot{\mathbf{R}}}\sum_{lm} b_{lm}^{jk}\delta(\mathbf{r}-\mathbf{R})\psi_l(E;|\mathbf{r}-\mathbf{R}|i^l Y_l^m(\widehat{\mathbf{r}-\mathbf{R}}) \tag{2.56}$$

where δ inside atomic sphere is unity and zero outside. Though this cellular method turned out to be too tough for applying boundary conditions, it gave rise to KKR (named after Korringa, Kohn and Rostoker) (and LMTO) method and Wigner-Seitz rule of energy band. Slater [35] in his Augmented Plane-wave(APW), inscribed a muffin-tin(MT) sphere in each atomic sphere. Inside the sphere, the potential is spherically symmetric and wave functions are expanded as Wigner-Seitz partial wave. Korringa [36], Kohn and Rostoker [37] expand the MT spheres similar to cellular and APW. The interstitial potential is flat and wave functions are expanded as phase shifted spherical wave. Boundary conditions are expressed as condition for self-consistent multiple scattering between the MT spheres. Andersen linearized this method which is one of the most used method of solving the KS equation.

2.7.1 Korringa, Kohn and Rostoker Method

In the KKR-ASA, MT and interstitial region is divided into overlapping atomic spheres (ASs). The total volume of the ASs thus equals the total crystal volume.

Any point r in the space is denoted by (r, R), where R is the index for the AS and $\mathbf{r} = (r, \hat{r}) = (r, \theta, \phi)(r < R)$ is the vector denoting the position in each AS. R denotes the radius of AS and here ϕ is azimuthal angle.

Starting point for KKR is an energy dependent orbital defined as

$$\chi_{lm}(E, \mathbf{r}) = i^l Y_l^m \begin{cases} \psi_l(E, r) + p_l(E)(\frac{r}{S}) & r < S \\ (\frac{S}{r})^{l+1} & r > S \end{cases} \tag{2.57}$$

where $\psi_l(E, r)$ is the solution of eqn. 2.57 and S is the radius of atomic sphere. This muffin-tin orbital(MTO) is regular, continuous and differentiable over all space. The potential function $p_l(E, r)$ and normalization of $\psi_l(E, r)$ requires continuity and differentiability at the sphere boundary with the boundary condition

$$p_l(E) = \frac{D_l(E) + l + 1}{D_l(E) - 1}, \tag{2.58}$$

$$where,\ D_l(E) = \frac{S}{\psi_l(E, S)} \frac{\partial \psi_l(E, \mathbf{r})}{\partial r}|_{r=S} \tag{2.59}$$

is the logarithmic derivative function.

The tail of the orbital, $(\frac{S}{r})^{l+1}$ is the solution of Poisson's equation $\nabla^2 X = 0$, which has zero kinetic energy. So, the tail centered at $\mathbf{R}$ can be expanded around the origin in terms of spherical harmonics with shifted in phase, which yields,

$$\sum_{R \neq 0} \exp i(\mathbf{k}.\mathbf{R})(\frac{S}{|\mathbf{r} - \mathbf{R}|})^{l+1} i^l Y_l^m (\widehat{\mathbf{r} - \mathbf{R}}) = \sum_{l'm'} \frac{-1}{2(2l'+1)} (\frac{r}{S})^{l'} i^{l'} Y_{l'}^{m'}(\hat{\mathbf{r}}) S^{\mathbf{k}}_{l'm',lm} \tag{2.60}$$

where $S^{\mathbf{k}}_{l'm',lm}$ is the canonical structure constant, converges inside the sphere of nearest neighbor.

The first term of MTO $i^l Y_l^m(\hat{\mathbf{r}})\psi_l(E,\mathbf{r})$ is already a solution of eqn. 2.55 and is the one-center expansion with origin at $\mathbf{r}$. For any other sphere, therefore, the term is

$$\sum_{lm} a_{lm}^{j\mathbf{k}} Y_l^m(\hat{\mathbf{r}})\psi_l(E,\mathbf{r}) \tag{2.61}$$

provided tails from all other sphere cancel the term

$$\sum_{lm} a_{lm}^{j\mathbf{k}} Y_l^m(\hat{\mathbf{r}})p_l(E)(\frac{r}{S})^l \tag{2.62}$$

where $a_{lm}^{j\mathbf{k}}$ is the expansion coefficient of MTO. From eqn. 2.60, the condition for this tail cancellation is

$$\sum_{lm} \left[P_l(E)\delta_{ll'}\delta_{mm'} - S_{l'm',lm}^{\mathbf{k}}\right] a_{lm}^{j\mathbf{k}} = 0 \tag{2.63}$$

where P_l is defined as

$$P_l(E) = 2(2l+1)\frac{D_l(E)+l+1}{D_l-1} \tag{2.64}$$

Solution of secular form of eqn. 2.63 gives eigenvectors $a_{lm}^{j\mathbf{k}}$ when

$$det\left[P_l(E)\delta_{ll'}\delta_{mm'} - S_{l'm',lm}^{\mathbf{k}}\right] = 0 \tag{2.65}$$

2.7.2 Muffin-tin potential

The basic assumption of muffin-tin orbital is that in the neighborhood of an ion-core the potential seen by the electron in a solid is not very different from that of the atomic ion-core. This neighborhood is spherically symmetric with radius S centered at R. In the interstitial region the potential is flat, called muffin-tin potential (V_{MTZ}). In muffin-tin potential is defined as

$$V_{MT}(\mathbf{r}-\mathbf{R}) = \begin{cases} \upsilon(|r-R|) - V_{MTZ} & r \leq S \\ 0 & r \geq S \end{cases} \tag{2.66}$$

is the muffin-tin potential where **R** and **r** are the positions of the ion-cores and electrons respectively. Thus Hamiltonian can be written as:

$$H = -\nabla^2 + \sum_R V_{MT}(|\mathbf{r}-\mathbf{R}|) - \kappa^2 + E \tag{2.67}$$

where κ is the kinetic energy in the extended region, $\kappa^2 = E - V_{MTZ}$. Eqn. 2.55 has been solved numerically for radial solution $\psi_l(E,\mathbf{r})$ written in terms of Hankel and Bessel function

$$\psi_L(\epsilon,\kappa,\mathbf{r}) = i^l Y_L(\hat{\mathbf{r}}) \begin{cases} \psi_l(\epsilon,\mathbf{r}) + \kappa cot(\eta_l(\epsilon)) j_l(\kappa r) & r \geq S \\ \kappa \eta_l(\kappa r) & r \leq S \end{cases} \tag{2.68}$$

with MT basis set

$$\chi_L^{MTO}(\epsilon,\kappa,\mathbf{r}) = i^l Y_L(\hat{\mathbf{r}}) \begin{cases} \psi_l(\epsilon,\mathbf{r}) + \kappa cot(\eta_l(\epsilon)) j_l(\kappa r) & r \leq S \\ \kappa \eta_l(\kappa r) & r \geq S \end{cases} \tag{2.69}$$

where S is the muffin-tin sphere radius. j_l and n_l are the spherical Bessel function is defined as

$$j_l(\kappa\mathbf{r}) \rightarrow \begin{cases} (\frac{(\kappa r)^l}{(2l+1)!}) & \kappa r \rightarrow 0 \\ \frac{\sin(\kappa r + \frac{l\pi}{2})}{\kappa r} & r \rightarrow \infty \end{cases} \tag{2.70}$$

and spherical Neumann function is given by

$$\eta_l(\kappa\mathbf{r}) \rightarrow \begin{cases} -\frac{(2l-1)!}{(\kappa r)^{2l+1}} & \kappa r \rightarrow 0 \\ -\frac{\cos(\kappa r + \frac{l\pi}{2})}{\kappa r} & r \rightarrow \infty \end{cases} \tag{2.71}$$

which means j_l is regular both at origin and at ∞ , where n_l is regular at ∞ only and diverges at origin. This yields a bound state envelop function which is real, and regular both inside (since $j_l(\kappa r)$ is regular at origin) and outside (since $n_l(\kappa r)$ is regular at infinity) the sphere. The inclusion of $j_l(\kappa r)$ in the single particle basis set includes the effect of neighbours so that the minimal basis set is capable of describing the full system. Anderson's method of linearized basis

$$\chi^{\alpha}_{RL} = \phi_{RL}(\mathbf{r_R}) + \sum \ddot{\phi}^{\alpha}_{R'L'}(\mathbf{r'_R}) h^{\alpha}_{R'L',RL} \tag{2.72}$$

where $\ddot{\phi}^{\alpha}_{R'L'}(\mathbf{r'_R})$ is linear combination of ϕ and $\ddot{\phi}$ and given by

$$\ddot{\phi}^{\alpha}_{R'L'} = \ddot{\phi}^{\alpha}_{R'L'} + \phi_{R'L'} o^{\alpha} \tag{2.73}$$

here, o^{α} is overlap matrix. Eq. 2.72 is used as starting point for our calculation of HS potential. Which subsequently used in evaluation of radial density, Fermi-Coulomb hole charge density. Evaluation of Fermi-Coulomb hole allows us to directly calculate electric field. Later electric field is utilized in evaluation of exchange-correlation potential.

2.8 Solution of the Kohn-Sham Equation

The Kohn-Sham orbitals are required to be expanded in a suitable basis set in order to be solved. The basis set can either be fixed energy dependent like plane waves or linear combination of the atomic orbitals or energy dependent partial wave-like basis. Plane wave basis has been found to be useful for the calculation of systems like clusters and solids. Plane wave basis expansion is mathematically simple. By using the pseudo-potential approach the size of the basis set required can be reduced making the calculation computationally less expensive.

2.8.1 Plane Waves and Pseudo-potentials

Plane wave basis are orthonormal and energy independent. Thus they convert the Kohn-Sham equation to a simple matrix eigenvalue problem for the expansion coefficients. Moreover, plane waves are atom and atomic position independent. In such calculations , the single electron wave function is expanded using plane wave basis $\exp[i(\mathbf{G}.\mathbf{r})]$, where the candidate G's are the reciprocal vectors of the unit cell used. The biggest advantage of plane wave basis is its ability to perform the exact variational calculation based on a discrete numerical grid, i.e., instead of doing actual real space integrations, we can do a summation over a real space grid, the results are exactly the same.

The plane wave calculations require that the wave function be described by plane waves within a certain energy cut-off E_{cut}. In order to reduce E_{cut} to a reasonable value the wave function should be smooth. While it is often smooth at the chemically important bonding area, near the nuclei, the valence wave functions often have a lot of wiggles. These wiggles must exist so that the valence wave functions are orthogonal to the deep level core wave functions. Besides, it is difficult to describe those chemically-not-important core wave functions using plane wave basis. To overcome these difficulties, pseudo-potentials are developed. Basically, using a Pseudo-potentials, the core states will no longer exist, and the valence pseudo-wave functions become smooth near the nuclei. Using this technique the unwanted singular behaviour of the ionic potential at the lattice points can be removed. A good pseudo-potential wave function should be soft and transferable. A pseudo-potential is soft if it requires less number of plane waves. A pseudo-potential is transferable if it works considerably well in different environments. However, to have these good properties, it is necessary to have different pseudo-potentials for s,p,d states, i.e, the pseudo-potential is angular momentum dependent (non-local pseudo-potential).

2.8.2 Projector Augmented Wave

The drawback of the pseudo-potential method is that all information on the full wave function close to the nuclei is lost. This can influence the calculation of certain properties, such as hyperfine parameters, and electric field gradients. Another problem is that one has no before hand knowledge of when the approximation yields reliable results.

A different approach is the augmented-plane-wave method (APW), in which space is divided into atom-centered augmented spheres inside which the wave functions are taken as some atom-like partial waves, and a bonding region outside the spheres, where some envelope functions are defined. The partial waves and envelope functions are then matched at the boundaries of the spheres. A more general approach is the projector augmented wave method (PAW) which is used in this thesis, which offers APW as a special case and the pseudo-potential method as a well defined approximation. The PAW method was first proposed by Blöchl [30].

The projector augmented wave (PAW) method separates the Kohn-Sham wave functions, which displays rapid oscillations in some parts of space, and smooth behaviour in other parts of space into auxiliary functions which are smooth everywhere and a contribution which contains rapid oscillations, but only contributes in certain, small, areas of space. Having separated the different types of waves they can be treated individually. Thus the Kohn-Sham total energy E can be separated into a part calculated on smooth functions, $\tilde{E}$, and some atomic corrections, ΔE^a, involving quantities localized around the nuclei only

$$E = \tilde{E} + \sum_a \Delta E^a \tag{2.74}$$

where the smooth part $\tilde{E}$ is the usual energy functional, but evaluated on the smooth functions $\tilde{\rho}$ instead of ρ and with the soft compensation charges $\tilde{Z}$ instead of nuclei charges $Z(\mathbf{r})$.

Chapter 3

A first-principles approach to band gap problems

[1]

3.1 Introduction

The many-body interacting system of valence electrons in a solid is one of the difficult problems in physics. Perhaps the most successful first-principles approach to the electronic structure of solids is density functional theory (DFT) [39, 40]. The ideas behind DFT are quite simple and remarkably easy to implement for numerical studies. However, the inaccuracy in predicting the band gap of semi-conductors and insulators has been one of the recurring problems in this approach. The crux of the matter lies in the setting up of the auxiliary, single particle Kohn-Sham equation

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[1] The contents of this chapter has been submitted for publication : P.Singh *et.al.*

[4, 6]. In the traditional DFT the auxiliary Hamiltonian is obtained variationally. As a result, DFT is applicable only to the ground state. It is well understood that the spectrum and orbitals of the Kohn-Sham equation have no specific significance beyond the fact that they are used to obtain the ground-state density and the kinetic energy contribution. Interpretation of the unoccupied part of the Kohn-Sham spectrum as the excitations of the many-body system does not have any basis. On the other hand, the energy eigenvalue of the highest occupied orbital is the exact ionization potential of the system [41]. Since adding an extra electron at the bottom of the conduction band would hardly change the density of a bulk system, it was expected that the difference in the Kohn-Sham orbital energies corresponding to the lowest unoccupied band and the top of the highest occupied band should give the correct band gap of semiconductors and insulators. However the results obtained by applying the traditional exchange-correlation functionals like the local density approximation (LDA) are contrary to this expectation and grossly underestimate the band gap with respect to experiments. We come up with a new class of exchange-only (EX) functionals developed by Harbola and Sahni (HS) [7], an orbital based exchange only functional. Harbola and Sahni provided its physical interpretation from electrostatics as the work done to bring an electron from infinity to some point against force field of the exchange hole depletion charges. HS-EX satisfies criteria required to replace LDA. The question arises : why is HS-EX important as there exist many functionals e.g. LDA+U, GGA [27, 28], meta-GGA [8], the exact exchange (EXX)

[42] functional and many hybrid functionals e.g. B3LYP [9] ? It has always been understood that the spectrum of orbitals of the Kohn-Sham (KS) equation have no specific significance beyond the fact that they are used to obtain the ground-state density and the kinetic energy contribution. KS obtained the Hamiltonian of this non-interacting system by a variational principle. As we know the Hamiltonian has higher order (excited) states as local minima, while the global minimum belongs to ground state. If we could make a starting guess quite close to he excited states then it would converge to this minimum. Alternatively, we could design the functional such that the excited states are global minimum. But contrary to LDA, HS-EX obtained the potential through clear physical arguments based on electrostatics. This is not a variational approach. Consequently, it allows us to apply HS-EX to calculate excited state properties e.g. band gap in semiconductors. Given the long available list of functionals it would not possible discuss all, nevertheless, we shall shed some light over some exchange-correlation functionals commonly used within KS-DFT along with HS-EX. There have been considerable efforts to improve the band gaps within the framework of Kohn-Sham DFT. Extending the idea of optimized effective potential (OEP), primarily proposed by Talman and Shadwick for atoms [42, 43], to solids by Kotani where exact exchange (EXX) combining with LDA correlation produces good band gaps in excellent agreement with the experiments [44]. EXX calculates the linear response function which is subsequently inverted, which makes the computation very cumbersome [47]. However, presently within first-principles approaches

for extended systems, the GW approximation (GWA) [45] explains electronic band properties most accurately while the computational efforts required for GW method are much heavier, thus limiting it's application to relatively smaller systems. We are proposing an alternative approach to obtaining the exchange-correlation potential. In this approach, the XC-potential is calculated as the work done in moving an electron in the electric field produced by its Fermi-Coulomb hole. The physical interpretation of this potential was provided by Harbola and Sahni (HS) [7]. Using HS approach within the exchange (EX) only approximation, where HS-EX is evaluated from Fermi hole, produces ground state as well as excited state properties comparable to EXX and GWA but with considerably reduced numerical efforts. The above physical picture and the vastly reduced computational effort make this approach worth following. With this in mind, we use HS approach to calculate the various properties of materials within TB-LMTO in the atomic sphere approximation (ASA) [48].

3.2 Methodology

In the post-Born-Oppenheimer many-body Hamiltonian of the interacting valence electron system, the contribution to the total energy by the electron-electron interaction terms is :

$$E_{\mathrm{ee}}[\rho] = \frac{1}{2}\int\int \frac{\Gamma(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

The joint probability density can be written as : $\Gamma(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')[1 - C(\mathbf{r},\mathbf{r}')]$ where $C(\mathbf{r},\mathbf{r}')$ is the correlation function. The electron-electron part of the total energy becomes :

$$E_{\text{ee}} = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \tag{3.1}$$

where, $\rho_{xc}(\mathbf{r},\mathbf{r}')$ is Fermi-Coulomb hole charge distribution defined as

$$\rho_{xc}(\mathbf{r},\mathbf{r}') = -\rho(\mathbf{r}')C(\mathbf{r},\mathbf{r}')$$

If we compare the Hartree and exchange-correlation terms in Eqs. 3.1, the physical interpretation of $\rho_{xc}(\mathbf{r},\mathbf{r}')$ is the deficit in the density of electrons at $\mathbf{r}'$ when another electron is at $\mathbf{r}$. Thus an electron at $\mathbf{r}$ causes a 'hole' in the electron density at $\mathbf{r}'$, which is the Fermi-Coulomb hole. We can approach the problem of defining the exchange part of the Kohn-Sham potential by its electrostatic definition as the work done to bring an electron from infinity to $\mathbf{r}$ against the electric field produced by the Fermi hole,

$$\mathcal{E}(\mathbf{r}) = \int \frac{\rho_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}(\mathbf{r}-\mathbf{r}')d\mathbf{r}'. \tag{3.2}$$

Here, $\rho_x(\mathbf{r})$ is Fermi hole (exchange) charge density and the exchange potential is obtained from the work done :

$$W_{HS}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{E}(\mathbf{r})\cdot d\ell \tag{3.3}$$

A question may be asked whether the field $\mathcal{E}(\mathbf{r})$ is curl free and the expression for the Harbola-Sahni potential is path independent. The kinetic energy correction to the exchange term does lead to a small solenoidal component in the field. This correction is necessary but may not be quantitatively important in many materials. However, indeed the field is curl free in the ASA. The virial theorem [50] gives the exchange energy from the HS-EX potential $W_{HS}(\mathbf{r})$

$$E_x = -\int \rho(\mathbf{r})\mathbf{r} \cdot \nabla W_{HS}(\mathbf{r}) d\mathbf{r}. \tag{3.4}$$

There have been several applications of these ideas [51, 52] to estimate accurately the ground state energies as well as the energies of excited states of several atomic systems. As is well known that latter are notoriously difficult to estimate theoretically. But the excellent results reported for both the ground and excited states encouraged us to apply this technique to solids. Using the approach outlined above, the Kohn-Sham like auxiliary equation in atomic sphere become

$$\begin{aligned} \left\{-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right\} \phi_{\lambda\sigma}(\mathbf{r}) &= \epsilon_\lambda \phi_{\lambda\sigma}(\mathbf{r}) \\ V_{\text{eff}} = V(\mathbf{r}) + \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' &+ W_{HS}(\mathbf{r}) \qquad . \end{aligned} \tag{3.5}$$

while for empty sphere we solve the equation with LDA

$$\begin{aligned} \left\{-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right\} \phi_{\lambda\sigma}(\mathbf{r}) &= \epsilon_\lambda \phi_{\lambda\sigma}(\mathbf{r}) \\ V_{\text{eff}} = V(\mathbf{r}) + \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' &+ V_{LDA}(\mathbf{r}) \qquad . \end{aligned} \tag{3.6}$$

Eq. 3.5 and eq. 3.6 are used to calculate various ground and excited state properties of solids. We have implemented the HS-EX potential in TB-LMTO within atomic sphere approximation (ASA) developed by Jepsen *et.al.*[48]. Within this methodology, the lattice space is divided into ion-core centric atomic spheres (AS) with overlap $< 10\%$, where ASA demands that the sum of AS volumes equals the cell volume. For open

Figure 3.1: Clockwise from top left, radial density (RD), LDA potentials for empty sphere (ES) and at bottom left HS-EX and LDA potential for silicon atomic sphere(Si-AS). Wigner-Seitz radius is kept fixed for both Si-AS and ES at 2.53Å.

lattices this is not possible and the remaining volume is filled with empty spheres which do not have associated ion-cores but is filled with charge. We shall replace the potential within the atomic spheres (AS) by the HS-EX. For the empty spheres (ES), we use the standard LDA potential because absence of core in ES, makes the electron gas reasonably homogeneous and application of LDA is justified.

3.3 Results and Discussion

3.3.1 Electronic Structure of Semiconductors: a first principles study

3.3.1.1 Silicon (Si)

In fig. 3.1, we have plotted potential inside Si-AS and ES with HS-EX (solid line) and LDA (dotted line). There is a discontinuity in the potential at the AS boundaries. This is an artifact of ASA. Contrary to HS-EX, LDA has a relatively positive contribution to exchange due to non-cancellation of self-interaction. In TB-LMTO the AS and ES orbitals have fractional charges which has been taken care of while calculating the radial and Fermi hole charge densities [53].Total valence electrons in Si-AS using HS-EX is 3.31, while EXX and LDA numbers are 3.34 and 3.21 respectively. HS-EX localizes the valence states by self-interaction correction. For band structure calculation, we started with Si having diamond structure, with indirect band gap. The diamond structure structure consist of two interpenetrating fcc lattices with Si atoms at (0,0,0) and (1/4,1/4,1/4), respectively, and we add two other fcc lattices of empty spheres to obtain closely packed structures within TB-LMTO-ASA. ES has been inserted as spherical scatterer in open shell region. The average Wigner-Seitz radius has been set for both Si-AS and ES to 2.53Å. Basis set used for this calculation is (3s3p3d) for Si-AS and (1s2p3d) for ES, which is complete under all symmetry operations and no additional basis atoms have been introduced. The tetrahedron integration is performed over the full Brilluoin zone with 29 irreducible k-points from

512 (8×8×8). The band structure of Si thus obtained is shown in fig. 3.2. The figure points out energy values along particular edges of the irreducible wedge, the energy dispersion along the straight line from point Γ to point X. A comparison of the dispersion curves obtained with HS-EX and LDA shows that the curvature of valence bands are hardly affected in HS-EX. However, definite shift has occurred in valence bands while conduction bands shifted and definite shift with some distortion has occurred which is not a rigid shift like scissor operator method. The energy dependent distortion invalidates the use of the scissors operator which empirically inserts a rigid shift [61] (in fig. 3.2 for LDA and HS-EX Fermi level has been set at zero). The conduction band minimum in silicon occur at about 0.85% of the way to the zone boundary from Γ to X. The difference between conduction band minimum and valence band maximum results into a correct indirect Γ-X gap for Si. Band gap for Si produced by HS-EX is 1.18 eV whereas LDA highly underestimates with 0.49 eV and some over-estimations in GWA [98] and EXX [44] with 1.37 eV and 1.98 eV respectively. For silicon, within HS-EX, the calculated effective electron mass ($\mathrm{m}_e^*/\mathrm{m}_0$) is 0.99 while Kittel *et.al.* reported a value of 0.97±0.02 [62]. Our calculated effective hole mass ($\mathrm{m}_h^*/\mathrm{m}_0$) is 0.44 while the calculations of Dexter *et.al.* [63] showed an average hole mass to be 0.39, where m_0 is the free electron rest mass. The same trend is clearly observed in the density of states.

Figure 3.2: Comparison between the band-structures and densities of states of Si using HS-EX and LDA potential.

A summary of the important features of the HS-EX band structure of Si at high-symmetry points in structure with respect to the valence-band maximum given in table 3.1. Total valence band width for Si is 11.80 eV.

3.3.1.2 Diamond (C)

The diamond and silicon posses similar structure which comes under same space group and the treatment of C follows that of Si. Basis set used for this calculation is (2s2p) for C-AS and (1s2s3d) for ES. The conduction band minimum in C occur at about 0.667% of the way to the zone boundary from Γ to X. The difference between conduction band minimum and valence band maximum results into a correct indirect Γ-X gap for C. Band gap for C produced by HS-EX is 5.56 eV whereas LDA highly

c-Silicon	band energies(eV)							
	HS-EX	Expt.		HS-EX	Expt.		HS-EX	Expt.
Γ_1^v	-11.80	-12.5±0.6	X_1^v	-7.88	-3.9	L_1^v	-9.64	
$\Gamma_{2,5}^v$	0.00	0.00	X_3^v	-7.88		L_1^v	-6.86	
$\Gamma_{1,5}^c$	2.58	3.4	X_5^v	-2.63		L_3^v	-1.10	1.21±0.4
Γ_1^c	3.69	4.2	X_1^c	1.42		L_1^c	1.48	2.3
			X_3^c	1.42		L_3^c	5.60	5.60
			X_5^c	10.49		L_1^c	9.40	

Table 3.1: Energy bands of Si at L, Γ and X high symmetry points with respect to $\Gamma_{2,5}$ point which is the valence-band maximum. Along with HS-EX band energies experimental energies for silicon has been shown.

Figure 3.3: Comparison between the band-structures and densities of states of diamond using HS-EX and LDA potential.

underestimates with 2.70 eV and some over-estimations in GWA [98] and EXX [44] with 6.03 eV and 5.12 eV respectively. HS-EX has slight overestimation of $\approx$ 2% while LDA and EXX underestimates by $\approx$ 51% and $\approx$ 7% respectively and GWA overestimates by $\approx$ 10%. Which shows our method is in better agreement with experiments. A summary of the important features of the HS-EX band structure of C at high-symmetry points in structure with respect to the valence-band maximum given in table 3.2. Total valence band width for C is 20.33 eV.

3.3.1.3 Zinc-blende and wurtzite aluminium nitride (AlN)

The high temperature electronics and optoelectronic applications require wide band gap semiconductors, aluminium nitride is one of the largest band gap semiconductors with 6.2 eV in wurtzite (WZ) phase. It usefulness can be attributed to it's high

c-Diamond	band energies(eV)					
	Γ_1^v	-20.33	X_1^v	-11.88	L_1^v	-14.69
	$\Gamma_{2,5}^v$	0.00	X_3^v	-11.88	L_1^v	-12.28
	$\Gamma_{1,5}^c$	6.01	X_5^v	-5.65	L_3^v	-2.57
	Γ_1^c	14.9	X_1^c	6.40	L_1^c	9.82
		X_3^c	6.41	L_3^c	10.61	
		X_5^c	16.35	L_1^c	16.70	

Table 3.2: Energy bands of diamond at L, Γ and X high symmetry points with respect to $\Gamma_{2,5}$ point which is the valence-band maximum.

temperature stability (melting temperature3000 C), high elastic stiffness and excellent thermal conductivity. In III-V group based Al-semiconductor compounds AlN with wurtzite (w-AlN) phase is only with direct band gap. The zinc blende (ZB) (cubic) form has been theoretically reported to be metastable [64, 65], and only the calculated lattice parameter (a = 4.37 $\mathring{A}$) is available [66, 67], obtained by assuming the same volume per atom as in the WZ structure. Both w-AlN and c-AlN have been the subject of extensive theoretical studies ranging from the semi-empirical to the first-principles methods within the density functional theory (DFT) framework [76]. We have explored in detail, common structural as well as electronic properties. The valence configuration in AlN of the Al is $3s^2 3p^1$ and N is $2s^2 2p^3$ shells. In WZ, the Al and N atoms are in (2b) positions as follows: Al (0, 0, 0), (1/3, 2/3, 1/2); N (0, 0, w), (1/3, 2/3, 1/2+w). For the WZ structure w is the internal parameter, described as the relative displacement between Al and N sub-lattices along the c direction, was fixed to be 0.385 and the c/a ratio at the value of 1.601. In ZB, the Al and N are in fcc positions as follows: Al (0, 0, 0); N (1/4, 1/4, 1/4). We have considered a set of lattice parameters for c-AlN is a=4.38 $\mathring{A}$ calculated by HS-EX approach developed by us. Theoretical calculations within the LDA give 4.32 [69] and 4.345 $\mathring{A}$ [70] using FLMTO and 4.342 $\mathring{A}$ using PWPP [71], and those within GGA give 4.394 $\mathring{A}$ using PWPP [72] and 4.40 $\mathring{A}$ using FLAPW [73]. For w-AlN, we started with experimental lattice parameter a = 3.11 and c = 4.98 [74] while the pseudo-potential calculations, slightly underestimates compared to the experiments, of Wright and Nelson [71] with values a = 3.08 $\mathring{A}$ and c = 4.94 $\mathring{A}$. The most prominent features of the calculated band structures (bandwidths, band gaps) of c-AlN and w-AlN are listed in Table 3.3. In c-AlN the conduction-band minimum (CBM) is located away from the Γ point, at the X point. Thus, we obtain an indirect band gap of 5.05 eV in agreement with other results (see Table 3.3 for comparison). The results of other approaches beyond the LDA, HartreeFock [75], GW quasi-particle [68] and self-interaction and relaxation correction pseudo-potential (SIRC-PP) [77] calculations are also listed for comparison. Only the GW quasi-particle calculation of Rubio et al [76] yields gap energies in reasonable agreement with experiment. The band gaps of AlN are underestimated in the LDA, when compared to the experimental data or GW calculations (Table 3.3). They are 30-50% smaller than the experimental values and this is an intrinsic feature of the DFT-LDA. In w-AlN, the band gap is 5.64 eV and direct at Γ; this is in close agreement with the results of experimental energy gap (6.28 eV) of w-AlN was determined by Berger [78]. Thus our HS-EX underestimates the band gap by 0.64 eV (≈ 10%). While LDA underestimates by 1.85 eV (≈ 30%). Total and the projected DOS integrated over the atoms (Al and N) and the interstitial region outside the atomic spheres for both WZ and ZB AlN. These plots (fig. 3.4) are very similar for both w-AlN and c-AlN. There is hardly any difference expected for the occupied states between DOSs obtained for the two structures, significant change for unoccupied levels has been expected. In particular, the total DOS for c-AlN has conduction band DOSs that are shifted toward lower energies as compared to that of w-AlN. It can be seen that the DOS in the interstitial region is not negligible. For both c-AlN and w-AlN, the total DOS presents three regions: firstly, N-2s state dominates the lower part of the valence band, secondly, N-2p and Al-3p states dominate the upper part of the valence band. The Al-3s states contribute to the lower valence bands. The first conduction band in Γ shows predominantly the Al-3s character. A summary of the important features of the HS-EX band structure of AlN at high-symmetry points in WZ structure and ZB structure with respect to the valence-band maximum has been given in table 3.3. The total valence bandwidths are 14.63 eV and 14.72 eV for w-AlN and c-AlN respectively.

w-AlN	band energies(eV)				c-AlN	band energies(eV)			
	Γ_1^v	-14.63	$H_{3'}^v$	-4.35		Γ_1^v	-14.72	L_1^v	-12.86
	Γ_3^v	-5.2	$H_{1,2}^v$	-3.10		$\Gamma_{2,5}^v$	0.00	L_1^v	-5.43
	Γ_5^v	-0.68	H_3^v	-0.75		$\Gamma_{1,5}^c$	5.20	L_3^v	-0.44
	Γ_1^c	5.64	H_3^c	10.16		Γ_1^c	14.74	L_1^c	8.26
	Γ_3^c	8.06	$A_{1,3}^v$	-3.25		X_1^v	-12.25	L_3^c	11.30
	$\Gamma_{1,6}^c$	12.84	$A_{5,6}^v$	-0.36		X_3^v	-4.67	L_1^c	15.47
	$L_{1',3'}^v$	-4.93	$A_{1,3}^c$	7.79		X_5^v	-1.62		
	$L_{1,3}^v$	-3.01	$A_{5,6}^c$	12.53		X_1^c	5.05		
	$L_{2,4}^v$	-3.01				X_3^c	9.79		
	$L_{1,3}^c$	7.74				X_5^c	14.97		
	$L_{1',3'}^c$	11.74							

Table 3.3: The eigen energies has been calculated with reference to the valence-band maximum.

Figure 3.4: Comparison between the band-structures and densities of states of diamond using HS-EX and LDA potential of w-AlN (wurtzite) and c-AlN (cubic)

3.3.1.4 Zinc-blende and wurtzite boron nitride (BN)

In recent years, the properties of boron nitrides (BN) have been studied in great detail, both theoretically and experimentally. This is mainly due to some of the fascinating properties of BN, such as extreme hardness, high melting point, low dielectric constant, large band gap, etc., that have many applications in modern microelectronic devices and its usefulness as a protective coating material[79]. At very high temperature range, BN emerged as a very strong competitor of diamond and SiC. Also, BN is the lightest III-V compound which is isoelectronic with the III-V semiconductors namely GaAs, but with quite different properties. BN exists in three crystalline forms [80]. We shall be studying zinc-blende and wurtzite phase of BN. There have been many studies on the electronic and structural properties of c-BN, but relatively few for w-BN. Early studies show vastly different results mainly because of deficiencies in the computational methods. In recent years, first-principles calculations in the local-density approximation (LDA) have provided much better and consistent results. These include the LCAO (linear combination of atomic orbitals) calculations with numerical basis by Zunger and Freeman [81]; LCAO Hartree-Fock study by Dovesi, Pisani, and Roetti [82]; calculations by Huang and Ching [83]; first-principles pseudo-potential calculations by Wentzcovitch and coworkers [84]-[87], and also by Van Camp, Van Doren, and Devresse. Park, Terakura, and Hamada studied the band structures and the equilibrium lattice constants of all three phases of BN using the full-potential linear augmented-plane-wave method (FLAPW)[88]. The band structure of BN is calculated self-consistently using the TB-LMTO method. A full basis set including the empty 3s and 3p atomic orbitals of both B and N is employed. Each atomic function is expanded in terms of tight binding atomic orbitals. 29-k points in the irreducible part of the Brilluoin zone (BZ) are used for self-consistent iterations in both the cases. The numerical accuracy achieved in these calculations is adequate and is comparable to similar calculations for other crystals. Our methodology predicts, c-BN and w-BN both are indirect band gap system, which is in agreement with the experiments. Our results compared with LDA and GWA are closest to experiments. HS-EX overestimates band gap only by $\approx$ 3%, while LDA underestimates by $\approx$ 50% and GWA overestimates by $\approx$ 11%. A summary of the important features of the HS-EX band structure of BN at high-symmetry points in WZ structure and ZB structure with respect to the valence-band maximum has been

Figure 3.5: Comparison of band-structure and densities of states using HS-EX and LDA potential of w-BN (wurtzite) and c-BN (cubic)

given in table 3.4.

3.3.1.5 Zinc-blende boron and aluminium phosphide (BP and AlP)

Stone and Hill [89] made the first optical transmission measurements on amorphous BP. A large abrupt decrease in the transmittance of 6.0 eV was taken to indicate a band gap of that width even though a small inflection occurred in their data at 2.0 eV. However, now it has been established that the experimental band-gap energy is only about 2.1 eV. The first report of this lower value was by Archer, Koyama, Loebner, and Lueas [90] who obtained agreement within 50 meV from room-temperature measurements of optical absorption, in-3ection electroluminescence, and photoelectric response of surface barrier contacts. At about the same time Wang, Cardona, and Fischer [91] determined from transmission measurements that the fundamental

w-BN	band energies(eV)				c-BN	band energies(eV)			
	Γ_1^v	-15.66	$H_{3'}^v$	-8.29		Γ_1^v	-18.05	L_1^v	-15.41
	Γ_3^v	-9.90	$H_{1,2}^v$	-7.10		$\Gamma_{2,5}^v$	0.00	L_1^v	-9.74
	Γ_5^v	-2.08	H_3^v	-2.77		$\Gamma_{1,5}^c$	9.04	L_3^v	-1.84
	Γ_1^c	8.08	H_3^c	11.30		Γ_1^c	11.57	L_1^c	11.11
	Γ_3^c	9.90	$A_{1,3}^v$	-5.17		X_1^v	-14.16	L_3^c	12.75
	$\Gamma_{1',6}^c$	11.74	$A_{5,6}^v$	-1.15		X_3^v	-8.25	L_1^c	16.45
	$\Gamma_{1,6}^c$	12.56	$A_{1,3}^c$	10.30		X_5^v	-4.47		
	$L_{1',3'}^v$	-9.33	$A_{5,6}^c$	11.23		X_1^c	6.02		
	$L_{1,3}^v$	-3.49				X_3^c	10.84		
	$L_{2,4}^v$	-3.22				X_5^c	17.64		
	$L_{1,3}^c$	8.51							
	$L_{1',3'}^c$	11.73							

Table 3.4: The eigen energies has been calculated with reference to the valence-band maximum.

absorption edge of BP is near 2 eV and caused by indirect transitions from the k= 0 top of the valence band to a conduction-band minimum at the X point. They attributed this small value of the energy gap to an extremely small ionicity. Fomichev, Z hukova, and Polushina [92] obtained a value of 2.0±0.2 eV for the band gap of BP by ultrasoft x- ray spectroscopy. In the literature, one finds completely different empirical predictions of the band gap of BP. For example, Manca [93] on the basis of the correlation between the value of the energy gap and the single bond energy, predicted a band gap of 4.2 eV. Scalar [94] predicted a gap of 6.2 eV based on an empirical formula connecting the energy gap with the ionic and covalent atomic radii of the constituent elements. However, Stearns [95] in considering these predictions, called attention to the fact that the III-V compounds are ordinarily more ionic than their group-IV analogs, but just the opposite is true of borides. Starting from these considerations, he predicted a band gap of 2.1 eV. BP is one of the promising IIIV semiconductors in the zinc-blende structure. This material exhibits excellent physical and chemical properties that make it attractive for device applications, including a wide band gap, a high melting point, high mechanical strength, etc. Technological interest in it has been stimulated in recent years by its potential use in optoelectronic and microelectronic devices working under extreme conditions. Using our methodology we predicted BP as an indirect band gap material with the band gap of 2.20 eV. This is in excellent agreement with the experiments but LDA predictions underestimate the band gap by $\approx$ 45%. The conduction band minimum in silicon occur at about 0.75% of the way to the zone boundary from Γ to X. The difference between conduction band minimum and valence band maximum results into a correct indirect Γ-X gap for BP. AlP also comes out to be a indirect band gap material in our method which is in agreement with the experiments. The calculated band gap is 2.49 eV which is in excellent agreement with experimental value of 2.51 eV with underestimation within 1% of latter.

Figure 3.6: Comparison between the band-structures and densities of states of diamond using HS-EX and LDA potential of zinc-blende c-BP and c-AlP

A summary of the important features of the HS-EX band structure of BP and AlP at high-symmetry points in ZB structure with respect to the valence-band maximum is given in table 3.5.

c-BP	band energies(eV)				c-AlP	band energies(eV)			
	Γ_1^v	-14.67	L_1^v	-11.67		Γ_1^v	-11.41	L_1^v	-9.87
	$\Gamma_{2,5}^v$	0.00	L_1^v	-8.43		$\Gamma_{2,5}^v$	0.00	L_1^v	-5.43
	$\Gamma_{1,5}^c$	4.79	L_3^v	-1.55		$\Gamma_{1,5}^c$	2.92	L_3^v	-0.73
	Γ_1^c	6.82	L_1^c	4.06		Γ_1^c	5.76	L_1^c	2.77
	X_1^v	-10.27	L_3^c	7.14		X_1^v	-9.26	L_3^c	7.30
	X_3^v	-8.19	L_1^c	11.41		X_3^v	-5.38	L_1^c	9.60
	X_5^v	-3.66				X_5^v	-1.97		
	X_1^c	2.53				X_1^c	2.49		
	X_3^c	2.73				X_3^c	2.97		
	X_5^c	12.44				X_5^c	11.67		

Table 3.5: The eigen energies has been calculated with reference to the valence-band maximum.

3.3.1.6 Polytypes 3C and 2H of silicon carbide (3C-SiC and 2H-SiC)

Cubic SiC has only one possible polytype, which is represented by 3C-SiC or β-SiC. Keeping tetrahedral bonding intact, each SiC bilayer can be oriented into only three possible positions with respect to the lattice. If these three layers are arbitrarily representation of X, Y and Z, and the arranged in sequence as ABCABC then the crystallographic structure comes out as cubic zinc blende. This arrangement is known as 3C-SiC. In 3C-SiC, 3 is the number of layers needed for periodicity. 3C-SiC possesses the smallest band gap ($\approx$ 2.4eV) [105]. Cubic SiC has been grown on Si with limited success and incorporated into heterostructure devices, despite the nearly 20% lattice mismatch between β-SIC and Si. Fig. 3.7 shows 3C-SiC is an indirect band gap material, where valence band maximum is at Γ and the conduction band minimum is at X. The $\Gamma^v_{2,5}$-X^c_1 indirect gap of 2.84 eV calculated form HS-EX is in good agreement with the value of 2.39 eV taken from optical absorption measurements made by Choyke, Hamilton, and Patrick [96] on relatively. We calculated band gap 1.56 eV using TB-LMTO-ASA within LDA. LDA underestimates gap approximately by $\approx$ 40%. While method developed by us TB-LMTO-ASA within HS-EX overestimates only approximately by $\approx$ 18%, whereas GWA overestimates it by $\approx$ 15%. We are very close to GWA values even in some cases we improved over GWA. 2H-SiC is another simple crystal structure found among SiC polytypes having largest band gap. The bi-layer stacking ABAB..., gives SiC hexagonal symmetry and referred to as 2H-SiC. All of the other SiC polytypes are a mixture of the zinc blende (cubic) and

Figure 3.7: Comparison between the band-structures and densities of states of diamond using HS-EX and LDA potential of 2H-SiC (wurtzite) and 3C-SiC (cubic).

wurtzite (hexagonal) bonding. There are four atoms in a unit cell with two positive and two negative ions. In 2H-SiC hexagonality h is unity which represents hexagonal close-packed structure. Again with reference to fig. 3.7 shows 2H-SiC is also an indirect band gap material, where valence band maximum is at Γ and the conduction band minimum is at M. The conduction band minimum in 2H-SiC occur at about 0.577% of the way to the zone boundary from Γ to M. Our calculated value is 3.39 eV which is in very close agreement with experiments 3.30 eV with over estimation about by $\approx$ 3%, where LDA underestimates by $\approx$ 53% while GWA overestimates by $\approx$ 14%.

A summary of the important features of the HS-EX band structure of 2H-SiC and 3c-SiC at high-symmetry points in WZ structure and ZB structure with respect to the valence-band maximum has been given in table 3.6. The maximum valence band width is -13.98 for 3H-SiC while -14.85 for 2H-SiC.

2H-SiC	band energies(eV)				3C-SiC	band energies(eV)			
	Γ_1^v	-13.98	$H_{3'}^v$	-7.10		Γ_1^v	-14.85	L_1^v	-11.59
	$\Gamma_{3'}^v$	-11.03	$H_{1,2}^v$	-4.41		$\Gamma_{2,5}^v$	0.00	L_1^v	-7.95
	Γ_3^v	-7.40	H_3^v	-1.51		$\Gamma_{1,5}^c$	6.66	L_3^v	-0.94
	Γ_5^v	-1.30	H_3^c	5.85		Γ_1^c	8.92	L_1^c	5.76
	Γ_1^c	3.58	$A_{1,3}^v$	-3.96		X_1^v	-10.24	L_3^c	10.46
	Γ_3^c	4.81	$A_{5,6}^v$	-0.71		X_3^v	-7.48	L_1^c	11.43
	$\Gamma_{1',6'}^c$	7.55	$A_{1,3}^c$	4.81		X_5^v	-2.85		
	$\Gamma_{1,6}^v$	8.07	$A_{5,6}^c$	8.41		X_1^c	2.84		
	$L_{1',3'}^v$	-7.30				X_3^c	5.34		
	$L_{1,3}^v$	-2.05				X_5^c	15.37		
	$L_{2,4}^v$	-1.99							
	$L_{1,3}^c$	4.04							
	$L_{1',3'}^c$	6.53							

Table 3.6: The eigen energies has been calculated with reference to the valence-band maximum.

Figure 3.8: Comparison between the band-structures and densities of states of diamond using HS-EX and LDA potential of Li and Na.

3.3.2 Comparison of HS-EX band gap with different methods

Table 3.7 shows us that our predictions are in excellent agreement with experiments, it also summarizes our arguments succinctly. Absence of self-interaction in HS-EX, contrary to LDA, localizes the valence bands comparatively more than conduction bands due to large exchange contribution by former. Consequently, instead of subsiding, HS-EX improves the band gaps which shows the applicability of Harbola-Sahni construct into the description of excited states.

3.4 A first-principles study of the Electronic structure of metals Li, Na, Al and V

The study of electronic structure of solids provides a fundamental basis for understanding their electronic properties. Study of electronic properties of metals shows negligible change in band structure except some fractional shift of energy bands and

Element	Band Gap(eV)			
	HS-EX	LDA	GW	Expt.
C	5.56	2.70	6.03	5.48
Si	1.18	0.49	1.37	1.17
AlN-ZB	5.05	2.44	4.90	5.11
AlN-WZ	5.64	4.43	5.80	6.28
AlP-ZB	2.49	1.16	2.86	2.51
AlP-WZ	2.01	4.43	—	—
BN-ZB	6.39	3.07	6.85	6.20
BN-WZ	7.82	4.90	—	5.92
BP-ZB	2.20	1.21	—	2.21
3C-SiC	2.84	1.38	2.76	2.42
2H-SiC	3.39	1.56	3.75	3.30

Table 3.7: The band gaps from HS-EX compared with LDA [97], GW [98]-[99] and experiments [100]-[106]. HS-EX and LDA are evaluated withing TB-LMTO-ASA. AlN, AlP, BN, BP refers to ZB structure and AlN, the two polytypes 3C and 2H of SiC were studied former with ZB while latter with WZ structure.

Figure 3.9: Comparison between the band-structures and densities of states of diamond using HS-EX and LDA potential of Al and V.

density of states level which localizes whole structure due to absence of self-interaction of orbitals in HS-EX. Although we have done the calculations over very simple metals Li, Na, Al and V shown in fig. 3.8 and fig 3.9, because our motivation was to develop a more efficient methodology to treat the semiconductor materials within TB-LMTO-ASA. We studied metals, to gauge the universal applicability of our methodology. Because underestimation of the excited states (band gap) in semiconductors and insulators almost by $\approx$ 30% to $\approx$ 50% concluded as one of classic failures of LDA. Implementation of HS-EX within TB-LMTO-ASA formalism shows good improvement over LDA. Results are shown in Table 3.7. In case of metals we got overestimated values of bulk moduli because of non-variational approach of method (HS-EX works better for quasi-particle states). Methodology, proposed by us gives as good structural properties as LDA does but in contrary to LDA it works at the places where LDA fails namely in electronic properties e.g. excited states in semiconductors (band gap problem).

3.5 Structural properties of metals and semiconductors

Further, we applied our method to calculate structural properties e.g. bulk moduli of semiconductors as well as metals. We chose to apply HS-EX based TB-LMTO to canonical semiconductors C, Si and few wide band gap system such as AlN, AlP, 3C-SiC (zinc-blende (ZB) structure) along with metals like Li, Na and Al has also been tested under this approach. Table 3.8 summarizes the BM for a series of elements (semiconductors and metals). HS-EX has been compared with LDA, HF and experiments. While good agreement is obtained for equilibrium lattice parameter (ELP) calculated within HS-EX with experiments except metals like Li and Na which differ by as much as 5%. The average deviation of the calculated ELP from the experiments is less than 1% for other systems under consideration. All the calculations performed self-consistently and non-relativistically. We used Murnaghan equation of states [54] to fit the lattice paprameter with eigen energies calculated by TB-LMTO-ASA within exchange only functional (HS-EX). The bulk modulus B is defined by the equation

$$B = V\frac{\partial^2 E}{\partial V^2} = -V\frac{\partial P}{\partial V} \tag{3.7}$$

where $E(V)$ is the total ground-state energy as a function of volume, P is the pressure, and B is evaluated at the minimum of $E(V)$. Although the bulk modulus is essentially the curvature of $E(V)$ at the equilibrium volume, it is customary, but not universal to go beyond a simple quadratic fit. As semiconductors have intriguing mechanical

Element	a(Å)		Bulk Modulus (GPa)			
Metal	HS-EX	Expt.	HS-EX	LDA	HF	Expt.
Li	3.27	3.45	17	16	12	11
Na	4.03	4.21	10	10	8	6
Al	3.98	4.02	93	99	–	76
V	2.98	3.02	209	196	–	162
Semiconductor	HS-EX	Expt.	HS-EX	LDA	HF	Expt.
C	3.60	3.57	429	457	438	442
Si	5.51	5.43	86	97	97	99
AlN-ZB	4.38	4.36	208	206	254	202
AlP-ZB	5.50	5.46	88	89	95	86
3C-SiC	4.41	4.36	211	227	218	224

Table 3.8: Equilibrium lattice parameters are shown from HS-EX and experiments. The bulk moduli have been evaluated by fitting the data to the Murnaghan equation of state [54]. Our results shall be compared with LDA [56, 55], HF [59, 60] along with experiments [58].

properties such as bulk moduli especially of very high value, we start by calculating elastic and electronic properties of semiconductors e.g.BM. Table 3.8 summarizes the BM for a series of elements (metals and semiconductors) and compounds. HS-EX has been compared with experiments and other theoretical calculations. We notice that with increasing atomic number equilibrium lattice parameter (ELP) shows good agreement with experiments. The HS-EX ELP values matches well with experiments which are within the accuracy of the calculations. For Li, Na deviation of ELP from experiments is (5, 5)% respectively while others within 1% of experimental values. We found underestimated ELP values in metallic systems with overestimated BM while opposite is case for the semiconductors. For semiconductors the HS-EX agrees closely with experiments. In case of metals we overestimate the BM. Structural properties of metals calculated within HS-EX produces almost similar results as LDA e.g. equilibrium lattice parameter and bulk moduli.

3.6 Conclusion

In summary, we have developed a first principles method to calculate accurately the band gaps of semiconductors, based on Harbola-Sahni exchange potential with TB-LMTO basis. Not only the calculated band gaps of several semiconductors are in very good agreement with experiments, but the ground state properties like the lattice parameters and bulk moduli. This computationally less expensive and the possibility of easy implementation in more accurate full potential methods should allow one to treat more complex systems. However, there are still issues to be settled, like systems with strong correlation effect needs more careful treatment e.g. oxides. We have estimated the local potential due to the Fermi-hole caused by the Pauli principle. However, the Coulomb hole in which even electrons with the different spins can not come near each other, needs to be incorporated. There is also difference between the true kinetic energy and the kinetic energy of the coupled system to be incorporated. Since the major part in the earlier discrepancy of the band gap has been completely taken care of, these extra correction may not be really necessary.

Chapter 4

Electronic structure of the binary alloy NiMo within augmented space formalism and its phase analysis

[1]

4.1 Introduction

The magnetic behaviour of disordered alloys in which a magnetic component is diluted with a non-magnetic one, or one in which the components have competing ferro- and antiferro-magnetic behaviour has been the subject of intense research for a long time [107]. By now the experimental picture is very well understood. In particular it is understood that in certain composition ranges one finds a phase in which there is

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no long-ranged magnetic order, in spite of the fact that locally magnetic moments exist. The susceptibility as a function of temperature shows a characteristic cusp, indicating freezing of magnetic degrees of freedom. In the same spin-glass phase one observes history dependence and anomalously slow relaxation, characteristic of glassy materials.

In this chapter we shall examine magnetic properties and phase transitions NiMo alloy to check the spin glass nature of NiMo within augmented space formalism [2]. This alloy can be prepared in the disordered phase by fast quenching from the melt. It's magnetic behavior are very different. NiMo is a random ferro-magnet in the Ni rich region, but keep losing magnetism as Mo concentration increases and suddenly goes to zero. It does not seem to exhibit a spin-glass phase. The aim of this communication, from a first-principles density functional based theory, is to map the problem onto an equivalent Ising model and describe the magnetic phases from the calculated pair energies of the model.

Although such alloy phases have been quite exhaustively studied by techniques of both equilibrium and non-equilibrium statistical mechanics, a first-principles, microscopic study based on realistic models of such systems will throw some light both on the suitability of some of the underlying assumptions of the simplified solvable models as well as differences in behaviour because of local chemistry.

Successful mean field approaches to the problem of spin-glasses vary from that of Sherrington-Kirkpatrick [108] to the sophisticated replica symmetry breaking ideas of

Parisi [109, 110]. Different ways of describing and dealing with the randomness have been suggested by Kaneyoshi [111], Plefka [112], Thouless *et.al.*[113] and the virial expansion of Morita and Horiguchi [114]. The virial expansion is valid either at low or very high temperatures [115] or when the spin pair energy parameter $J \sim O(N^{-1/2})$. It is, in fact, invalid in the parameter range and coupling type of our interest. Most of these solvable models assume specific type of spin pair energies like infinitely weak, infinitely long-ranged ($J \sim O(1/N)$) and further assume Gaussian distribution of these pair energies in an ad hoc manner. It would be interesting to examine these simplified models in light of our first-principles analysis.

This chapter will be arranged as follows : in the section 2 we shall study the electronic structure of NiMo alloy at varying compositions and extract information about the density of states and local magnetic moment. In section 3 we shall use our electronic structure and the generalized perturbation expansion formalism to map the problem of emergence of magnetic order onto a classical Ising model and obtain the effective pair energies. We shall examine the nature of these pair energies in detail. In the final section we shall use our mapped random Ising model to examine the phase diagram basing our analysis on mean-field theories.

4.2 Electronic structure of NiMo alloy

Our starting point will be the Kohn-Sham equation for the motion of electrons in the alloy. We can choose any of the methods for generating Hamiltonians from first principles in which the basis is labeled by lattice points. Such a tight-binding description is ideal for describing the substitutional disorder in the alloys of our interest. We shall choose the tight-binding, linear muffin-tin orbitals method (TB-LMTO) [116]. The TB-LMTO is a standard technique by now and we shall refer the interested reader to the above reference for details. In a random alloy the LMTO 'potential' parameters are random and we shall have to describe the properties of the system from the viewpoint of configuration averaging. Extensive work on methods dealing with configuration averaging exists. An extended discussion on the successful averaging techniques and a comparison between their estimates (for FeCr) has been given in a recent paper by Tarafder *et.al.*[117] In the present work we have chosen to use the augmented space recursion (ASR) [11] introduced by one of us.

The augmented space formalism deals with configurational averaging going beyond mean-field approaches like the CPA. It takes into account the effect of configurational fluctuations of the immediate neighbourhood of a site and can deal with inhomogeneous disorder like clustering [119], short-ranged ordering [120]-[121] and local distortions arising out of size mismatch of constituents [122]. The augmented space formalism is exact and approximations arise only in the recursion part. Recursion expands the configuration averaged Green function as a continued fraction and the approximation is in the number of continued fraction steps accurately calculated before the asymptotic part is 'terminated' by one of the terminators suggested by Haydock [123] or Beer and Pettifor [124]. We shall terminate with the Beer-Pettifor terminator after 11 steps of recursion. This will mean that 20 moments of the density of states will be accurate, as compared with only 8 moments in the CPA. The other major source of error is in the atomic sphere approximation of the TB-LMTO. One way out is to replace the TB-LMTO with full-potential LMTO. But then the Hamiltonian will no longer be sparse and recursion will lose accuracy. We shall stick with the TB-LMTO-ASR. The limit of accuracy of the total energy calculations is about a few mRyd/atom. For energy differences less than this our statements will be qualitative.

The calculations are LSDA-self-consistent and the Madelung energy is constructed according to the ideas of Ruban and Skriver [125]. Their screening parameters were obtained using the SQS technique as suggested by Ruban *et.al.*[126]. Within the TB-LMTO procedure the solid is partitioned into atom centric atomic spheres (AS) labeled by $\mathbf{R}_i$. $\Phi(\mathbf{r}-\mathbf{R}_i)$ is the wavefunction projected in an AS at $\mathbf{R}_i$. Once we have calculated the configuration averaged Green function $\ll G^{\sigma}_{\mathbf{R}_iL,\mathbf{R}_i,L}(E) \gg$ we immediately obtain the following:

The local spin-resolved density of states :

$$n^{\sigma}(E,\mathbf{R}_i) = -\frac{1}{\pi}\Im m \mathrm{Tr}_L \ll G^{\sigma}_{\mathbf{R}_iL,\mathbf{R}_iL}(E+i0^+) \gg \tag{4.1}$$

The charge and the magnetization densities :

$$\begin{aligned}
\rho^{\sigma}(\mathbf{r}-\mathbf{R}_i) &= \int_{-\infty}^{E_F} |\Phi(\mathbf{r}-\mathbf{R}_i)|^2 \; n^{\sigma}(E,\mathbf{R}_i) \\
\rho(\mathbf{r}-\mathbf{R}_i) &= \rho^{\uparrow}(\mathbf{r}-\mathbf{R}_i) + \rho^{\downarrow}(\mathbf{r}-\mathbf{R}_i) \\
m(\mathbf{r}-\mathbf{R}_i) &= \rho^{\uparrow}(\mathbf{r}-\mathbf{R}_i) - \rho^{\downarrow}(\mathbf{r}-\mathbf{R}_i)
\end{aligned} \tag{4.2}$$

and the magnetic moment within an atomic sphere (AS) :

$$m(\mathbf{R}_i) = \int_{AS} d^3\mathbf{r} \; m(\mathbf{r}-\mathbf{R}_i)$$

$\rho(\mathbf{r}-\mathbf{R}_i)$ is the charge density and $m(\mathbf{r}-\mathbf{R}_i)$ is the magnetic moment density in AS at $\mathbf{R}_i$. From this description it is clear that the magnetic moment is not localized at $\mathbf{R}_i$ but smeared across the AS. $m(\mathbf{R}_i)$ integrated over an AS is the average magnetic moment associated with it. These magnetic moments are thus built up out of itinerant electron charge densities associated with different spins.

Fig.-4.1 shows the atom and spin projected densities of states for $\mathrm{Ni}_{1-x}\mathrm{Mo}_x$ at two characteristic compositions : one with low Mo content and another with a higher one. The electronic structure of NiMo has been studied earlier using the CPA by Abrikosov *et.al.*[128] and using the locally self-consistent Green function (LSGF) by Abrikosov *et.al.*[129].

We have earlier studied this alloy system both from the point of view of electronic structure [130] and atomic ordering [131]. Unlike other canonical spin glass alloys,

Figure 4.1: Projected densities of states for Ni (red) and Mo (black) in $\mathrm{Ni}_{1-x}\mathrm{Mo}_x$ alloys (left) x=0.08 and (right) x=0.18

the Ni and Mo bands overlap considerably. In addition Ni is a fragile magnet whose moment is lost if it is surrounded by too many non-magnetic neighbours. Local magnetic moments on Ni and Mo and the total magnetic moment per atom are shown in Fig.-4.2. We see that Mo does carry some magnetic moment in the alloy, although rather small. Also the moment carried by Mo is oppositely oriented to that of Ni. As in all systems in which magnetism is predominantly itinerant, the Mo PDOS becomes narrower as its concentration decreases and its local moment increases. Effect on Ni, however, is rather different. Because of the fragility of its moment, as its concentration decreases and Mo occupying its neighbourhood becomes more probable, Ni moment also decreases. Fig.-4.2 shows that the total magnetic moment of the alloy also decreases as Mo concentration increases and finally vanishes at $x \simeq 0.15$. This is clearly reflected in the experimental data of Asgar *et.al.*[132]. Spin-glass phase has not been reported in NiMo, although careful experimentation is still required around

$x \simeq 0.15$ *before* where the Ni loses its local moment.

Figure 4.2: Local magnetic moments at Ni and Mo (AS) sites in $Ni_{1-x}Mo_x$ as a function of Mo concentration x.

4.3 Magnetic ordering and the random Ising model

The analysis of magnetic order forming out of the paramagnetic phase is similar to that of atomic ordering from a chemically disordered phase. To describe the magnetic phases of an itinerant magnetic alloy we shall follow the generalized perturbation method first introduced by Ducastelle and Gautier [12]. We shall begin with a completely disordered paramagnetic arrangement of atomic spheres each with its own magnetic moment pointing randomly along the quantization direction or opposite to it. Into that system introduce local perturbations and expand the total energies:

$$E = E_{\mathrm{dis}} + \sum_{Q,\mathbf{R}_i} E^{(1),Q}(\mathbf{R}_i)\ \delta\xi_i^Q + \frac{1}{2}\sum_{QQ'}\sum_{\mathbf{R}_i,\mathbf{R}_j} E^{(2),QQ'}(\mathbf{R}_i,\mathbf{R}_j)\ \delta\xi_i^Q\ \delta\xi_j^{Q'}\ldots \tag{4.3}$$

Q, Q' are the species of atom Ni or Mo. The summation of $\mathbf{R}_i$ is over those AS occupied by specie Q, and that of $\mathbf{R}_j$ over AS occupied by specie Q'. The scalar variable $\delta\xi_i^Q$ takes the value ±1 according to whether the atomic sphere labeled by $\mathbf{R}_i$ is occupied by a Q specie of atom and its average moment (constructed out of the itinerant electron charge densities as discussed before) points in the quantization direction or opposite to it. Note that $\delta\xi_i^Q$ are not spin variables but occupation numbers. Once the averaged magnetic moment in the AS labeled by $\mathbf{R}_i$ is built up from itinerant electron densities, the variables $\{\delta\xi_i^Q\}$ describe how the AS are arranged on the lattice. Consequently, they are scalar, classical variables. Our aim is to determine which arrangement is free-energetically the most favourable.

The terms $E^{(1),Q}(\mathbf{R}_i)$, $E^{(2),QQ'}(\mathbf{R}_i,\mathbf{R}_j)$ are called the renormalized single-site and pair energies. The former plays no role in ordering of the AS, while the higher terms like triplet and quadruplet energies are assumed to be small enough to be ignored. It is easy to note from the above definition that :

$$E^{(2),QQ'}(\mathbf{R}_i,\mathbf{R}_j) = \frac{1}{2}\sum_{\sigma}\sum_{\sigma'}(2\delta_{\sigma\sigma'} - 1)\ E^{Q\sigma,Q'\sigma'}_{\mathbf{R}_i,\mathbf{R}_j} \tag{4.4}$$

where $E^{Q\sigma Q'\sigma'}_{\mathbf{R}_i,\mathbf{R}_j}$ is the total energy of a paramagnetic background with the sites $\mathbf{R}_i$ and $\mathbf{R}_j$ occupied by Q and Q' type of atoms, with σ and σ' being the alignments of the averaged magnetic moments in the AS, either along or opposite to the quantization direction. Since $E^{(2),QQ'}(\mathbf{R}_i,\mathbf{R}_j)$ are very small energy differences (of the order of mRy) of large energies (of the order of 10^3 Ry), a separate calculation of each component energy will produce errors larger than the small differences themselves. These the pair energy parameters will be calculated, following the suggestion by Lichtenstein *et al.* [14, 15], as :

$$E^{(2),QQ'}(\mathbf{R}_i,\mathbf{R}_j) = \frac{1}{4\pi}\int_{-\infty}^{E_F} dE\ \Im m\ \mathrm{Tr}_L \left\{ \underline{\underline{\delta}}^{Q}_{\mathbf{R}_i}\ \underline{\underline{T}}^{Q\sigma Q'\sigma}(\mathbf{R}_i-\mathbf{R}_j)\ \underline{\underline{\delta}}^{Q'}_{\mathbf{R}_j} T^{Q\sigma' Q'\sigma'}(\mathbf{R}_j - R_i)\right\} \tag{4.5}$$

where $\sigma \neq \sigma'$ and $\underline{\underline{\delta}}^{Q}_{\mathbf{R}_i} = \underline{\underline{P}}^{Q\sigma}_{\mathbf{R}_i} - \underline{\underline{P}}^{Q'\sigma'}_{\mathbf{R}_i}$. $\underline{\underline{P}}^{Q\sigma}$ is the on-site potential function of TB-LMTO while $\underline{\underline{T}} = (\underline{\underline{P}} - \underline{\underline{S}})^{-1}$ is the Green operator in a disordered system in which the sites $\mathbf{R}_i$ and $\mathbf{R}_j$ are occupied by species $Q\sigma$ and $Q'\sigma'$. $\underline{\underline{S}}$ is the LMTO structure matrix. We should note that these energy calculations are also from an itinerant electron viewpoint.

In Ising model parlance $E^{(2)QQ'}(\mathbf{R}_i,\mathbf{R}_j) = J^{QQ'}(R)\ R = |\mathbf{R}_i - \mathbf{R}_j|$. Let us examine the behaviour of $J^{QQ'}(R)$ in greater detail. To quantify this variation we use the spatial moments of the scaled pair energy :

$$\begin{aligned} I_0^{QQ'} &= \sum_R W(R) J^{QQ'}(R) \\ I_{n-1}^{QQ'} &= \sum_{R\geq a} W(R) \left\{ J^{QQ'}(R)/I_0^{QQ'} \right\}^n \qquad n = 2,3\ldots \end{aligned} \tag{4.6}$$

$W(R)$ are the coordination numbers on the face-centered cubic lattice.

Unlike canonical spin glass materials where alloying with magntic atoms leave the non-magnetic atoms with negligible moment, on other hand in NiMo, Mo gains a small moment and the pair energy between Ni and Mo and Mo and Mo are not negligible. Fig.-4.3 shows these pair energies as functions of distance. The Ni-Ni pair energy in NiMo has significant differences from the pair energies of pure and robust magnetic atoms in canonical spin glasses. Although the nearest neighbour pair energy is still ferro-magnetic, the anti-ferromagnetic second nearest neighbour pair energy is very small and dominated by the ferro-magnetic third nearest neighbour one. Both the Ni-Ni and Ni-Mo pair energies show the characteristic decay due to disorder scattering. The Ni-Mo pair energy is ferromagnetic, but at low Mo concentrations most of the neighbours of Ni are also Ni. It is more probable to find Mo at the next-nearest neighbour positions. The relatively large next-nearest neighbour antiferro-magnetic Ni-Mo pair energies may then explain why the Mo and Ni atoms have moments anti-parallely aligned.

However, a look at Fig.-4.4 shows us that the moments of $J^{\mathrm{NiNi}}(R)$ are all positive and strongly decreasing as x increases. As for NiMo the local 'Weiss' field has a distribution which becomes more Gaussian as x increases and increasingly sharp. The positive sign of the third and fifth moments indicate that the pair energies are predominantly ferro-magnetic. This means that frustration is negligible exactly in the compositions where spin-glass may become possible. This coupled with the fact that exactly in this region the Ni atoms lose their local moments, may be the reason

Figure 4.3: Pair energies $J^{QQ'}(R) = E^{(2)QQ'}(R)$ for $Q, Q' =$ (top) Ni-Ni, (middle) Ni-Mo and (bottom) Mo-Mo in $\mathrm{Ni}_{1-x}\mathrm{Mo}_x$.

Figure 4.4: First four m‘oments of $J^{NiNi}(R)$ $R \geq a$ with R for different compositions of NiMo

why spin glass phase has not been observed in NiMo.

A comment must be made regarding the oscillatory pair energies in these alloy systems. Ling *et.al.*[134]-[135] have discussed the pair energies in CuMn, another spin-glass alloy. They argue that if the Fermi energy straddles the local DOS peak of the magnetic component, then ferromagnetism is favored, whereas antiferro-magnetism is stabilized if the local DOS peaks are away from the Fermi-energy. In CuMn the t_{2g} states are more nearly filled and provoke a ferromagnetic tendency while the e_g states being away from the Fermi energy stabilizes anti-ferromagnetism. The competition between these two tendencies suppresses direct magnetic interactions between the magnetic atoms and enhances the role of indirect interactions. The outcome is the interpretation of magnetic interactions in terms of damped, oscillatory RKKY-like interactions. This may not be reflective of actual RKKY interactions. For NiMo too a similar argument can be made. A look at the Ni projected DOS shown in Fig.-4.1 shows us that the e_g and t_{2g} structures in the DOS are well separated : one straddling the Fermi energy and the other away from it.

4.4 Phase analysis of NiMo

Our model consists of N_A, A and N_B, B atoms uniformly distributed over M lattice sites and interacting via our estimated pair energies $J(\mid R_i - \mathbf{R}_j\mid)$. These may vary in sign as a function of distance providing the main ingredient, frustration, in the system. The probability of an atom A occupying a specific site $\mathbf{R}_k$ is $1/M$, as every site has equal probability of occupation. Similarly, the probability that a site is occupied by a A atom is N_A/M and a B atom is N_B/M. In the thermodynamic limit, in the absence of any clustering or segregating effects,

$$\lim_{N_A,M\to\infty} \frac{N_A}{M} = x_A \qquad \lim_{N_B,M\to\infty} \frac{N_B}{M} = x_B$$

x_A, x_B being the atomic concentrations of A and B constituents. The random 'Hamiltonian' is the same as shown in Eqn. (3):

$$\Delta E = \frac{1}{2}\sum_{QQ'}\sum_{\mathbf{R}_i,\mathbf{R}_j} J^{QQ'}(|\mathbf{R}_i - \mathbf{R}_j|)\ \delta\xi_i^Q\ \delta\xi_j^{Q'}$$

where,

$$J^{QQ'}(R) = E^{(2),QQ'}(R)$$

For a binary alloy, Q, Q' can be either A or B. $J^{QQ'}(|\mathbf{R}_i - \mathbf{R}_j|)$ is random depending upon which type of atoms occupy the sites $\mathbf{R}_i$ and $\mathbf{R}_j$. It can take on the values $J^{AA}(|\mathbf{R}_i - \mathbf{R}_j|)$, $J^{BB}(|\mathbf{R}_i - \mathbf{R}_j|)$ or $J^{AB}(|\mathbf{R}_i - \mathbf{R}_j|)$.

Introducing the single-site mean field approach by replacing the quadratic term $\delta\xi_i^Q\delta\xi_j^{Q'}$ by $\delta\xi_i^Q m_j^{Q'} + \delta\xi_j^{Q'} m_i^Q - m_i^Q m_j^{Q'}$ where m_i^Q is the thermal average $< \delta\xi_i^Q >$, we can obtain the Free energy as :

$$F \;=\; -\frac{1}{2}\sum_{QQ'}\sum_{\mathbf{R}_j,\mathbf{R}_j\in QQ'} J^{QQ'}(|\mathbf{R}_i - \mathbf{R}_j|) m_i^Q m_j^{Q'} + \frac{1}{\beta}\sum_{Q}\sum_{\mathbf{R}_i\in Q} \log\cosh(\beta h_i^Q) \quad (4.7)$$

where the local 'Weiss' fields are :

$$h_i^Q = \sum_{Q'}\sum_{R_j\in Q'} J^{QQ'}(|\mathbf{R}_i - \mathbf{R}_j|) m_j^{Q'} \qquad (4.8)$$

In an ordered alloy we can define a homogeneous order parameter corresponding to the occupation variable of a Q type of atom as $m^Q = (1/N_Q)\sum_{i\in Q} m_i^Q$ and an average global order parameter as $m = \sum_Q x_Q m^Q$. In our disordered system inhomogeneities are in a macroscopic scale and this prevents us from introducing such an idea prior to some kind of configuration averaging. Rather we picture the system as follows : the net result of random pair energies connecting a local order parameter with its neighbourhood is that it experiences a local random 'Weiss' field along which the average AS moment aligns. This leads to a *set of local order parameters* $\{m_i^Q\}$. In order to describe the local order parameters we need to know the distribution of the local 'Weiss' fields. This interpretation links our work with that of Thouless [113] and Mookerjee [137]. The free energy is a function of the whole set of *local* order parameters. The stable phase solution comes from the equations $\partial F/\partial m_i^Q = 0$ for all i. This leads to :

$$m_j^Q = \tanh\left[\beta h_j^Q\right] \qquad Q, Q'\text{can be } A \text{ or } B \tag{4.9}$$

For sufficiently high temperatures, the only consistent solution will be $m_i^Q = 0\ \forall i$. At low concentrations of the magnetic constituent and as we lower the temperatures some of the local order parameters become non-zero and they are distributed randomly on the lattice. Moreover, there could be several different configurations of ± order parameters which have the same free energy. This implies that rather than having a unique stable phase with non-zero global order parameter, we have a very corrugated free energy landscape with many minima differing in random distributions of ± moment carrying AS separated from each other by energy barriers. The resulting 'phase' may consist of domains with differing local AS configurations. One way of describing such an inhomogeneous picture is to find the distribution function of the scaled local 'Weiss' field. The scaling is carried out as follows : all $J(R)$ is replaced by $I(R) = J(R)/I_0$. In case there is only one magnetic constituent, the scaling is done with : $I_0 = \sum_R W(R)J(R)$. In case both the constituents are magnetic we have three factors I_0^{AA}, I_0^{AB} and I_0^{BB} and we scale with respect to $I_0 = \text{Max}\ \{I_0^{AA}, I_0^{AB}, I_0^{BB}\}$. Here $W(R)$ is the coordination number at a distance R from an origin.

The scaled 'Weiss' fields are given by :

$$\widehat{h}_i^Q = \sum_{Q'} \sum_{\mathbf{R}_j \in Q'} I^{QQ'}(|\mathbf{R}_i - \mathbf{R}_j|)\ m_j^{Q'}$$

The technique for the derivation of distribution function has been described earlier by Klein [138] and Mookerjee [137] and the reader is referred to those papers for details. Here we shall quote the procedure and the main results. The probability is first expressed as a Radon transform of the Eqn.(4.8) and then the approximation is introduced in which we replace the delta-functional kernel of the Radon transform by its configuration average. Under the assumption that local 'Weiss' fields at different sites are uncorrelated : so that there is no clustering or short-ranged correlations between the local order parameters, we get

$$\mathcal{P}_Q(\widehat{h}_i^Q) = \frac{1}{2\pi} \int dk\ e^{ik\widehat{h}_i^Q} \prod_{Q'} \left[1 - \frac{F_{QQ'}(k)}{M}\right]^{N_{Q'}}$$

where,

$$F_{QQ'}(k) \;=\; \sum_R \int dz \mathcal{P}_Q(z) \left[1 - \exp\left\{-ikI^{QQ'}(R)\tanh(\beta J^{QQ'}(R) z)\right\}\right]$$

In the thermodynamic limit :

$$\mathcal{P}_Q(\widehat{h}_i^Q) = \frac{1}{2\pi}\int dk \exp\left\{ik\widehat{h}_i^Q - \sum_{Q'} x_{Q'} F_{QQ'}(k)\right\}$$

The direct calculations of the $F_{QQ'}(k)$ are tough as it stands, but let us expand the exponential and examine the terms :

$$\begin{aligned} F_{QQ'}(k) = \int dz\ \mathcal{P}_Q(z) \Big[& ikI_0^{QQ'}\tanh(\beta J_0^Q z) + \frac{k^2}{2} I_1^{QQ'}\tanh^2(\beta J_0^Q z) \ldots \\ & \ldots + \frac{(-ik)^3}{6} I_2^{QQ'}\tanh^3(\beta J_0^Q z)\ldots \Big] \end{aligned}$$

where

$$\sum_R W(R) I^n(R) = I_{n-1} \quad n = 1, 2\ldots$$

We define :

$$\begin{aligned} J_0^Q &= \sum_{Q'} x_{Q'} m^{Q'} \sum_R J^{QQ'}(R) = \sum_{Q'} k_B T_{QQ'} m^{Q'} \\ J_1^Q &= \sum_{Q'} x_{Q'} q^{Q'} \sum_R J^{QQ'}(R)^2 = \sum_{Q'} k_B^2 T^{g2}{}_{QQ'} q^{Q'} \end{aligned}$$

Figure 4.5: Phase diagrams for NiMo alloy

and

$$
\begin{aligned}
m^Q &= \int dz\ \mathcal{P}_Q(z)\ \tanh(\beta J_0^Q z) \\
q^Q &= \int dz\ \mathcal{P}_Q(z)\ \tanh^2(\beta J_0^Q z)
\end{aligned}
\tag{4.10}
$$

Comparing Eqns. (4.9) and (4.10) we note that we can interpret m^Q and q^Q as the configuration averages $\ll m_i^Q \gg$ and $\ll\left(m_i^Q\right)^2\gg$. Our frozen disordered local moment picture envisages spin-glass in NiMo as a quaternary alloy $\mathrm{Ni}^{\uparrow}_{1-x/2}\mathrm{Ni}^{\downarrow}_{1-x/2}\mathrm{Mo}^{\uparrow}_{x/2}\mathrm{Mo}^{\downarrow}_{x/2}$. For this phase $m^Q = 0$ but $q^Q \neq 0$. Thus the frozen disordered moment picture is consistent with our model for a spin-glass.

The equations (4.10) then reduce to the standard mean-field equations :

$$m^Q = \frac{1}{\sqrt{2\pi}} \int dz e^{-z^2/2} \tanh \left[\sum_{Q'} \frac{T_{QQ'}}{T} m^{Q'} + \frac{T^{g2}_{QQ'}}{T^2} q^{Q'} z \right]$$

$$q^Q = \frac{1}{\sqrt{2\pi}} \int dz e^{-z^2/2} \tanh^2 \left[\sum_{Q'} \frac{T_{QQ'}}{T} m^{Q'} + \frac{T^{g2}_{QQ'}}{T^2} q^{Q'} z \right]$$

The results are similar to many earlier works based on the distribution of local 'Weiss' fields, but it must be emphasized that our derivation has throughout made assumptions that take into account both a correct description of substitutional disorder and correct form of the pair energies. The scaling of both the mean and variance of the local 'Weiss' field with concentration of the magnetic component naturally arises in our results. Moreover, in this derivation we emphasize on the distribution of local 'Weiss' fields, so that the inhomogeneous picture of the system remains intact. m^A, m^B, q^A, q^B are being related to the moments of the local 'Weiss' field distribution.

One phase is characterized by $m^Q = 0, q^Q = 0$ so that the 'Weiss' field distribution is a delta function at $h^Q = 0$. This is obviously a paramagnetic phase with no local or global magnetization. Another phase is characterized by $m^A = 0, m^B = 0, q^A \neq 0, q^B \neq 0$. Here the distribution of the 'Weiss' fields are Gaussian with means at zero but with a non-zero spread. How can such a phase be described ? Since the mean is zero the local magnetization positive at as many sites as it is negative. This is exactly the frozen disordered moment picture described earlier. The spin-glass phase boundary is given by :

$$T_g = \frac{1}{2}\left\{(T^g_{AA} + T^g_{BB}) + \sqrt{(T^g_{AA} - T^g_{BB})^2 + 4T^g_{AB}T^g_{BA}}\right\} \tag{4.11}$$

Finally there is a third phase where $m^A \neq 0, m^B \neq 0, q^A \neq 0, q^B \neq 0$. For this phase the distribution of the local 'Weiss' fields are shifted Gaussians with a non-zero mean. So not only is there a distribution of different local moments, the global averaged moment is also non-zero. This is the random ferro-magnetic phase. This boundary is given by :

$$T_c = \frac{1}{2}\left\{T_{AA} + T_{BB} + \sqrt{(T_{AA} - T_{BB})^2 + 4T_{AB}T_{BA})}\right\} \tag{4.12}$$

The Fig.-4.5 plots phase boundaries for NiMo. Now both the constituents carry moment, so we shall use the more general Eqns.(4.11) and (4.12). The paramagnetic-random-ferromagnetic boundary agrees very well with the experimental results of Asgar *et.al.*[132]. We note that in most of the temperature-concentration domain the spin-glass boundary lies well below the random-ferromagnetic one. Only in a small region around Mo concentration 11-13% (atomic) is there a possibility of these boundaries to cross and a spin-glass transition possible.

4.5 Conclusion

In NiMo alloy with increasing Mo concentration, Ni loses it's local moment and suddenly goes to zero at close to 13 at.% of Mo. NiMo does not show any signature of spin glass which may be the artifact of mean-field approach followed by us. So very careful experimental observation is required at 11-13 at.% of Mo as there is a competition between the formation of the spin-glass and collapse of both magnetic moment and frustration with dilution.

Chapter 5

Comparison between magnetic transitions in NiMo and NiW alloys

[1] In this chapter we shall switch from TB-LMTO-ASR formalism to KKR-CPA. Our aim would be to apply different approximations to similar problems in order to get a feel for their individual applicabilities. We shall study $Ni_{1-x}Mo_x$ and $Ni_{1-x}W_x$ alloys where concentration of Mo varies from 0 to 12 percent and that of W varies from 0 to 10 percent respectively. We shall present composition dependence of pair energies, spatial moments of scaled pair energies and magnetic phase behaviour of these alloys and then making a detailed analysis and comparison to conclude with arguments of non-existence of spin-glass phase in above two in contrast with canonical spin-glass systems like AuFe.

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5.1 Introduction

Transition metals like Fe, Co and Ni alloy with non-magnetic metals like Au,Ag or Cu to form disordered solid solutions. For certain composition ranges in these alloys we observe the spin-glass phase at low temperatures. Ni is an exception to this class. Alloyed with Mo or W, it does exhibit a disordered phase. However, no experimental signature of the spin-glass phase is seen in either $\mathrm{Ni_{1-x}Mo_x}$ or $\mathrm{Ni_{1-x}W_x}$.

We shall study magnetic transitions and magnetic phase diagrams of these two alloy systems based on the ideas of the generalized perturbation method (GPM) [12, 13]. We begin with a completely disordered nonmagnetic background and perturb it with magnetic fluctuations. We expand the total energy of this perturbed state about the nonmagnetic background in a power series in the small perturbations. In this expansion, retaining terms only till the pair energies, we map the problem onto an effective Ising model. This will be the basis of our phase analysis.

This energy expansion involves coefficients which are small differences of large energies. We use the Lichtenstein formula [14, 15] for a direct and hence accurate calculation of these small energy differences. We obtain the local magnetic moments from the Korringa-Kohn-Rostocker based coherent potential approximation (KKR-CPA) [144, 145]. The pair energies has been calculated from the more accurate exact muffin-tin orbital based CPA (EMTO-CPA) [146]. These techniques have been described in detail in the references provided.

5.2 Formation of moments and magnetic ordering

In order to understand the onset of magnetic ordering in random alloys, we need a derivation of the lowest magnetic configurational energy. The KKR partitions the lattice space into atom centric atomic spheres. Within each sphere we treat the electrons as itinerant and the magnetic moment associated with an atomic sphere is obtained from the configurational averaged Green functions as shown Chapter 4, eqns (4.1)-(4.2).

The problem of magnetic ordering is then the ordering of these atomic spheres carrying their moments. This is exactly the problem described in Chapter 4, eqns. (4.3)-(4.4).

The one-site energy $E^{(1),Q}$ is unimportant for bulk ordered structures emerging from disorder. It is important for emergence of inhomogeneous disorder at surfaces and interfaces [147]. The pair energies $E^{(2),QQ'}$ are the most important factors governing emergence of bulk ordering. The interpretation of equation (4.3) immediately allows us to introduce a method to obtain the pair potentials directly rather than calculate the total energies and then subtract them. Since they are small differences (of the order of mRy) of large energies (of the order of 10^3 Ry), a direct calculation will produce errors larger than the differences themselves. The Lichtenstein formula was introduced to calculate such small differences directly. This has been described and given in Chapter 4, eqn. (4.5).

Figure 5.1: Magnetic moments per atomic spheres for $\mathrm{Ni_{1-x}Mo_x}$ (top) and $\mathrm{Ni_{1-x}W_x}$ (bottom)

5.3 Mean-field analysis of transition temperatures

The generalized perturbation maps the problem onto an effective Ising model. Chapter 4 section 4.3 describes the analysis in detail. We shall follow the same procedure as described in that section.

In fig. 5.1, we have shown the local Ni magnetic moments as functions of alloy composition. We note at around 12% dilution with Mo and 10% dilution with W, the Ni atoms in the alloy lose their individual magnetic moments. This is in sharp contrast with Fe diluted with Au or Ag, or Mn diluted with Cu. In an earlier communication we have shown [148] that with increasing dilution the local magnetic moment of Fe actually increases to that of an isolated Fe atom. For these canonical spin-glass alloys, although at around 10-20% dilutions the alloys go into a spin-glass phase and the net magnetization vanishes, the individual local moments on the magnetic atoms remain robust (as seen from Mössbauer experiments). The moment on Ni, on the other hand,

Figure 5.2: (Top panels) Pair energies for $\mathrm{Ni_{1-x}Mo_x}$ and their variation with composition. (Bottom panels) Pair energies for $\mathrm{Ni_{1-x}W_x}$ and their variation with composition. In the right panels pair energies are shown starting from the second nearest neighbors in the face-centered cubic lattice.

is fragile and is lost on dilution. There can, therefore, be a competition between loss of local moment on Ni and an onset of the spin-glass phase in these alloys which we wish to examine in greater detail.

In fig. 5.2 shows the exchange couplings as a function of composition. We note that the exchange couplings are strongly composition dependent. The right panels show pair energies starting from the next-nearest neighbours and their composition

Figure 5.3: Moments of the exchange energies for (top) $\mathrm{Ni_{1-x}Mo_x}$ (bottom) $\mathrm{Ni_{1-x}W_x}$

variation in greater detail. We note the following points :

(i) If we compare the results for NiMo with those obtained in Chapter 4, we note that ASR and CPA almost mirror each other. In this alloy system the two methods give comparable results.

(i) The pair energies are dependent on the composition. The simplified models of spin-glass alloys without exception assumed that the pair energy depended only on the components of the alloy. The nearest neighbour exchange energies are ferromagnetic and decreases on dilution mirroring the collapse of Ni local magnetic moment. The second nearest neighbour exchange energies change from anti-ferromagnetic to just ferromagnetic on dilution, while the next three collapses to zero with dilution. This feature has to be incorporated in any realistic model of the spin-glass.

(ii) The pair energy $J(\widehat{R})$ oscillates in sign with increasing $\widehat{R}$ so that the possibility of frustration is present. The nearest neighbour pair energy is strongly ferromagnetic and quite a bit larger than the next nearest neighbour one. The behaviour of the pair energies exhibits exponential decay characteristic of disorder damping. With increasing dilution disorder scattering increases and so does the damping. A model with damped, oscillatory interaction seems suitable for these alloys.

Let us examine the behaviour of $J(\widehat{R})$ in greater detail. To quantify the variation of $J(\widehat{R})$ with $\widehat{R}$ we use the spatial moments of the scaled pair energy :

$$I_n = \sum_{R>a} W(\widehat{R}) \left\{ J(\widehat{R})/J(a) \right\}^n \quad n = 1, 2, \ldots \tag{5.1}$$

$W(\widehat{R})$ are the coordination numbers on the face-centered cubic lattice and a is the nearest neighbour distance on it.

From fig. 5.3 we note that the third moments of both $\mathrm{Ni_{1-x}Mo_x}$ and $\mathrm{Ni_{1-x}W_x}$: M_3 are positive which is characteristic of distributions which are asymmetric with more weightage towards ferro-magnetic pair energies. This asymmetry decreases and at around $10-12\%$ dilution becomes zero. This is in sharp contrast with AuFe, where this moment is negative and changes to positive only at around 84% dilution of Fe with Au. The anti-ferromagnetic pair energies are the source of frustration on the lattice. The third and fourth moments M_3 and M_4 go to zero with increasing dilution indicating that the distribution (whose moments these are) becomes more Gaussian (free from asymmetry and kurtosis), while the second moment M_2 also decreases and the distribution about the mean becomes sharp (delta function like). The first moment also goes to zero at around $10-12\%$ dilution, indicating that the distribution becomes a delta function centered at the origin.This is characteristic of a paramagnetic phase and there is a strong indication that a paramagnetic phase with no local Ni moments may be the stable low temperature phase at 12% dilution for $\mathrm{Ni_{1-x}Mo_x}$ and 10% dilution for $\mathrm{Ni_{1-x}W_x}$

These results throw some light on the nature of frustration in the systems and their behaviour with composition. Khmelevskyi *et al.* [149] have used the partial moments

Figure 5.4: Frustrated plaquettes on a face-centered cubic lattice which lose their frustration on dilution

$K(R_0) = \sum_{R>R_0} W(\widehat{R})J(\widehat{R})$ to illustrate frustration. The moments by themselves cannot give full information about frustration unless we couple them with the lattice topology. Antiferro-magnetic pair energies indicates the possibility of frustration. But antiferro-magnetic pair energies themselves may not lead to frustration until we couple it to frustrated plaquettes on the lattice. On bipartite lattices even completely antiferro-magnetic pair energies lead to no frustration at all.

Fig. 5.4 shows a few of the smallest triangular and quadrilateral plaquettes within a cubic unit cell of the face-centered cubic lattice. The signs shown are that of the corresponding $J(\widehat{R})$. Given the exponential decay of $J(\widehat{R})$ with $\widehat{R}$, these smaller plaquettes are energetically the most important. With increasing dilution all these plaquettes lose their frustration. This is another phenomenon that competes with formation of a spin-glass phase on dilution.

Finally, we shall make use of the eqn.(4.10) to eqn.(4.11) and eqs. 5.1 to generate

Figure 5.5: The magnetic phase diagram for $\mathrm{Ni_{1-x}Mo_x}$ and $\mathrm{Ni_{1-x}W_x}$

the phase diagram for $\mathrm{Ni_{1-x}Mo_x}$ and $\mathrm{Ni_{1-x}W_x}$. This is shown in fig. 5.5. The collapse of Ni magnetic moment on dilution leads to the paramagnetic phase extending all the way down to T=0K below 88% Ni in $\mathrm{Ni_{1-x}Mo_x}$ and 90% Ni in $\mathrm{Ni_{1-x}W_x}$. For $\mathrm{Ni_{1-x}Mo_x}$ there is a small region around 88% Ni composition where $\mathrm{T}_g > \mathrm{T}_c$. However, we have to remember that these are mean field estimates of T_c and T_g, and the local Ni moment just vanishes here. Therefore the existence of a spin-glass phase in $\mathrm{Ni_{1-x}Mo_x}$ in this corner of the phase diagram is doubtful. So far no experimental report on the spin-glass in $\mathrm{Ni_{1-x}Mo_x}$ is available. For $\mathrm{Ni_{1-x}W_x}$, on the other hand, no such possibility seems to exist and there is no signature of any spin-glass phase in the phase diagram.

5.4 Conclusion

We conclude that Ni based binary alloys behave differently from canonical spin-glasses. In NiMo and NiW, contrary to canonical spin-glass material, as the concentration of Mo or W increases, the *local* magnetic moment on Ni goes to zero. In Ni based alloys there is a competition between the formation of the spin-glass and collapse of both magnetic moment and frustration with dilution and the phase diagram does not indicate the possibility of a spin-glass phase.

Chapter 6

Effect of impurity doping on pristine clusters

[1]

6.1 Introduction

Magnetic clusters and nano-particles are interesting not only because of their possible technological applications, but also because in these systems we can systematically study the effect of diminishing size and dimension on magnetism. Semiconductors with dilute magnetic impurities (DMS) [16] have opened up a possibility of manipulating the spin degree of freedom of electrons through interaction between the local moments of the doping magnetic ions and the spins of the charge carriers of the host

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semiconductors. By definition conventional DMS is a diamagnetic semiconductor which is doped with a transition metal with unfilled d-levels. Content of magnetic transition metal dopant varies from few to several atomic percent. These magnetic dopants add some spins which are coupled with several kinds of dopant−dopant interactions. Ferromagnetic (FM) ground state is result of such couplings in a DMS. Mainly super-exchange and double exchange phenomenon are involved. However, super exchange occurs principally in oxides with oxygen as mediating agent between two dopants, and in double exchange ionic dopants with unequal charges exchange an electron. In both the mechanisms defined previously exchange occur through the bond between the dopants with mediator, where FM in semiconductors is independent of free carriers. Third mechanism, surfaced in last few years, says if crystal has lattice defects then there will be associated electrons which will couple the dopant spins. Still not very much clear. Finally, the DMS, which posses very important mechanism, carrier-induced exchange arises by co-dping $(ZnTe)_{12}$ cluster (wide band gap) with donor or acceptor impurity introduces itinerant electrons or holes in the host wide band gap semiconductor, which are coupled with transition metal magnetic impurity spins. Magnetic and electrical transport properties has strong link with last mechanism, providing the bigger horizon for functionalizing spintronic material. In a majority of DMS materials FM occurs well below the room temperature, this puts a limitation on their practical use. As two important criteria for selecting the most promising materials for semiconductor spintronics are: first, existence of FM at room temperature and second, if application of the material is already known at industrial level. A rapid progress in doping II-VI wide band-gap semiconductors by substitutional impurities has recently been achieved. For example, donor or acceptor doping in case of solids has been performed for ZnSe:I [150] and ZnTe:N [151]. The motivation behind studying the Cr doped $(ZnTe)_{12}$ clusters [24] with either donor or acceptor impurities is to take a step towards the search for room temperature FM and also tuning of the band gap at nano-scale. $(ZnTe)_{12}$ with stable cage structure like fullerene with 8 hexagons and 6 rhombi, have HOMO-LUMO gap of $\sim$2.33 eV. Doping with magnetic material make non-magnetic cluster properties interesting. In this chapter we shall study the effect of impurity co-doping of Cr doped $(ZnTe)_{12}$ clusters with acceptor (N) or donor (I) type of impurities. We shall emphasis over the electronic properties of such co-doped clusters to understand how structural, energetic and magnetic changes take place. Effects of doping on the FM of bulk $Zn_{1-x}Cr_xTe$ have already been studied. Iodine (I), which is found to be an electron dopant, enhances the FM while Nitrogen (N), which is expected to be a hole dopant, suppresses it [152, 23]. These effects have been explained on the basis of the double exchange mechanism [153]. However, carrier-induced FM in $Zn_{1-x}Cr_xTe$ thin films is in doubt because these films are highly insulating. In $Ga_{1-x}Mn_xAs$, on the other hand, FM is enhanced with increased hole concentration. Clusters are finite systems and do not have extended carrier states. In them the situation may be rather different. Here the local environment of the Cr dopant may play an important role in its magnetism. It would therefore be instructive to study such co-doped clusters. To our knowledge a theoretical investigation into impurity co-doping of $(ZnTe)_{12}$ clusters with magnetic dopant is not available.

6.2 Computational Details

We shall use the density functional theory (DFT) based plane wave method implemented in the Vienna *ab initio* simulation package (VASP) [154] with projector augmented waves (PAW) [30, 158]. The PAW formulation is suitable for transition metals. We have used the exchange-correlation energy functional of Perdew-Burke-Erhnzerhof [155]. The 3d and 4s electrons of Zn anc Cr, the 6s and 5p electrons of Te, the 5s and 5p electrons of I and 2s and 2p electrons of N are treated as valence electrons respectively and the wave functions are expanded in plane wave wave basis set with default kinetic energy cut-offs. At the Γ point reciprocal space integrations has been done. We have kept the cluster in a large enough super-cell (a cube with sides of length 15Å) so that there is no effect of interaction between periodic images of the cluster. We have used the Kosugi algorithm [156]. It is a new and efficient iteration method for simultaneously obtaining several eigensolutions of a large real-symmetric matrix by modifying the simultaneous expansion method by Davidson and Liu. The method is basically the Ritz iteration method to correct trial vectors simultaneously using correction vectors. However, the number of the correction vectors determined in each iteration need not be the same as the number of the desired solutions. It is advantageous for the former number to be smaller than the latter when many eigensolutions are sought. We have chosen Kosugi algorithm (special Davidson block iteration scheme) over RMM-DIIS because it optimizes a subset of selected bands simultaneously. This is approximately a factor of 1.5-2 slower than RMM-DIIS, but always stable. We have also applied the Vosko-Wilk-Nusair interpolation [157]. Usually VASP uses the standard interpolation for the correlation part of the exchange correlation functional. The interpolation formula according to Vosko-Wilk-Nusair, usually enhances the magnetic moments and the magnetic energies. Because the Vosko-Wilk-Nusair interpolation is the interpolation usually applied in the context of gradient corrected functionals, it is desirable to use this interpolation whenever the PW(91) functional is applied. The accuracy of Hellman-Feynman forces were set to 0.001 eV/Å- atom. The automatic Monkhorst-Pack $\underline{k}$-mesh generator was used. For transition metals with large magnetic moments, the PAW method seems to be more appropriate (comparable to all-electron calculations) than the ultra-soft pseudo potential(US-PP) method [158]. The magnetization energies are overestimated in US-PP approach and for generalized gradient approximation (GGA) these overestimations are even larger than local-spin density approximation (LSDA). This overestimation is attributed to the dependence of GGA on shape of the wave functions compared to LSDA functionals. However, the difference lies in pseudization of the augmentation charges in US-PP approach. Judicious selection of accurate psuedized augmentation function can make US-PP as good as PAW but on the cost of expensive computations. While in PAW introduction of radial grids avoids any such expenses. The formation energy of the cluster is calculated as,

$$\begin{aligned} E_{\text{form}} &= E[\text{Zn}_\text{p}\text{Te}_{12}\text{Cr}_\text{n}\text{X}_\text{m}] - E[\text{Zn}_{12}\text{Te}_{12}] + n\ \mu_{\text{Cr}} + m\ \mu_{\text{X}} \ldots \\ & \quad \ldots - \begin{cases} (n+m)\ \mu_{\text{Zn}} & \text{case (a) if } p = 12 - n - m \\ n\ \mu_{\text{Zn}} & \text{case (b) if } p = 12 - n \\ 0 & \text{case (c) if } p = 12 \end{cases} \end{aligned} \tag{6.1}$$

where, n and m are total number of magnetic impurity atoms and total number of donor (I) or acceptor (N) type impurities respectively. X represents type of donor or acceptor impurity. E_{form} is the difference of the total energy of doped and pure parent pristine cluster and the chemical potential of dopants. μ_X is the chemical potential of the element X. Formation energy tells us how easily we can construct a stable cluster by adding or substituting atoms. The higher (lower) the formation energy lower (higher) is the probability to form a stable cluster. At a nano-scale it differs from the cluster binding energy which is the energy required to disassemble the cluster into free atoms.

6.3 Results and Discussions

Among the smaller clusters, pristine $(\text{ZnTe})_n$ with n=12 is the most stable with binding energy of 2.07 eV. It has a fullerene-like cage structure as shown by Yadav *et. al.* [24]. Its HOMO−LUMO gap is 2.33eV, wider as compared to the bulk value of 2.26 eV. Increase of band gap with reduced dimension leads to an idea of band gap tuning by impurity doping. In our problem we tried various isomeric structure of the cluster doped with impurities in three different ways, namely

1. **Substitutional**: We replace the atom from the host cluster, preferably at zinc sites. We found Zn site energetically more stable.
2. **Endothermal**: Dopants occupy the center of the cage of the host cluster.
3. **Exothermal**: Absorbed on the surface of the host cluster.

Two type of dopants has been used. Firstly, 3d-transition metal Cr as magnetic impurity and secondly, co-dopants of group V-A (N) as acceptor and VII-A (I) as donor. These dopants and co-dopants have various possible doping positions.

(a) We did the substitutional doping n atoms of Cr and m atoms of X both may be substituted either at Zn-site or Te-site. Substituting Cr, I (or N) or both at Te site is energetically not feasible.

(b) n atoms of Cr may substitute Zn and m atoms of X sit in interstitial or surface positions. The cluster size becomes $24 + m$.

(c) Both n atoms of Cr and m atoms of X may sit in interstitial or surface positions. The cluster size changes to $24 + n + m$.

In the calculations $(ZnTe)_{12}$ cluster either mono-doped or bi-doped with magnetic impurity (Cr) and mono-doped with donor (I) or acceptor (N). $(ZnTe)_{12}$ cluster mono-doped with Cr have only possibility of FM while bi-doping with Cr may favour FM or or anti-ferromagnetism (AFM). Our goes like

1. $(ZnTe)_{12}$ mono-doped with Cr and I or (N).
2. $(ZnTe)_{12}$ bi-doped with Cr and mono-doped with I.
3. $(ZnTe)_{12}$ bi-doped with Cr and mono-doped with N.

In second and third points feasibility of both FM and AFM coupling between Cr atoms has been investigated.

6.3.1 Pristine cluster $(ZnTe)_{12}$ mono-doped with magnetic Cr and donor (I) impurities

We have started with the $(ZnTe)_{12}$doped with magnetic impurity (Cr), latter co-doped with donor (I) impurities. After structural optimization until the Hellman-Feynman forces on each atom are less than the error bar described in the earlier section. The Fig.-6.1 and Table-6.1 describe and illustrate the final geometric structures and their magnetic moments respectively. Each of the structures represents a local minimum in the energy landscape.

Among various isomeric combinations studied, we have considered six different clusters with the lowest energy. They have been arranged in the order of increasing stability and formation energy.

1. MF1-I : a Cr and an I atom substituting two Zn atoms (24 atoms).
2. MF2-I : a Cr atom inside the cage substituting a Zn atom and an I on the surface (25 atoms).

3. MF3-I : a Cr and an I atom kept outside the cage (26 atoms).
4. MF4-I : a Cr and an I atom kept outside the cage but with interchanged positions (26 atoms).
5. MF5-I : a Cr atom on surface and an I inside the cage substituting a Zn atom (25 atoms).
6. MF6-I : a Cr outside the cage and I inside the cage (26 atoms).

MF1-I is the most stable structure with 1.051 eV formation energy while Cr and I have replaced Zn-host from the surface.

In Table-6.1 different structures has been arranged in order of increasing formation energy. The formation energy is minimum when two Zn atoms are substituted by Cr and I from the cage. There is slight bond distortion in the neighbourhood of the Cr atom. In MF1 the Cr-Te distance is reduced approximately by 4-8% from parent pristine cluster, indicating increase in bond strength and accumulation of charges in the Cr-Te bond. The donor (I) impurity mostly sits next to the Cr site but energy minimization process takes I to the center of the cage. There is decrease in local as well as global moment which is due to increased co-ordination of Cr in the cluster. Co-doping with donor (I) gives an extra electron to the cluster . When it delocalizes within cluster, it can jump from one atom to one of its neighbours [11]. This intra-cluster electron hopping reduces the HOMO-LUMO gap. We found that replacing Te sites instead of Zn with dopants was energetically rather unfavorable. Earlier Yadav

Figure 6.1: Zn-atom in gray, Te-atom in shade of dark-yellow, Cr-atom in blue and I-atom in magenta. $(ZnTe)_{12}$ cluster mono-doped with Cr and I. The spin direction at Cr signifies presence of moment at Cr-site. Ordering of optimized structures has been done with increasing formation energy.

				Magnetic Moment		
	$\mathbf{d_{Cr-I}}$	$\mathbf{E_{form}}$	$\mathbf{E_{gap}}$	**Cr**	**I**	**Total**
MF1-I	2.58	1.051	0.69	2.11	-0.03	1.42
MF2-I	2.58	2.373	0.78	3.57	-0.19	3.00
MF4-I	7.98	3.568	0.64	3.35	0.00	2.98
MF5-I	2.70	3.583	0.24	3.11	-0.01	2.87
MF3-I	6.71	3.600	0.54	3.31	0.00	3.04
MF6-I	3.01	4.787	1.44	3.97	0.27	4.25

Table 6.1: The six different clusters of $(ZnTe)_{12}$ mono-doped with Cr and I, described in the text and their characteristic properties. Distance between Cr and I atoms d_{Cr-I} is in Å, E_{form} and HOMO-LUMO gap (smallest of the two spin channels) E_{gap} are in eV and magnetic moments in bohr-magnetons.

et. al.[24] showed the magnetic moment for the structure with minimum formation energy for Cr doped $(ZnTe)_{12}$ to be $3.62\mu_B$. I co-doping reduces this to $1.42\mu_B$ for MF1. Only in the relatively unstable MF6 structure we see the increase in moment. In the bulk, donor (I) doping i.e. introduction of extra electron in $Zn_xCr_{1-x}Te$ is supposed to enhance the magnetic moment on site occupying Cr-atom. In $(ZnTe)_{12}$ cluster donor(I) doping lowers the magnetic moment on site Cr because I has tendency to go to Cr-site consequently donating an electron and reducing number of unpaired spins at Cr-site. This effect is attributed to diminishing size of cluster due to increased surface to volume ratio. We conclude that the local environment of Cr in the doped cluster plays an important role in determining the moment on it.

6.3.2 Pristine cluster $(ZnTe)_{12}$ mono-doped with magnetic Cr and acceptor (N) impurities

We have considered six different optimized structures out of several isomers we have tested in our calculation of $(ZnTe)_{12}$ mono-doped with a magnetic impurity (Cr) and an acceptor (N).

1. MF1-N : a Cr and a N atom substitute two Zn atoms (24 atoms).
2. MF2-N : a Cr atom substituting a Zn atom inside the cage and N on surface (25 atoms).
3. MF3-N : a Cr and a N atom kept outside the (26 atoms).
4. MF4-N : a Cr and a N atom kept outside the cage with interchanged positions (26 atoms).
5. MF5-N : a Cr atom on surface and N substituting a Zn atom inside the cage (25 atoms).
6. MF6-N : a Cr outside the cage and N inside the cage (26 atoms).

Table-6.2 shows the properties of the six lowest possible energy structures of $(ZnTe)_{12}$ mono-doped with Cr and N arranged according to increasing formation

Figure 6.2: Zn-atom in gray, Te-atom in shade of dark-yellow, Cr-atom in blue and N-atom in cyan. $(ZnTe)_{12}$ cluster mono-doped with Cr and I. The spin direction at Cr signifies presence of moment at Cr-site. Ordering of optimized structures has been done in increasing formation energy.

	$\mathbf{d_{Cr-N}}$	$\mathbf{E_{form}}$	$\mathbf{E_{gap}}$	**Magnetic Moment**		
				Cr	**N**	**Total**
MF1-N	3.36	1.874	0.67	3.725	0.240	4.079
MF2-N	1.93	3.374	0.82	3.663	0.093	4.069
MF4-N	3.29	3.752	1.16	4.055	0.075	4.226
MF5-N	6.21	4.121	0.26	3.759	-0.151	3.094
MF6-N	3.80	5.432	0.40	3.670	0.404	4.241
MF3-N	5.63	5.714	0.47	3.706	-0.439	2.982

Table 6.2: The six different clusters of $(ZnTe)_{12}$ mono-doped with Cr and N described in the text and their characteristic properties. Distance between Cr and N atoms d_{Cr-N} is in Å, E_{form} and HOMO-LUMO gap (smallest of the two spin channels) E_{gap} are in eV and magnetic moments in bohr-magnetons.

energies. Fig.-6.2 displays the structurally optimized structures of the six possibilities mentioned in Table-6.2. If we compare Cr-I and Cr-N doped pristine cluster $(ZnTe)_{12}$, the structure of the latter have higher formation energies than the corresponding ones of the former. In MF1-I and MF1-N, Cr-I and Cr-N replaces two Zn atoms on same rhombus. The donor (I) always try to bond with magnetic impurity (Cr) due to its high electron affinity, since Cr needs to saturate in terms of bonding to get to the minimum energy state. The donor impurity I leaves the surface and gets bonded with Cr. But acceptor N remains on the surface and just distorts the rhombus on which it sits and also the nearby hexagon into a distorted rectangle. The

Cr-N distance in comparison to Cr-I is enhanced by 23 % which means there is less charge accumulation between Cr and N. MF1-N forms a comparatively stable cage like structure with slight distortion from $(ZnTe)_{12}$ doped with Cr. Formation energy is minimum for both these clusters in their respective groups. But as we can see, contrary to expectation, the magnetic moment is higher for N-doped $(ZnTe)_{12}$ with Cr as compared to pure Cr doping. Doping with acceptor (N) impurity is expected to suppress magnetism in bulk $Zn_{1-x}Cr_xTe$. N has three unpaired electrons in its valence state. Doping it in the bulk will reduce the number of unpaired electrons and hence magnetism. However, in many similar cases the opposite has been observed [159]. Wang and Zunger [160] showed, using thermodynamic arguments, that if we dope ZnO with Ga and N from a N_2 source, then N centric dopant clusters N-Ga_4 and N-Ga_3Zn which promote n-type doping are favored. On the other hand, doping ZnO with Ga and N from a NO source favors Ga centered dopant clusters Ga-N_4 and Ga-N_3O which promote p-type doping. This explains the surprising observation [161] that the type of doping and therefore enhancement or suppression of magnetism does depend upon the local environment in which the N sits after doping. In our case, in the MF1-N cluster, there is a clustering of N-Cr-Te_3. Since we have structurally minimized geometry, we can argue that the N-Cr-Te_3 clustering is energetically favourable and could be the source of the moment enhancement.

6.3.3 Pristine cluster $(ZnTe)_{12}$ bi-doped with magnetic impurity (Cr) and mono-doped with donor (I) or acceptor (N) impurities

$(ZnTe)_{12}$ bi-doped with magnetic impurity (Cr) and donor impurity (I) leads to several isomeric structures. After structural optimization we have chosen following five cluster compositions in the order of increasing formation energy.

1. F1/AF1-I : Two Cr atoms substituting Zn atoms on opposite vertices of a rhombus and an I atom substituting a Zn atom nearest to one of Cr atoms. The moments on the Cr atoms are either aligned (F) or anti-aligned (AF)(24 atoms).

2. F2/AF2-I : Two Cr atoms substitute Zn and an I substitutes a Te on the same rhombus (24 atoms).

3. F3/AF3-I : Two Cr atoms and an I atom replace three Zn atoms on same hexagon (24 atoms).

4. F4/AF4-I : Two Cr atoms substitute Zn on the same rhombus and an I atom sits outside the cage (25 atoms).

5. F5/AF5-I : Two Cr atoms substitute Zn on opposite vertices of two rhombi with an I atom sitting outside the cage (25 atoms).

The starting structures are such that the Cr atoms may be arranged either in FM or AFM coupling. After structural optimization by limiting the Hellman-Feynman forces below the error bar, the final moments and geometrical structures are described in Table-6.3 and Fig.-6.3 (for FM arrangement of Cr moments) and Fig.-6.4 (for AFM arrangement of Cr moments) respectively.

				Magnetic Moment			
	$\mathbf{d_{Cr-Cr}}$	$\mathbf{E_{form}}$	$\mathbf{E_{gap}}$	$\mathbf{Cr_1}$	$\mathbf{Cr_2}$	**I**	**Total**
F1-I	7.05	1.291	0.12	4.04	3.895	-0.02	7.86
F2-I	2.92	1.564	0.54	4.01	4.01	-0.003	7.92
F3-I	3.23	2.062	0.13	3.59	3.52	-0.02	6.59
F4-I	3.04	4.337	0.51	3.63	3.54	-0.06	6.57
F5-I	7.73	4.674	0.51	3.75	3.12	-0.06	6.51
AF1-I	7.01	1.248	0.45	4.04	-3.897	-0.02	0.197
AF2-I	2.62	1.432	0.42	3.67	-3.76	-0.01	-0.098
AF3-I	4.68	1.965	0.72	3.69	-3.22	-0.01	0.715
AF4-I	2.81	4.140	0.24	3.57	-3.37	-0.07	0.636
AF5-I	7.73	4.666	0.55	3.75	-3.11	-0.06	0.766

Table 6.3: Distance between Cr atoms $\mathrm{d_{Cr-Cr}}$ is in Å, $\mathrm{E_{form}}$ and HOMO-LUMO gap (smallest of the two spin channels) $\mathrm{E_{gap}}$ are in eV and magnetic moments in μ_B.

In Table-6.3, the five energetically minimized structures are arranged according to the lowest (F1/AF1) to the highest (F5/AF5) formation energies. For the FM structures of Cr1-Cr2, the most favourable cluster has a large Cr-Cr distance in which the Cr atoms sit on opposite vertices of two rhombi facing each other across the cluster. The I replaces a Zn in the neighbourhood of one of the Cr atoms. Clusters bi-doped with Cr at Te-sites are s energetically unfavorable. The structures with AFM spin-arrangements have lower formation energies in compared to FM spin-arrangmentss. In the AFM structures the two Cr atoms are not equivalent, as one has an I atom in its vicinity. The moments on the two are therefore not equal in magnitude and we have essentially a ferri-magnetic arrangement. Yadav *et. al.*[24] showed that for Cr doped $(ZnTe)_{12}$ cluster FM stability decreases with increase in distance between Cr-Cr atoms. Doping that cluster with I changes this order. This now depends on at which position the I sits with respect to the Cr atoms. The HOMO-LUMO gaps in these clusters are reduced by I-doping. The donor I contributes an electron to system which is delocalized within it. In case of $(ZnTe)_{12}$ cluster bi-doped with Cr and monodoped with N. We have chosen four lowes energy cluster compositions to describe the low energy states out of several isomeric structures.

1. F1/AF1-N : Two Cr atoms replacing Zn at opposite vertices of two facing rhombi and a N atom replacing a Zn in the neighbourhood of one of the Cr atoms (24 atoms).

2. F2/AF2-N : Two Cr atoms substituting two Zn on same rhombus and a N atom sitting outside the cage (25 atoms).

3. F3/AF3-N : Two Cr atoms and a N atom substituting three Zn atoms on same hexagon (24 atoms).

Figure 6.3: Zn-atom in gray, Te-atom in shade of dark-yellow, Cr-atom in blue and I-atom in magenta. $(ZnTe)_{12}$ cluster bi-doped with Cr and mono-doped with I. The spin direction at Cr1 and Cr2 signifies presence of moment at Cr-site which are FM coupled. Ordering of figures has been done in increasing formation energy.

Figure 6.4: Zn-atom in gray, Te-atom in shade of dark-yellow, Cr-atom in blue and I-atom in magenta. $(ZnTe)_{12}$ cluster bi-doped with Cr and mono-doped with donor (I). Spin-up at Cr-1 and spin-down at Cr-2 couple them AFM aligned. Ordering of optimized structures has been done with increasing formation energy.

4. F4/AF4-N : Two Cr atoms substituting two Zn on same rhombus with a N atom substituting a Zn in an adjacent rhombus (24 atoms).

				Magnetic Moment			
	$\mathbf{d_{Cr-Cr}}$	$\mathbf{E_{form}}$	$\mathbf{E_{gap}}$	$\mathbf{Cr_1}$	$\mathbf{Cr_2}$	**N**	**Total**
F1-N	6.81	2.98	0.23	3.77	3.88	0.14	7.78
F2-N	2.96	3.33	0.59	3.74	3.47	1.58	9.10
F3-N	3.30	3.33	0.39	3.66	3.56	-0.11	6.63
F4-N	2.93	3.57	0.78	3.65	3.65	-0.15	6.65
AF1-N*	6.77	3.08	0.69	3.75	3.63	-0.16	6.73
AF2-N	2.85	3.22	0.24	3.59	-3.51	0.16	1.97
AF3-N	2.58	3.35	0.55	3.36	-3.69	-0.11	-0.63
AF4-N*	2.93	3.57	0.78	3.65	3.65	-0.15	6.65

Table 6.4: Distance between Cr atoms d_{Cr-Cr} is in Å, formation energy E_{form} and HOMO-LUMO gap (smallest of two spin channels) E_{gap} are in in eV and magnetic moments in μ_B. * these structures cannot sustain anti-aligned moments (see text).

We started with $(ZnTe)_{12}$ clusters bi-doped with Cr and mono-doped with N. The Cr-moments are either FM or AFM aligned. After structural optimization and restricting the Hellman-Feynman forces to below the imposed error bar, we obtained clusters whose magnetic structures and geometry are described in Table-6.5 and Fig.-6.7 for FM arrangement of Cr1 and Cr2 moments and Fig.-6.8 for AFM arrangement

Figure 6.5: Zn-atom in gray, Te-atom in shade of dark-yellow, Cr-atom in blue and N-atom in cyan. $(ZnTe)_{12}$ cluster bi-doped with Cr and mono-doped with N. The spin direction at Cr1 and Cr2-sites signifies FM coupling of moment at Cr-sites. Ordering of structures has been done with increasing formation energy.

Figure 6.6: Zn-atom in gray, Te-atom in shade of dark-yellow, Cr-atom in blue and N-atom in cyan. $(ZnTe)_{12}$ cluster bi-doped with Cr and mono-doped with N. Spin direction at Cr-1 and Cr-2 signifies AFM coupling between two Cr-atoms. Ordering of optimized structures has been done with increasing formation energy.

of Cr1 and Cr2 moments respectively. In the Table-6.5 for structures AF1-N and AF4-N we started with AFM coupled Cr moments, whcih after optimization yield FM like Cr-moments. Unlike other cases the AF moment configuration in these structures is not even locally stable. As discussed earlier, same as in case of cluster mono-doped with Cr and acceptor (N), the effect on magnetic moment of these clusters too depend on the environment in which the dopant N sits. In the clusters with least formation energy FM arrangement is preferred and the moments are bolstered above prtistine cluster doped with Cr. The HOMO-LUMO gap is also reduced from the pure pristine cluster significantly. When Cr-Cr distance is minimum, gap is larger in case of N-doping. The Zn or Te atoms surrounding Cr-atoms have very small moments induced on them. Cr-atoms acquire larger moment than bulk due to reduced co-ordination.

6.3.4 Analysis of cluster energy spectra

Fig.-6.7 and Fig.-6.8 shows the energy spectra of the minimum formation energy pristine clusters of $(ZnTe)_{12}$ mono-doped and bi-doped with Cr and mono-doped with I or N respectively. In the left columns, magenta and green-color corresponds to Cr-3*d*, blue-color to I-5*p* and black-color to N-2*p* partial density of states. In the right columns plot belongs to total density of states where magenta-color indicates the spin-up-channel while green-color is down-spin-channels. Fermi-level (E_F) has been set at zero. The top left panels of Fig.-6.7 and Fig.-6.8 show the spectra for the clusters MF1-I and MF1-N respectively. We note that $(ZnTe)_{12}$ mono-doped with Cr along with the I or N impurities, specifically substituting at Zn-sites, changes the electronic structure at the E_F significantly. In the right column, top panel of Fig.-6.7 we see that the occupied 3*d*-levels in the up-channel due to I doping shifts towards higher energies above E_F, i.e. they now become unoccupied. While in the down-spin-channel unoccupied 3*d*-levels were shifted towards lower energies with 5*p*-orbital contribution near E_F. In up-spin-channel just above E_F large number of states are available but in the down-spin-channel HOMO-LUMO gap is larger. The right

Figure 6.7: Energy spectrum of (ZnTe)$_{12}$ cluster with (left column, top) Cr-3*d* and I-5*p* projected spin-resolved DOS and (right column, top) total spin-resolved DOS for Cr-I doping for MF1-I structure; (left column, middle) Cr1-3*d*, Cr2-3*d* and I-5*p* projected spin-resolved DOS and (right column, middle) total spin-resolved DOS for Cr2-I doping for F1-I structure ; (left column, bottom) Cr1-3*d*, Cr2-3*d* and I-5*p* projected spin-resolved DOS and (right column, bottom) total spin resolved DOS doe Cr2-I doping for AF1-I structure.

Figure 6.8: Energy spectrum of $(ZnTe)_{12}$ cluster with (left column, top) Cr-3*d* and N-2*p* projected spin-resolved DOS and (right column, top) total spin-resolved DOS for Cr-N doping for MF1-N structure; (left column, middle) Cr1-3*d*, Cr2-3*d* and N-2*p* projected spin-resolved DOS and (right column, middle) total spin-resolved DOS for Cr2-N doping for F2-N structure ; (left column, bottom) Cr1-3*d*, Cr2-3*d* and N-2*p* projected spin-resolved DOS and (right column, bottom) total spin resolved DOS doe Cr2-I doping for AF2-N structure.

column top panel of Fig.-6.8 shows that doping with acceptor (N) impurity, occupied and unoccupied states both in up as well as down spin-channels are shifted towards lower energies. Band gap is larger in the up-spin channel. Thus it seems possible that, doping appropriately, the gaps can be reduced to a level where either the up or down or both spin-channels become gapless i.e. half-metallic like in nature. The middle left panels of Figs. 6.7 and 6.8 show $(\mathrm{ZnTe})_{12}$ bi-doped with Cr and mono-doped with I or N respectively, with Cr1 and Cr2 having moments with FM alignment. For the case of I-doping the picture is quite like the case mono-doped with Cr, with smaller gap in the up-channel and larger gap in the down-channel. For FM alignment of Cr1-Cr2 in case of N-doping, gaps are almost same. The bottom left panels of Figs. 6.7 and 6.8 show $(\mathrm{ZnTe})_{12}$ bi-doped with Cr and mono-doped with I or N respectively, Cr1 and Cr2 have AFM arrangment. For I-doping in the AF case gap in up-spin as well as down-spin channel are same, while for N-doping the down-channel has the larger gap. If we compare Fig.-6.7 and Fig.-6.9 for FM case where $(\mathrm{ZnTe})_{12}$ bi-doped with Cr, Cr up-3*d* states populate the HOMO-LUMO gap of pristine $(\mathrm{ZnTe})_{12}$. While for the AFM case both the up-3*d* and down-3*d* Cr states are pushed above and below the HOMO-LUMO gap of $(\mathrm{ZnTe})_{12}$ cluster giving significant gaps for both the up and down spin-channels. Referring to Fig.-6.8 we note that with N-doping both N up-2*p* and down-2*p* states populate the HOMO-LUMO gap of $(\mathrm{ZnTe})_{12}$ giving much smaller gaps than that for AFM case with I-doped clusters. Partial and total density of states of I and N doped $(\mathrm{ZnTe})_{12}$ clusters with FM and AFM arrangements of Cr-atoms show difference in moments due to varying hybridization between Cr-3d and I-5p (or N-2p) states which also results into changed chemical bonding of Cr-Te2-I(or N) type of clustering. We can clearly see the difference in majority and minority electrons on integrating partial density of states which significantly differs from one cluster arrangement to another showing substantial change in moment.

			Magnetic Moment
	$\mathbf{E_{g_{up}}}$	$\mathbf{E_{g_{dn}}}$	$\mu_{\mathrm{B}}/atom$
F0	2.73	2.73	0.00
F1	0.74	2.37	3.64
F2	0.69	1.06	1.42
F3	0.28	1.67	2.20
F4	0.16	1.70	3.40

Table 6.5: HOMO-LUMO gaps in the up and down channels in eV, magnetic moments in bohr magneton μ_B.

Fig-6.9 shows the spin-resolved energy spectrum of pristine $(\mathrm{ZnTe})_{12}$ cluster (F0). Fig.-6.10 shows (top pannel from left to right) the energy spectrum in the two spin channels for $(\mathrm{ZnTe})_{12}$ mono-doped with Cr (F1), mono-doped with Cr and co-doped with I (F2), and (bottom pannel from left to right) bi-doped with Cr and co-doped with I (F3) and finally tri-doped with Cr and co-doped with I (F4). A systematic study of the five cases shows that there is considerable change in the spectrum near

Figure 6.9: Total spin-resolved DOS of the pristine $(ZnTe)_{12}$ cluster.

the Fermi level in the up-spin-channel as compared to that in the down-spin-channel with respect to pristine $(ZnTe)_{12}$ cluster. Band gap of up-spin-channel decreases with increasing number of Cr atoms keeping I fixed but in down-spin-channel once the co-doped with I the change is much smaller. The up-spin-channel is fully spin polarized and only one spin type of electrons can pass through it. This is characteristic of half-metallic systems. We have summarized this in Table-6.5. The decrease in moment for Cr-I doping is due to *p*-*d* hybridization in Cr-3*d* and I-5*p* orbitals. In contrast to this similar doping of Cr-atoms and co-doping with an acceptor (N) atom both energy gaps reduce with increased doping of Cr-atom with fixed N. Both up and down spin-channel have only partial spin polarization.

If we wish to synthesize these clusters at room temperature then the HOMO-LUMO gap should be of the order of $E_g \simeq \kappa_B T$ where $T \simeq 300K$. That is, the

Figure 6.10: Total spin-resolved DOS of $(ZnTe)_{12}$ cluster doped with Cr, Cr-I, Cr2-I and Cr3-I. In the top panel(from left to right): $(ZnTe)_{12}$ cluster doped with Cr and CrI respectively and in the bottom panel(from left to right): $(ZnTe)_{12}$ cluster doped with Cr2-I and Cr3-I respectively.

larger HOMO-LUMO gap in the spin channels should be greater than 0.025 eV. In our case we have smaller HOMO-LUMO gap in the up-spin channel in comparison to the down-spin channel and for all configurations this larger gap is more than the above limit. We believe, it may be possible to synthesize the described clusters in the laboratory at room temperatures.

6.4 Conclusion

We have shown that pristine cluster $(\mathrm{ZnTe})_{12}$ doped with magnetic impurities and co-doped with charged impurities changes the energetics as well as the magnetic properties and may stimulate half-metallic nature into it. For clusters doped with two or more Cr atoms, both I or N co-doping enhances magnetic moments. Moreover most stable configurations are those with FM aligned Cr moments. Enhancement of magnetic moments by N co-doping has been attributed to specific cluster environments of the dopants and co-dopants. Unlike the bulk, there are no extended electronic states in the cluster and local environment plays the crucial role here. This is a characteristic of reduced dimensions.

Chapter 7

Conclusion

In this chapter we shall discuss what and how we researched, along with the findings in compared to other methods which were motivation of work done for this thesis.

In the chapter 3 we have developed a first principle method with non-variational approach to calculate ground-state as well as excited-state properties of semiconductor materials and reporting an adaptation of the Harbola-Sahni exchange (HS-EX) potential to the tight-binding linear muffin tin orbital (TB-LMTO) method. There has been several methods available which considerably improve the band gaps within the framework of Kohn-Sham DFT, but why we bank upon HS-EX only? Like the idea of optimized effective potential's (OEP) extension to solids where exact exchange combining with LDA correlation produces reasonably good band gaps in agreement with the experiments. Computational cost involved in exact exchange is high because of inversion of linear response function which makes the computation very cumbersome and heavy. Presently, more accurate methods in first-principle approaches for extended systems exists, the GW approximation (GWA) explains electronic band properties most accurately but computationally GW method is very heavy which restricts it's uses for relatively smaller systems. Keeping in mind we have proposed HS-EX potential an alternative approach to obtaining the exchange-correlation potential. In this approach, the XC-potential is calculated as the work done in moving an electron in the electric field produced by its Fermi-Coulomb hole.

Using HS approach within the exchange (EX) only approximation, where HS-EX is evaluated from Fermi hole, produces ground state as well as excited state properties comparable to EXX and GWA but with considerably reduced numerical efforts. The above physical picture and the vastly reduced computational effort make this approach worth following. With this in mind, we use HS approach to calculate the various properties of materials within TB-LMTO in the atomic sphere approximation (ASA). The electrostatic basis of derivation of the Harbola-Sahni potential allows this non-variational approach to study different excited state properties like band gap. We replaced LDA from TB-LMTO with HS-EX. HS-EX completely cancels the self-interaction part, contrary to LDA. As filled shells contribute more to exchange thus potential obtained using HS-EX is better over LDA, giving more clear picture of shell closing in atoms. Consequently, localizing the valence band and conduction band levels resulting into better excited state properties e.g. band gap. We shall also emphasize on calculated ground state properties like equilibrium lattice parameter, bulk modulus for metals and semiconductors are in very close agreement with the experiments. The clear physical interpretation of HS-EX potential coupled with the fact that it is very simple to implement in numeric calculations leads us to suggest its preferential use over other computationally cumbersome techniques. These new results improve substantially over local density approximation results, bringing them very close to experimental values.

In the chapter 4 and chapter 5 we studied Ni (Nickel) based alloys doped with Mo (molybdenum) and W (tungsten) as non-magnetic impurities. As we know alloys has always been very important because of their industrial use and among them searching for some specific properties make them more interesting e.g. spin glass nature. Both alloy system we studied using augmented space formalism and coherent potential approximation methods does not show any signature of spin glass. In our studies we attribute this to the artifact of mean-field approach followed by us. Fragile moment of Ni in NiMo or NiW alloy which suddenly disappears when Mo or W concentration reaches $\approx$ 13 at.% and $\approx$ 10 at.% respectively. So, we proposed for very careful experimental observation at 11-13 at.% of Mo and at 10 at.% of W as there is a competition between the formation of the spin-glass and collapse of both magnetic moment and frustration with dilution.

In chapter 6 we have studies pristine cluster comprised of Zn (Zinc) and Te (Tellurium) atoms in a most stable cage structure of it type. We have shown that pristine cluster $(ZnTe)_{12}$ doped with magnetic impurities e.g Cr (Chromium) and co-doped with charged impurities e.g. I (Iodine of n-type) and N (Nitrogen of p-type). In our study charged impurities play major role and changes the energetics as well as the magnetic properties and in some of isomers they stimulated half-metallic nature which is very important feature we found in DMS materials. We have doped the clusters with maximum of two magnetic atoms, both I and N has been taken as mono-dopants. We studied both ferromagnetic as well as anti-ferromagnetic properties and ferrmomagnetism came out as most stable configurations in these systems. Enhancement of magnetic moments by N co-doping has been attributed to specific cluster environments of the dopants and co-dopants. Unlike the bulk, there are no extended electronic states in the cluster and local environment plays the crucial role here. This is a characteristic of reduced dimensions.

To conclude on positive node *"The Past: Our cradle, not our prison; there is danger as well as appeal in its glamour. The past is for inspiration, not imitation, for continuation, not repetition."*-annonymous

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