CHAPTER-1
INTRODUCTION:

There are a rich variety of disordered alloys having diverse electrical, magnetic, transport, optical and super conducting properties in nature; these properties make them very useful for technological applications. For understanding these properties knowledge of their electronic structure is essential. In disordered alloys due to the lackness of translational invariance, which is a characteristic of ordered solids, Bloch’s theorem, which greatly simplifies the electronic structure calculation of ordered solids, is inapplicable to these systems. In other words, the standard band theory method developed for ordered solids cannot be applied to disordered alloys.

The main subject of this thesis is the calculations of electronic structure of substitutional random binary alloys which are the simplest kind of disordered systems. In such alloys there exists a lattice structure but each lattice point can be occupied by either of the constituent atoms. Examples of such systems are \( \alpha \)-brass Cu-Zn, Cu-Ge, Cu-Pd, Cu-Ni, Cu-Au, Ag-Pd, Nb-Mo, Cr-V and Cr-Mo etc. Such an alloy will be denoted by \( A_xB_y \), Where \( X \) and \( Y \) are concentrations of \( A \) and \( B \) types of atoms in the alloy, respectively.

A great progress has been made in understanding the electronic structure of the disordered alloys during last three decades, by the application of Coherent Potential Approximation (CPA)\(^{1-3} \). The CPA is a mean field approximation, which for the sake of configurational averaging replaces a disordered alloy \( (A_xB_y) \) by an ordered solid of effective atoms. These effective atoms are determined by using the self-consistent condition
that if an A (B) atom is embedded in this effective medium, the average scattering with respect to the medium is zero i.e.

\[ xJ_A^{\text{CPA}} + yJ_B^{\text{CPA}} = 0 \] (1.1)

where \( J_{A(B)}^{\text{CPA}} \) is atomic scattering operator for an A or B atom embedded in the effective medium. A simpler approximation is average t-matrix approximation (ATA)\(^1\) in which the t-matrix corresponding to the effective atom is

\[ t^{\text{ATA}} = xJ_A + yJ_B \] (1.2)

where \( t_{A(B)} \) is atomic scattering operator for an isolated A(B) atom. Another simple approximation is virtual crystal approximation (VCA)\(^4\) in which the potential corresponding to the effective atoms is assumed to be

\[ \nu^{\text{VCA}} = x\nu_A + y\nu_B \] (1.3)

where \( \nu_{A(B)} \) is the potential of A(B) atom. This approximation is good only when the difference between the two constituents potential is small. Note that all these approximations (CPA, ATA, VCA) are single-site approximations; i.e. they neglect correlated scattering from clusters of atoms. The CPA has been found to be the best single-site approximation for calculation of electronic structure of disordered alloys.

A frequently quoted model in alloy theory is the rigid band model\(^5\). In this model the potentials of the constituent atoms are assumed to be the
same. However, Fermi energy ($E_F$) is adjusted to give the required number of valence electrons ($N^V$) per atom in the alloy as

$$N^V = \int_{-\infty}^{E_F} \rho(E) \, dE \quad \text{(1.4)}$$

where $\rho(E)$ is the density of states (DOS) per atom of the host system. The rigid band model is a crude approximation and does not explain many experimental results. Because of its simplicity, it is frequently used as a first step to get an idea of the electronic structure of the alloy.

There is very large number of interacting electrons ($\approx 10^{23}$) interacting with nuclear potentials in a solid. Therefore, the calculation of energy levels of such a system is a many-body problem, which cannot be solved exactly. However, this problem can be solved to a great degree of accuracy by using the one electron approximation. In this approximation, the many-body problem is reduced to a problem of one electron moving in some effective potential which is determined self-consistently. Muffin-tin approximation is further used to simplify the calculation of this potential. In this approximation the potential is assumed to be spherically symmetric within a sphere and Wigner-Seitz cell as

$$V(\tilde{r}) = \begin{cases} 
V_{A(B)}(r) & \text{for } r < r_m \\
V_{A(B)}^I & \text{for } r > r_m
\end{cases} \quad \text{(1.5)}$$

The $V^I$ is a constant interstitial potential as

$$V_{A(B)}^I = 3 \int_{r_m}^{r_s} V(r) r^2 \, dr \left/ \left( r_{ws}^3 - r_m^3 \right) \right. \quad \text{(1.6)}$$
where $V(r)$ is a spherically symmetric potential, which, it is hoped, will be slowly varying in the region between the muffin-tin sphere and the Wigner-Seitz sphere of radius $r_{WS}$. For a pure A(B) solid, $V_{A(B)}^I$ defines muffin-tin zero, i.e. this constant is subtracted from the potential (1.5) making interstitial potential zero. For the alloy, this is calculated as

$$V_{ALLOY}^I = xV_A^I + yV_B^I$$  \hspace{1cm} (1.7)

Note that muffin-tin potentials are non-overlapping. The muffin-tin approximation is a reasonably good approximation for the potential as can be seen by referring to the book by Moruzzi et al.\textsuperscript{7} Using this approximation, they have calculated various properties such as cohesive energy, bulk modulus, density of states and Fermi energy. They got very good agreements with experimental results and were able to explain general trends. Recent experience with alloys show that the muffin-tin approximation is also a good approximation for metallic alloys\textsuperscript{1-3, 8-14}. The muffin-tin potentials for the constituent atoms are constructed by using the local density approximation (LDA) of the density functional theory\textsuperscript{15}. The potential can be written as\textsuperscript{3}

$$V_{A(B)}(\vec{r}) = V_{Coul}^{A(B)}(\vec{r}) + V_{Nuc}^{A(B)}(\vec{r}) + V_{XC}^{A(B)}(\vec{r})$$  \hspace{1cm} (1.8)

where coulomb, nuclear and exchange-correlation contributions are

$$V_{Coul}^{A(B)}(\vec{r}) = \int d\vec{r}' \frac{\rho_{A(B)}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$  \hspace{1cm} (1.9)

$$V_{Nuc}^{A(B)}(\vec{r}) = -e^2 Z_{A(B)} / r$$  \hspace{1cm} (1.10)
\[ V_{M^{A(B)}}^\alpha(\vec{r}) = \frac{\delta E_{X\cdot C}(\rho_{M^{A(B)}}(\vec{r}))}{\delta \rho_{M^{A(B)}}(\vec{r})} \]  

(1.11)

where \( \rho_{M^{A(B)}} \) is the electron charge density in A(B) cell, Z is the atomic number and \( \Omega \) denotes the integral over the Wigner-Seitz unit cell. Here, \( E_{X\cdot C} \) is the exchange-correlation energy functional, which in the local density approximation is given by\(^{15}\)

\[ E_{X\cdot C}(\rho) \approx \int \rho(\vec{r}) \varepsilon_{X\cdot C}(\rho(\vec{r})) d\vec{r} \]  

(1.12)

where \( \varepsilon_{X\cdot C}(\rho) \) is the contribution of exchange and correlation to the total energy (per electron) in a homogeneous but interacting electron gas of density \( \rho \). For paramagnetic case, von Barth-Hedin form of \( \varepsilon_{X\cdot C} \) is\(^{16}\)

\[ \varepsilon_{X\cdot C}^{(v)}(r_s) = -\frac{0.91633}{r_s} - 0.045F\left(\frac{r_s}{21}\right) \]  

(1.13)

where \( r_s \) is given by

\[ \frac{4\pi}{3}(r_s)^3 = \left(\frac{1}{\rho}\right) \]  

(1.14)

and function

\[ F(x) = (1 + x^3)ln(1 + 1/x) - x^2 + x/2 - 1/3 \]  

(1.15)

Gunnarsson and Lundqvist form of \( \varepsilon_{X\cdot C} \) for paramagnetic case is\(^{17}\)

\[ \varepsilon_{X\cdot C}^{(C)}(r_s) = -\frac{0.458}{r_s} - 0.0333F\left(\frac{r_s}{11.4}\right) \]  

(1.16)

Vosko et.al. form of \( \varepsilon_{X\cdot C} \) for paramagnetic case is\(^{18}\)
\begin{align*}
\epsilon^0_{\text{ex}}(r_S) &= \frac{-0.91633}{r_S} + A \left[ \ln \left\{ \frac{x^2}{X(x)} \right\} + \frac{2b}{Q} \tan^{-1} \left[ \frac{Q}{2x + b} \right] \\
&\quad - \frac{bx_0}{X(x_0)} \left[ \ln \left\{ \frac{(x - x_0)^2}{X(x)} \right\} + \frac{2(b + 2x_0)}{Q} \tan^{-1} \left[ \frac{Q}{2x + b} \right] \right] \right)
\end{align*}

where

\[ X(x) = x^2 + bx + c, \quad Q = \left(4c - b^2\right)^{1/2} \quad \text{and} \quad x = (r_s)^{1/2} \quad (1.17) \]

Here, \( A = 0.0621814, \ x_0 = -0.10498, \ b = 3.72744 \) and \( c = 12.9352 \)

It has been seen that use of different exchange-correlation does not give large differences in the calculation of various properties\textsuperscript{15}. For example differences in cohesive energies in Li, Na, K and Rb were found to be less than 8 mRy\textsuperscript{18}. Because Moruzzi et al\textsuperscript{7}, have found good agreement between theory and experiment for several metals including Cr and Al, using von Barth-Hedin form of the exchange-correlation potential. Therefore, We have used this form in our calculations for above reason as will be discussed in detail in Chapter 3.

The CPA theory has been very successful as a single-site approximation to calculate the electronic structure of random substitutional disordered alloys during last thirty years. This theory when applied to muffin-tin model of disordered alloys, is known as Korringa-Kohn-Rostoker–CPA (KKR-CPA) theory\textsuperscript{1}. In the perfect crystal limit, the KKR-CPA theory reduced to the standard KKR band theory\textsuperscript{1}. In earlier stage of application, potentials \( V_A \) and \( V_B \) were not determined self-consistently. In the most sophisticated application of the KKR-CPA, within the framework of the local density approximation \( V_A \) and \( V_B \) are determined self-consistently described in Chapter 2. This fully charge-self-consistent
KKR-CPA theory is a first principle parameter-free theory of the electronic structure of random alloys.

The outline of the thesis is as follows. In Chapter 2, we will present the brief formulation of charge self-consistent KKR-CPA. Section 2.1 presents the introduction of the chapter. In section 2.2, we derive the KKR-CPA equation in multiple scattering formalism. In section 2.3, we present the charge self-consistent KKR-CPA method.

In Chapter 3, we will apply the charge self-consistent KKR-CPA method in calculation of electronic structure of Cr-Al alloy. Section 3.1 present the introduction of the chapter, we will give the computational details of our calculation in section 3.2. The Green’s function method is used to calculate charge densities of constituent atoms in the alloy. The flow chart of charge self-consistent KKR-CPA is also given in this section. The mixing scheme for CPA and charge self-consistency loop are discussed. The study of charge self-consistent potentials, charge densities and the density of states as a function of Cr concentration in the CrₙAlₙ⁺ for X= 0.95, 0.85 and 0.75 are given in section 3.3. In this section we also compare the results of charge self-consistent KKR-CPA density of states with the density of states using Cr-based rigid band model. We have chosen von Barth-Hedin exchange correlation potential to calculate the new crystal potentials of constituent atoms in the alloy. For Cr-Al alloy, we compare the results of density of states calculated by using the charge self-consistent KKR-CPA method with the X-ray photo spectra experimental results. We find that there is a very good agreement between our results and experimental results for different concentration of alloy. It is also found that Cr-based rigid band model fails
in the calculation of electronic structure of Cr-Al alloys. In the final section 3.4 we summarize our main conclusions.

In Chapter 4, we apply the KKR-CPA to the s-phase shift double peak semicircular model. Section 4.1 provides an introduction of this chapter. In section 4.2 we discuss the s-phase shift semicircular model in the KKR framework. In section 4.3, the path operators and t-matrices for the s-phase shift double peak semicircular model is derived. In section 4.4, formula for the KKR-CPA density of states to the s-phase shift double peak semicircular model is derived. In section 4.5, we present the CPA equation and computational details for this model with programme. In section 4.6, we discuss our results for s-phase shift double peak semicircular model. In section 4.7, we summarize our main conclusions.

Finally, in Chapter 5, we give the summary of the achievements of the present work. Some suggestions for further improvements are also given and some possible remaining problems are mentioned.