A Study of the Electronic Structure of Spin Glass Alloys

A dissertation submitted for the
partial fullfillment for the
degree of Master of Philosophy

April, 1999
Dhaka University, Dhaka

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AIN-UL HUDA
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I like to dedicate this thesis paper to the following kind persons, who allowed me to work with them as their co-author in some research papers published in different International Journals.

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Publications

1. Augmented Space Recursion of Spectral Functions for disordered binary alloys: some comments International Journal of Modern Physics **B,** vol. 11. No. 31(1997), 3715-3721

2. A study of the Spectral Functions and Complex Band Structures for the Disordered Binary Alloys: AgPd and AuFe, International Journal of Modern Physics **B,** vol. 11 No. 31(1997), 3703-3713

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Contents

Abstract

In this work, we have studied the electronic structure of spin glass alloys, i.e. the binary alloys composed of the transition metals (Ni, Fe, Co) and noble metals (Au, Ag, Cu). We have calculated the density of states of the spin glass alloys with different combination of them such as 25% of transition metals with 75% of rare earth metals, 50% of the former and 50% of the latter, and similarly 75% and 25% combination. For this purpose, we use the TB-LMTO packages together with augmented space recursion technique. We developed codes for calculating the fermi energy, total energy and magnetic moments of the alloys from the density of states data. We present the DOS of above mentioned binary alloys, magnetic moments and totol energy of the system. We found that magnetic moments decreases almost linearly with concentration of non magnetic components. We also obtained a linear variation of energy with concentration. It can be concluded that there are no short ranged ordering in these concentrations.

Chapter One
INTRODUCTION

1.1 The problem of structure of Matter

The microscopic description of the physical and chemical properties of a material system is a complex problem. In general, we have a collection of atoms interacting with forces that derive from some potential field. The ensemble of particles may be isolated (molecules and clusters), extended (Solids, surfaces, wires and liquids), or a combination of both (molecules in solution). However in all cases we can unambiguously describe the system by a number of nuclei and electrons interacting through Coulombic (electrostatic) forces. Formally we can write the hamiltonian of such a system in the following general form:

$$\hat{H} = -\sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\nabla_I^2 + \sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{2}\sum_{I=1}^{P}\sum_{J\neq I}^{P}\frac{Z_I Z_J}{|R_I - R_J|} + \frac{e^2}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|r_i - r_j|} - e^2\sum_{I=1}^{P}\sum_{i=1}^{N}\frac{Z_I}{|R_I - r_i|} \qquad (1.1)$$

where $R=\{R_I\}$, $I=1.....P$, is a set of P nuclear coordinates, and $r=\{r_i\}$, $i=1.....N$, is a set is a set of N electronic coordinates. Z_I and M_I are the P nuclear charges and masses respectively. Electrons are fermions, so that the total electronic wave function must be anti symmetric with respect to exchange of two electrons. Nuclear can be fermions, bosons or distinguishable particles, according to the particular

problem under examination. All the ingredients are perfectly known and, in principle, all the properties can be derived by solving the following Schrodinger equations;

$$\hat{H}\psi_i(r,R) = E_i\psi_i(r,R) \tag{1.2}$$

However, only in a few cases a complete analytic solution of equation (1.2) is available, and numerical solutions are also limited to a very small number of particles. There are several features that contributing to this difficulty. First, this is a multicomponent many body system, where each component (each nuclear species and the electrons) obeys a particular statistics. In other words, the full Schrodinger equation can be easily decoupled into a set of equations so that; in general, we have to deal with 3P+3N coupled degrees of freedom. Using the many body theory, rather than using such a huge number of Schrodinger equation we can deal with stationery Schrodinger equation of an N-electron system

$$\left[-\frac{\hbar^2}{2m}+V(r)\right]\psi(r_1,r_2,r_3.....r_N) = E\psi(r_1,r_2,r_3.....r_N) \tag{1.3}$$

(alongwith the appropriate boundary conditions), which allows us to take into account the interactions among the electrons, among the nuclei and between the electrons and nuclei. It is not hard to realize that the solution of the Schrodinger equation under an all inclusive form of potential, V, is by no means an easy task. One has to invoke approximations to get approximate solutions. The exact wavefunctions containing the interactions and motions of say Avogadro's number of particles could hardly be presented in a recognizable from to yield any useful information. But with the invent of fast computers and also the innovative ideas of the leading physicist leads the electronic structure calculation to a new era and it can

be pre-assumed that it will replace the costly experimental verification of experimental electronic calculation in future.

The Electronic Structure Calculations are important for the following purposes:

1. Verifying large amount of experimental data in material science, solid state electronic devices, Ultra Violate and X-ray synchrotron Spectroschopies etc.
2. Extracting parameters (U, Δ , etc.) of model hamiltonians used for studying strongly correlated systems and phenomena.
3. Predicting material properties and their trends prior to actual experiment, which may be prohibitively difficult or expensive (e. g. behaviors of solids under extreme conditions: ultrahigh pressure, ultra low temperature, and high magnetic field)
4. Search for new materials (multi-layers, nanostructures etc.) with novel structural, electronic, magnetic, opto-electronic, photonic, superconducting properties.

1.2 Electronic structure calculations: brief history

Computer experiments plays a very important role in science today. The electronic structure calculation became so powerful with the advent of the Computer. The electronic structure calculation was originated from the Density Functional Theory by Hohenburg-Kohn-Sham in 1965, which was one of the three breakthroughs of its history. In the Density functional theory, the ground-state properties of an interacting many-electron system in an external potential v(r), using the particle density, n(r), as the basic variables. Thus we shall be concerned with system which obey the many-body Schrödinger equation. The complicated and

unmanageable many-electron problem was transformed to an effective one-electron problem, which in turn can be solved within the so-called local density approximation. The local density approximation is applicable for a system whose density n(r) is a slowly varying function of position.

The second breakthrough came from the Linear Band Structure Method introduced by O. K. Andersen in 1975. The linearization of Muffin Tin Orbital and Augmented Plane Wave are ideal tools for first principles determination of material properties. These tools can effectively evaluate the electron density n(r) and total energy E_{tot}, two most fundamental ground state quantities, from which cohesive and other properties can be derived. Moreover the tight binding linear version can effectively handle the ordered and disordered solids, which is the main theme of this thesis paper.

Car-Parrinello (1995) Molecular Dynamics-Density functional theory was the third breakthrough of electronic structure calculations. Ab-initio Molecular Dynamic simulation of atomic aggregates where forces acting on atoms are evaluated within the framework of Density Functional Theory. Numerical experiment of simulated annealing allows one to track the trajectory of motion with temperature; and hence find the global minimum in Born-Oppenheimer total energy surface, or even some of the metastable local minimum.

1.3 The One Electron Problem

One of the approaches which is usually adopted in the present day first principles electronic calculations is the so called one-electron or single-particle

picture. In this case one can assume that it is meaningful to study the behaviour of a single electron in an average field V(**r**), produced by other electrons and nuclei. The Hohenburg-Kohn-Sham (1964, 1965) density functional formalism provides a self consistent prescription for calculating the one electron potential V(**r**), that can be constructed from the electron density alone and which includes important quantum mechanical effects of exchange and correlation. In practice, one use the local density approximation for the exchange correlation part V_{xc} which at a given position depends only on the local charge and spin-charge densities. The total potential V(**r**) is a sum of the external potential $V_{ex}(\mathbf{r})$, the electron-electron coulomb repulsion $V_c(\mathbf{r})$ as seen by a given electron due to the charge distribution in the system and the exchange correlation part V_{xc}. One solve for one electron approximation

$$\left[-\nabla^2 + V(r)\right]\varphi_j(r) = E_j\varphi_j(r) \tag{1.4}$$

(in atomic Rydberg Units) for one electron moving in the three-dimensional condensed-matter potential V(**r**). In that case the charge density

$$\rho(r) = \sum_{j \in occ} \left|\varphi_j(r)\right|^2 \tag{1.5}$$

is obtained in such a form that it can be used to construct the input potential V(**r**) for a next iteration towards charge (and spin) self-consistency. The main problem is here to solve *Poisson's equation,*

$$-\nabla^2 V_c(r) = 8\pi\left[\rho(r) - \sum_R Z_R\delta(r_R)\right] \tag{1.6}$$

for the electronic and proton charge densities. **r** are the electronic and **R** the nuclear positions. The relative electronic positions are $\mathbf{r_R}=|\mathbf{r}-\mathbf{R}|$ with the distances from the nuclei. After self consistency has been achieved for the potential one can proceed to calculate all physical properties of interest with it. Thus the calculation of the electron structure reduces to the self consistent solution of the Hohenberg-Kohn-Sham equations.

1.4 Different Methods of One Electron band Structure Calculation

For crystalline solid, the self consistent solution of Hohenberg-Kohn-Sham Equation is more complex. In that case, one has Bloch periodicity and the computational effort can be reduced by performing the calculation in reciprocal space for determining the band-structure or energy dispersion relation, E (**k**) for a **κ** vector in the first Brillouin zone of the reciprocal lattice. The various existing band structure methods can be broadly categorized as:

(a) ***Fixed basis set methods***: here the wavefunction is determined as an expansion in some set of fixed basis functions, like linear combination of atomic orbitals (LCAO), plane wave, Gaussian orbitals etc.

(b) ***Partial wave method***: here the wave function is expanded in a set of energy and potential dependent partial wave like the Wigner-Seitz cellular method, the augmented plane wave method (APW) and the Korringa-Kohn-Restoker (KKR) method.

Methods using fixed basis-functions:

In a fixed-basis method, such as LCAO method the Schrödinger equation is solved by seeking the wave function $\psi_j(\mathbf{r})$ as an expansion,

$$\sum_G \chi_G(\mathbf{r}) u_{G,j} \approx \psi_j(\mathbf{r}) \tag{1.7}$$

in some energy-independent set {G} of basis functions χ_G . The coefficient $u_{G,j}$ and the one electron energies E_j are then obtained with the help of the Rayleigh-Ritz variational principle as the eigenvectors and eigenvalues of the algebric eigenvalue problem

$$(\mathbf{H} - E\mathbf{O})\mathbf{u} = 0 \tag{1.8}$$

With the Hamiltonian matrix

$$\mathbf{H}_{G',G} = \left\langle \chi_{G'} \middle| -\nabla^2 + V \middle| \chi_G \right\rangle \tag{1.9}$$

and the overlap matrix

$$\mathbf{O}_{G',G} = \left\langle \chi_{G'} \middle| \chi_G \right\rangle \tag{1.10}$$

The essential disadvantage of the classical fixed basis-sets is that they must be large in order to be reasonably complete. Atomic orbital-or *Gaussian* sets, for instance, must include several radial functions per atom and angular momentum, that is, the index n takes several values. For example, a compound containing 99 sodium atoms and one uranium atom per cell, the number of plane wave needed in the basis is the same as had all atoms been uranium and hence unmanageable. On the other hand, when their size can be managed, plane wave method is the simplest to work with.

Methods using partial waves and the muffin-tin approximation

An important simplifying feature of the problem with an all-electron (deep) potential is that inside the atoms where the "Kinetic energy", ε_j=v(r), is numerically large and the wave-functions varied rapidly, the potential is essentially spherically symmetric. The muffin tin approximation (MTA) retains only this part of the potential inside atom-centered muffin spheres and as a consequence, Schrödinger equation become separable in this part of space. The potential around the atomic site

$$V_{MT}(r) = V_i(r_i) + \sum_R V_R(r_R) \approx V_0 + \sum_R V_R(r_R) \qquad (1.11)$$

where $V_R(r_R)$ and $v_R(r_R) = V_R(r_R) - V_0$ are spherical symmetric inside the sphere of radius S_R centered at **R** and vanishes outside and $V_i(r_i)$ takes the constant value V_0 (the muffin tin zero (MTZ)) in the interstitial region and vanishes outside. This kind of potential is designed to facilitate matching condition of the wave function from cell to cell through the assumption that the electron moves freely between spheres with a constant wave number $\kappa = (\varepsilon - V_{MTZ})^{1/2}$. This assumption is valid only if the wavelength $2\pi/\kappa$ is large compared to the thickness of the interstitial region i.e. the distance $S_E - S_{MT}$. This wavenumber criterion is satisfied for all closed packed solids. For such potential, it is possible to solve Schrodinger equation exactly in terms of energy-dependent partial wave expansion

$$\psi_j(r) = \psi_i(\varepsilon_i, r_i) + \sum_{RL} \varphi_{RL}(\varepsilon_i, r_R) c_{RL,j} \qquad (1.12)$$

the partial wave

$$\varphi_{RL}(\varepsilon, r) \equiv \varphi_{RL}(\varepsilon, r_R) Y_L(r_R) \qquad (1.13)$$

for the MT well of type **R**, the angular momentum L≡lm and the energy ε has a radial part which is easily obtained by integrating the corresponding radial Schrödinger equation,

$$\left|r\varphi_{RL}(\varepsilon,r)\right|'' \equiv \left|V_R(r)+l(l+1)r^{-2}-\varepsilon\right|r\varphi_{RL}(\varepsilon,r). \qquad (1.14)$$

In practice, the radial scalar relativistic Dirac equation is solved rather than the Schrödinger equation. The wave function in the interstitial region $\psi_i(\varepsilon_i, \mathbf{r_i})$, may be obtained by a plane wave expansion or by analytic continuation of the partial wave expansion from a near site. A partial wave is taken to vanish outside the sphere and an interstitial function is taken to vanish outside the interstitial region. The main drawback of the methods based on partial wave is that, for the evaluation of the one-electron energies, it involves the solution of a secular equation of the form

$$\mathbf{M}(\varepsilon).u_j = 0$$

with a secular matrix $\mathbf{M}(\varepsilon)$ which has a complicated non-linear energy dependence. Even for moderately sized matrices this requires orders of magnitude more computation in the solution of an eigen value problem with the same matrix size. In general, the partial wave methods provides solution of arbitrary accuracy for the MT potential and in the case of closed-packed systems, this makes the far more accurate than any traditional fixed basis method.

1.5 Current Status

In the previous sections we have discussed the different methods of calculating the electronic structure calculations. Although the partial wave methods are accurate tools for 1-electron band structure method, these cost expensive computations.

In course of the last decade or so the LMTO method was introduced and developed by OK Andersen and coworkers and emerged as very convenient and accurate scheme for studying the electronic structure of solids within the density functional formalism. The LMTO is physically transparent and computationally convenient and indeed possesses a number of very attractive features.

Firstly, the method is cast in the form of standard algebraic eigenvalue problem and therefore has the speed required in a self-consistency calculation which often has to run through a number of cycles.

Secondly, like all other linear methods, such as the linearized augmented plane wave method (LAPW) or, the linearized augmented spherical wave method (LASW) it is an approximate method but it has the required accuracy over a chosen energy window.

Thirdly, it employs the same type of basis functions for all elements in the periodic table thus leading to a conceptually consistent description of physical trends throughout the periodic table.

Fourthly, as indicated before the method is physically transparent and can be used in several levels of approximations.

We have also employed the recursion method of Haydock (1980), Heine and Kelly (1980) in this thesis. This method calculate the local electronic structure by evaluating the various diagonal elements of the real space Green Function and can supply information of charge densities, local bond order, magnetic moments, band energy etc. The method does not require lattice periodicity and can be applied to amorphous systems. defects in crystals and random alloys. and is useful even for periodic solids with very large number of atoms per unit cell. The computational and approximation schemes are well developed and calculation labour is moderate.

We have also used the augmented space formalism to the problem of expressions for configuration averaged Green function and other related quantities mainly of substitution binary alloys.

The augmented space formalism was first introduced by Mookerjee and thercafter developed by Mookerjee and coworkers is a method of configuration averaging a function of a set of random variables. The disordered medium in the real Hilbert space is transformed to a larger Hilbert space called the augmented space and various approximation schemes are introduced therein.

1.6 Present Work

In this thesis, we present the Density of states of the spin glass alloys. The density of states (DOS) for electrons in a band yields the number of states in certain energy range. If $g(\varepsilon)d\varepsilon$ denotes the number of electron states per unit volume in the energy range ε, $\varepsilon+d\varepsilon$, then

$$g(\varepsilon)=\frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}E^{1/2} \tag{1.15}$$

It is evident that g(ε) is intimately related to the shape of the energy contour and hence the band structure. The complexities of this structure are reflecting in the form taken by g(ε). Using the density of states we can calculate the Fermi Energy, Magnetic moment and the Total energy of the alloy.

The fermi Energy satisfy the condition,

$$\int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon = n \tag{1.16}$$

where n is the number of electron.

Substituting value of g(ε) of equation (1.15) we obtain,

$$\varepsilon_F=\frac{\hbar^2}{2m^*}(3\pi^2 n)^{2/3} \tag{1.17}$$

The order of fermi energy is few electron volts.

The total energy of the binary alloys can be given by the following equations:

$$E = E_{kin} + E_{mad} + E_{pot} \tag{1.18}$$

where

$$E_{kin} = \sum_{j \in occ} E_j - \sum_R \int_0^S V_R(r)\,\rho_R(r)(4\pi r^2 dr)$$

$$E_{mad} = \sum_R \sum_{R'} Z_R Z_{R'} |R-R'|^{-1}$$

$$E_{pot} = \sum_{0}^{s}(4\pi r^2 dr)\,\rho_R(r)\left\{\varepsilon_{xc}\left|\rho_R(r)\right| - 2z_R / r + \int_{0}^{s}(4\pi r'^2 dr')\,\rho_R(r')|r-r'|^{-1}\right\}$$

Here the charge density $\rho_R(r)$ within the muffin-tin sphere is constructed out of the wave functions of the occupied states: $\rho(r) = \sum_{j\in occ} q_j|\varphi_j(r)|^2$ spherically averaged inside the muffin tin.

We describe the basic features of the LMTO method in Chapter-2. We introduced the Augmented Space formalism in Chapter-3. In the same Chapter, we discussed the basic features of the recursion method developed by Haydock and the formalism to use the recursion method in Augmented Space.

An Introduction to Spin Glass Alloys is given in Chapter-4 and the results and discussion are presented in the Chapter-5.

Chapter Two

Linearized muffin tin orbital method

2.1 Introduction

According to Born-Oppenheimer [1927] approximation, the time scale associated to the motion of the nuclei is usually much slower that associated with electron. In fact the smaller mass of the electrons as compared to that of the protons (in the most unfavorable case) is about 1 in 2000, meaning that their velocity is much larger. the electrons are light particles which in their motion immediately follows the motion of nucleus. So one first solves for the electronic structure and at later stage use the energy of the electronic ground state obtained as a function of nuclear positions as a potential energy for the motion of nuclei. The different approach of electronic structure calculations is discussed in the previous section.

In course of the last decade or so the Linearized Muffin Tin Orbital method introduced by Andersen and coworkers [1975] has emerged as a very convenient and accurate scheme for studying the electronic structure of solids within the density

functional formalism. In this chapter we shall describe the formalism behind the linearized muffin tin orbitals method **(LMTO).**

2.2 Schematic Description of the LMTO method

The objective of the method is first to solve the Schrödinger equation of the one electron problem. The potential V(**r**) is characteristic of an infinite periodic solid and is often approximated by a collection of muffin tin well potential. Thus,

$$V(r) = \sum_R V_{MT}(r_R) + V_0 \qquad (2.1)$$

Here $r_R = r - R$ *and* $V_{MT}(r_R)$ is spherically symmetric about R in a sphere of radius S and zero outside. V_0 is the flat potential in the interstitial region alone.

Then one has to construct the charge density is constructed as

$$n(r) = \sum_j^{occ} \left|\psi_j(r)\right|^2 \qquad (2.2)$$

and in the same time use it to find the potential $V(r)$ for the next self-consistency iteration by solving the Poisson equation for the Hartree part and by using the local density description for the exchange-correlation part. After achieving the self-consistency for the potential, with its help various quantities of physical interest can be evaluated such as the total energy of the electrons and the nuclei in the Born-Oppenheimer approximation, the pressure, the magnetic moment etc. The one-electron states are significant for physical and chemical properties and range from

the energy where an electron can tunnel from one atom to the next upto the Fermi level. The relevant energy range thus extends approximately half a rydberg on either side of the potential energy maximum and the latter is about a rydberg below the Fermi level.

The fixed basis set methods used the LCAO, the plane waves and the Gaussian orbital pseudopotential methods Schrodinger equation is solved by expanding the wave functions in the fixed basis as ,

$$\sum_{R_n, L} \chi_{R_n, L_{ij}} u_{R_n, L_{ij}} \approx \psi_j(r) \tag{2.3}$$

where $\{\chi\}$ is the energy independent basis set. The coefficient and the one electron energies E_js are obtained with help of the Rayleigh-Reitz variational principle as the eigenvalues and eigenvectors of the algebraic eigenvalue problem

$$(H - E_j O) u_j = 0 \tag{2.4}$$

The procedure discussed above is highly convenient and is employed in the MTO method with the hamiltonian matrix

$$H_{R'_n, L'; R_n, L} = \left\langle \chi_{R'_n, L'} \middle| (-\nabla^2 + V) \middle| \chi_{R_n, L} \right\rangle \tag{2.5}$$

and the overlapping matrix

$$\mathbf{O}_{R'_n, L'; R_n, L} = \left\langle \chi_{R'_n, L'} \middle| \chi_{R_n, L} \right\rangle \tag{2.6}$$

For crystal structure the above basis functions can be transferred into Bloch functions

$$\chi = \sum_{T} \chi_{R_n L}(r - R - T)\exp(ikT) \tag{2.7}$$

so that for each Bloch vector the matrix obtained is of convenient size. In (2.7) the vector R runs over the atoms in the primitive cell only, T are the translational vectors of the lattice, and the Bloch function is normalized to unity in the primitive cell. Since the atomic orbitals or Gaussian sets must include several radial functions per atom and angular momentum component, the plane waves needs exceedingly large basis sets for material having other than broad bands.

In the partial wave methods, since the muffin tin is considered to be spherically symmetric about the atomic sites in the muffin tins, the Schrödinger equation is separable in radial and angular parts. In terms of partial wave expressions,

$$\psi_j(r) = \psi_{\text{int},j} + \sum_{RL} \phi(E_j, r_R) C_{RL,j} \tag{2.8}$$

where $\psi_{int,j}$ is the interstitial part of the wave function.

The radial part for the partial wave $\phi_{RL}(\varepsilon, \boldsymbol{r})\ Y_{LM}(\boldsymbol{r})$ for the MT well at $\boldsymbol{R}$ may be obtained by numerically integrating the corresponding Schrodinger equation.

The wave function in the interstitial region may be obtained by a plane wave expansion or by an analytical continuation of the partial wave expansions from a

near site. It can be assumed that the partial wave vanishes outside its own sphere and the interstitial function vanishes outside the interstitial region i.e. inside the spheres. The partial waves are functions of energy variable E and one electron energies are those E_j for which coefficients c_j can be found such that the partial wave expansions from various spheres join continuously and differentiably together. The way this matching condition are formulated differs algebraically from one method to another, but in general the result is a set of linear homogeneous equations

$$M(E)c_j = 0 \qquad (2.9)$$

having a secular matrix $M(E)$. This matrix in contrast to the $(H\text{-}EO)$ matrix of the earlier method has a complicated non-energy dependence and the procedure for determining the one electron energies and the corresponding coefficients c_j is by first tracing a root E_j of $M(E)$ and then solving the linear homogeneous equations by substituting $E = E_j$. Even for moderately sized matrices this require an order of magnitude more computation than the eigenvalue method. The partial wave methods have a number of positive sides; the solution provided by them for the MT potential is highly accurate and for closed-packed, high point symmetry structures they are in general more accurate than the corresponding fixed basis methods. The partial waves apply equally well to any atom in the periodic table.

Now let us illustrate the question of incorporation of energy dependent partial waves in an energy independent basis set with a simple model of bonding in a diatomic molecule. We shall employ only one energy independent orbital $\chi_L(\mathbf{r})$.

In an LCAO type description the bonding and antibonding states are approximately expressed as

$$\psi_A^B(r) \approx \chi_L^\alpha(r) \pm (-1)^l \chi_L^\alpha(r-R) \tag{2.10}$$

where the meaning of the superscript α will be clarified soon and their energies may be estimated from equation (2.4)

Inside the atomic spheres, the exact states can be expressed by partial wave expansions,

$$\psi_A^B(r) = \sum_L \phi_L^\alpha(B,r) h_L^\alpha \tag{2.11}$$

where the subscript indicates that we have included the energy dependence of the expansion coefficients h_L^α is arising from the choice of the orbitals in the normalization of the partial waves.

The function χ_L should be augmented by $\phi_L(E,r)$'s and if we augment the tail $\chi_L(r-R)$ by

$$\frac{1}{2}(-1)^{l'} \sum_{L'} \left| \phi_{l'}^\alpha(B,r) - \phi_{l'}^\alpha(A,r) \right| Y_{L'}(\hat{r}) h_{L'}^\alpha$$

and the head $\chi_L(r)$ by

$$\frac{1}{2} \left| \phi_L^\alpha(B,r) + \phi_L^\alpha(A,r) \right| Y_L(\hat{r})$$

We may approximately obtained equation (2.11) from (2.10). Now the tail function are therefore augmented by the energy derivative functions

$$\dot{\phi}_L(E_\nu,r) \equiv [\partial\phi_l(E,r)/\partial E]_{E=E_\nu} \tag{2.12}$$

evaluated at some E_ν at the centre of interest. The heads are similarly augmented by an appropriate linear combination of $\phi_l(E_\nu,r)$ and $\dot{\phi}_{RL}(E_\nu,r)$. The augmented orbital thus takes the form

$$\chi^{\alpha}_{RL}(r_R) = \chi^{\alpha,i}_{Rl}(r_R) + \phi^{\alpha}_{RL}(r_R) + \sum_{R'L'}\sum \dot{\phi}^{\alpha}_{RL}(r_R)h^{\alpha}_{RL,R'L'} \tag{2.13}$$

The augmented orbitals may be used as basis functions in a variation calculation. For closed-packed systems the potential is spherically symmetric for a large volume around each atom and one may thus choose the augmentation spheres as large as possible either as touching muffin-tin spheres or as slightly overlapping, space filling Wigner-Seitz spheres.

For such large augmentation spheres the radial degree of freedom is sufficiently described by the ϕ, $\dot{\phi}$ augmentation only (i.e. only one orbital per lm value and thus a minimal basis set is obtained in this manner). The Taylor series of the radial function truncated after the first two terms

$$\phi_l(E,r) \approx \phi_l(E_\nu,r) + \dot{\phi}_l(E_\nu,r)(E-E_\nu) \tag{2.14}$$

can describe fairly well the change of radial wave function throughout the atomic sphere ($r \leq S$).

Further since the ϕ, $\dot{\phi}$ augmentation are used in the variational scheme, the error of the radial wave function which is of the second order in ($E-E_v$) gives rise to errors in the fourth order in ($E-E_v$) in the energy bands. We thus see that to set up the linear muffin tin orbital method one starts with the muffin tin orbitals that are the solutions of Helmholtz equation

$$\left(\nabla^2 + \kappa^2\right)\psi = 0 \tag{2.15}$$

as the envelope set. Each linear method use a characteristic envelope set. The chosen envelope set should be reasonably complete in the interstitial region. After a set is chosen each basis function is then expanded in spherical harmonics about all atomic sites **R** and each component is continuously and differentiably augmented inside spheres of chosen radii S_R. In the above we give the schematic description of the whole method. In the next section we shall discuss elaborately the methodology of LMTO.

2.3 Detailed formulation of the LMTO

In the section we will give the detailed formulation with mathematical expression whenever necessary of the basic aspects of the LMTO.

The radial wave functions and the potential function.

As indicated before the one-electron wave functions inside a muffin tin sphere are the solutions of the radial Schrodinger equation

$$(H-E)\left|\psi_l(E,r)\right\rangle = 0 \tag{2.16}$$

Let us define a radial function normalized to unity in the sphere

$$\phi_l(E,r) \equiv \left\langle \psi_l^2(E,r) \right\rangle^{-\frac{1}{2}} \psi_l(E,r) \tag{2.17}$$

Where the normalization integral can be written as,

$$\begin{aligned} \left\langle \psi_l^2(E,r) \right\rangle &\equiv \int \psi_{lm}^*(E,r)\psi_{lm}(E,r)dr \\ &= \int_0^s \psi_l^2(E,r)r^2 dr \int\int \left|Y_{lm}(\hat{r})\right|^2 d\Omega \\ &= \int_0^s \psi_l^2(E,r)r^2 dr \end{aligned} \tag{2.18}$$

In the LMTO, out attention will be focused upon energy range centered around some energy E_υ, which will be decided by us according to our problem. Thus for every angular momentum l we choose an energy $E_{\upsilon l}$ and use the energy independent basis set formed by normalized radial wave function

$$\phi_{\nu l}(r) \equiv \phi_{\nu l}(E_\nu, r) \tag{2.19}$$

and its energy derivative

$$\dot{\phi}_{\nu l}(r) \equiv \left[\frac{\partial \phi_l(E_\nu, r)}{\partial E}\right]_{E=E_\nu} \tag{2.20}$$

It should be noted that in the next section we represented this functions as ϕ (**r**) (ϕ_l(**r**)) or and here for convenience of discussion we write that as $\phi_{\upsilon l}(r)$ etc. The corresponding logarithmic derivatives at the sphere boundaries (r=s) are

$$D_{\nu l} = S\phi'_{\nu l}(s) / \phi_{\nu l}(s) = S\psi'_{\nu l}(S) / \psi_{\nu l}(S) \tag{2.21}$$

$$D_{vl} = S\phi'_{vl}(S)/\phi_{vl}(S) \tag{2.22}$$

where the dash($'$) indicates spatial derivative. By (2.17), the normalization integral in the sphere is unity, i. e.

$$\langle \phi(E) | \phi(E) \rangle = 1 \tag{2.23}$$

One can obtain by successive differentiation

$$\langle \phi_v | \phi_v \rangle = 0 \tag{2.24}$$

and also $$\langle \phi^2 \rangle = -\langle \phi_v | \ddot{\phi}_v \rangle \tag{2.25}$$

From (2.16) we obtain the relations between the u-th energy derivative of the partial wave $\phi_v^u(S)$ and the corresponding logarithmic derivative $D\{\phi_v^u(S)\}$ and their integral $\langle \phi_v | \phi_v^u \rangle$ in the sphere.

Differentiating the Schrodinger equation(2.16) successively with respect to energy one can obtain

$$(H - E_v) | \psi_v^u \rangle = u | \psi_v^{u-1} \rangle \tag{2.26}$$

Using the Green's second identity it can be shown that,

$$\begin{aligned}
&\left\langle \psi_2 \middle| H-E \middle| \psi_1 \right\rangle - \left\langle \psi_1 \middle| H-E \middle| \psi_2 \right\rangle \\
&= \int_{Sphere} \left| \psi_1^*(r)\nabla^2\psi_2(r) - \psi_2^*(r)\nabla^2\psi_1(r) \right| \\
&= \int_{Surface} \left[\psi^*{}_1(r)\frac{\partial\psi_2(r)}{\partial n} - \psi^*{}_2(r)\frac{\partial\psi_1(r)}{\partial n} \right] \\
&= \left| D_2 - D_1 \right| S\psi_1(S)\psi_2(S)
\end{aligned} \tag{2.27}$$

Here $\psi_1(r)$ and $\psi_2(r)$ are arbitrary functions of the form $\psi_{lm(r)}Y_{lm(r)}$ with the same l, m and radial logarithmic derivatives D_1, D_2 respectively. $\frac{\delta}{\delta n}$ means differentiation with respect to the normal to the surface of the sphere and also in the first step we have inserted the hamiltonian $H=-\nabla^2+V(r)$ and used

$$\left\langle \psi_1 \middle| E-v(r) \middle| \psi_2 \right\rangle = \left\langle \psi_2 \middle| H-E \middle| \psi_1 \right\rangle$$

If we set $\psi_1 = \psi_\nu^\mu(r), \psi_2 = \psi_\nu(r)$ we obtain from (2.28)

$$\begin{aligned}
&\left\langle \psi_\nu \middle| H-E \middle| \psi_\nu^\mu \right\rangle - \left\langle \psi_\nu^\mu \middle| H-E \middle| \psi_\nu \right\rangle \\
&= \left| D_\nu - D\{\psi_\nu^\mu\} \right| S\psi_\nu(S)\psi_\nu^\mu(S)
\end{aligned} \tag{2.28}$$

Also from (2.26) we obtain the result,

$$\begin{aligned}
u\left\langle \psi_\nu \middle| \psi_\nu^{\mu-1} \right\rangle &= \left\langle \psi_\nu \middle| H-E \middle| \psi_\nu^\mu \right\rangle \\
&= \left| D_\nu - D\{\psi_\nu^\mu\} \right| S\psi_\nu(S)\psi_\nu^\mu(S)
\end{aligned} \tag{2.29}$$

By putting $u = 1$ we get

$$D_{\dot{\nu}} = D_{\nu} - \left| S\phi_{\nu}(S)\,\phi_{\nu}(S) \right|^{-1} \tag{2.30}$$

Now it can also be proved that is orthogonal to the core states defined by,

$$H\phi_n = E_n\phi_n$$

$$D\{\phi_n\} = D_{\nu} \quad \text{with } n \neq \nu \tag{2.31}$$

$$\phi_n(S) << \phi_{\nu}(S)$$

ψ_n and ψ_{ν} are orthogonal and thus

$$0 = <\phi_n | \phi_{\nu}> = <\phi_n | H-E | \phi_{\nu}> .$$

Interchanging the function in the last integral and also from (2.29) we obtain,

$$<\phi_n | H-E | \phi_{\nu} > = <\phi_{\nu} | H-E | \phi_n> + [D_{\nu}-D_{\nu}]\, S\phi_n(S)\dot{\phi}_{\nu}(S)$$

$$0 = <\phi_{\nu} | H-E | \phi_n> + [D_{\nu}-D_{\nu}]\, S\phi_n(S)\dot{\phi}_{\nu}(S)$$

$$= (E_n-E_{\nu})<\dot{\phi}_{\nu} | \phi_n> + \phi_n(S)/\phi_{\nu}(S) \quad \text{[Using 2.30]}$$

From (2.31) we have the second term on the right hand side approximately zero, and hence we obtain the desired result

$$<\dot{\phi}_{\nu} | \phi_{\nu} > = 0 \text{ for } n \neq \nu \tag{2.32}$$

Any linear combination of $\dot{\phi}_{\nu}$ and ϕ_{ν} is thus orthogonal to the core states and augmentation of the muffin tin orbital by ϕ_{ν} - $\dot{\phi}_{\nu}$ functions is a suitable way of orthogonalization of the core states. Also as mentioned at the end of last section by

augmenting tails with $h_{RL,R'L'}\phi_{vl}(r)$at the neighboring sites they are also made orthogonal to the core states of these neighboring atoms also.

To define ϕ^{α} , $\dot{\phi}^{\alpha}$, one may choose the following relation with ϕ and $\dot{\phi}$

$$\phi^{\alpha} \equiv \left|1+(E-E_{v})o_{Rl}^{\alpha}\right|\phi_{Rl}(E,r) \tag{2.33}$$

and therefore

$$\phi_{Rl}^{\alpha}(E_{v},r)=\phi_{Rl}(r)+\phi_{Rl}o_{Rl}^{\alpha} \tag{2.34}$$

also $$\phi_{Rl}^{\alpha}(r)\equiv\phi_{Rl}(r) \tag{2.35}$$

The constants o_{Rl}^{α} is to be defined such that the linear combination of ϕ_{Rl}^{α} functions in (2.13) in previous section matches continuously and differentially to the tail of $\chi_{R'L'}(r_R)$.

We now wish to introduce the potential functions which is very important for our subsequent work. The potential function for energy E and angular momentum l defined by

$$P_{l}(E)=2(2l+1)\frac{D_{l}(E)+l+1}{D_{l}(E)-l} \tag{2.36}$$

The log-derivative $D_l(E)$ is a monotonically increasing function of energy except at its singularities. The potential function is therefore an increasing function of energy. For each l, both the functions consists of periods in energy (Andersen 1975, Skriver 1984) labeled by the principal quantum number and separated by energy V_{nl} decided to be those for which

$$D_l(V_{nl})=l \tag{2.37}$$

Also within each period we further define three parameters

$$D_l(B_{nl}) = 0$$

$$D_l(C_{nl}) = -l-1$$

$$D_l(A_{nl}) = -\infty \qquad (2.38)$$

The energies V_{nl}, B_l, , C_l , A_l represent the square well pseudopotential, the bottom, the centre, the top respectively of the nl-th energy band.

According to the Wigner-Seitz rule an l-band is formed in the energy range where the logarithmic derivative is negative i.e. from $D_l(B_{nl})=0$ to $D_l(A_{nl})= -\infty$. Now

$$P_l(B_l) = -\frac{l+1}{l} X 2(2l+1)$$

and

$$P_l(A_l) = 2(2l+1)\frac{D_l + l + 1}{D_l - l} = 2(2l+1)$$

So according to Wigner Seitz rule, the band is formed in terms of potential function in the range,

$$-(2l+1)(l+1)/l < P_l < 2(2l+1) \qquad (2.39)$$

and has hence a width on the P-scale of $2(2l+1)^2/2l$

We further observe that $P_l(C_l) = 0$

In the LMTO formalism as noted before, the Schrodinger equation is treated as an eigenvalue problem subject to the boundary condition of a special log-derivative at the sphere boundary. One can further consider parametrizatoin of the

function $E_l(D)$ inverse to $D_l(E)$. For this purpose we shall use the Rayleigh-Reitz variational principle with a radial trial function of arbitrary log-derivative D at the sphere boundary given as

$$\phi(D,r) = \phi_\nu(r) + \omega(D) \tag{2.40}$$

where

$$\omega(D) = -\frac{\phi_\nu}{\dot{\phi}_\nu}\frac{D - D_\nu}{D - D_{\dot{\nu}}}$$

Here $\phi_\nu = \phi_\nu(S)$, $\dot{\phi}_\nu \equiv \dot{\phi}_\nu(S)$. Further we see that

$$\phi_\nu(D,S) = \phi_\nu \frac{D_\nu - D_{\dot{\nu}}}{D - D_{\dot{\nu}}} \tag{2.41}$$

With the basis $\phi_{lm}(D, \boldsymbol{r}) = i^l Y_{lm}(\boldsymbol{r})\phi_l(D, \boldsymbol{r})$ the matrix elements of the Hamiltonian in the sphere,

$$\left\langle \phi_{l'm'}(D') \middle| H - E_{\nu l} \middle| \phi_{lm}(D) \right\rangle = \omega_l(D)\delta_{l'l}\delta_{m'm}$$

$$\left\langle \phi_{l'm'}(D') \middle| \phi_{lm}(D) \right\rangle = \delta_{l'l}\delta_{m'm}\left[1 + \omega_l(D')\omega_l(D)\left\langle \phi^2_{\nu l} \right\rangle\right]$$

With these we obtain the variational estimate

$$E_l(D) = E_{\nu l} + \frac{\left\langle \phi_{lm}(D) \middle| H - E \middle| \phi_{lm}(D) \right\rangle}{\left\langle \phi^2_{lm}(D) \right\rangle}$$

$$= E_{\nu l} + \frac{\omega_l(D)}{1 + \left\langle \phi^2_{lm} \right\rangle \omega^2_l(D)} + O(\varepsilon^3) \tag{2.42}$$

where $\varepsilon = E - E_V$

The variational estimate $E_l(D)$ is thus a single valued function confined to an energy-window

$$E_\nu - \left(\frac{1}{2}\right)\left\langle \phi_\nu^2 \right\rangle^{-1/2} \le E(D) \le \left(\frac{1}{2}\right)\left\langle \phi_\nu^2 \right\rangle^{-1/2} \qquad (2.43)$$

2.4 Envelope Function and Structure Constant

In this subsection we will discuss the envelope function and structure matrix. The envelope function should be reasonably complete in the interstitial region i.e. in the region between atomic spheres. For closed packed lattices the interstitial region is small, and the atomic sphere approximation mentioned earlier can be applied before this region need not to be considered. In such cases the above requirement is mild but even then each envelope function should be smooth so that the radius of convergence of the one Centre expansion exceeds the atomic sphere radius. For last l-convergence each envelope function should be a reasonable solution of the Schrodinger equation, in a large region between the atoms. The augmentation then needs to take place only for the few lower l-components i.e. s-, p-, and for the transition and noble metals the d-, and for rare earth and actinides the f-components. Also the potential between the atoms is rather flat and kinetic energy $\kappa^2 = E - V(\mathbf{r})$ is rather small. One may thus choose for the envelopes the solution of the Helmholtz equation $(\nabla^2 + \kappa^2)\, \chi^{(e)} = 0$ with κ^2 is small. In the partial wave methods like the KKR or the APW method, the potential is approximated by a muffin tin potential and κ^2 is chosen equal to $E - V_{MTZ}$ such

that $\chi^{(e)}$ is an exact solution of Schrödinger equation. For evaluating the hamiltonian and overlapping integrals we must include the integrals over the interstitial region or eliminate these by employing ASA. The simplest choice is to set $\kappa^2=0$ and in this work we shall mainly discuss with this set. The envelope function $\chi_{RL}(\varepsilon)$ of a MTO is thus defined to be atom centered angular momentum eigenfunctions of the Laplaces equation and this has the form of static multipole field given by

$$K_{RL}(r_R)=\left(\frac{r_R}{\omega}\right)^{-l-1} Y_L(r_R) \tag{2.44}$$

where $r_R = r-R$, and L≡composite angular momentum index.

Equation (2.44) is irregular at $\boldsymbol{r}=\boldsymbol{R}$ and is the irregular solution of the Laplace's equation the regular solution is,

$$J_{RL}(r_R)=\left(\frac{r_R}{\omega}\right)^{-l} Y_L(r_R) \tag{2.45}$$

where $K_{RL}(r_R)$ may be expanded in terms of $J_{RL}(r_R)$ as,

$$\begin{aligned} K_{RL}(r_R) &= -\sum_{L'}\left(\frac{r_R}{\omega}\right)^{l'} \frac{Y_{L'}(r_{R'})}{2(2l'+1)} S_{RL,R'L'} \\ &= \sum_{L'} J_{R'L'}(r'_R) S_{RL,R'L'} \end{aligned} \tag{2.46}$$

valid for $r_R \le |\, r-\boldsymbol{R}' \,|$. All distances are measured in terms of an arbitrary length ω, which may be the lattice constant or the Wigner-Seitz radius of the lattice. The expansion coefficient $S=[S_{R'L',RL}]$ are called the structure constants. These are

actually bare canonical structure constants for reason to be clarified soon. They only depend on atomic positions in units of ω and are thus independent of the atomic sphere potential and the lattice parameters of Wigner-Seitz sphere radius. The structure constants thus can be fixed for a particular lattice type and hence to be calculated only once for a bcc, fcc or sc system. They may expressed as two centre integrals with the z-axis chosen along the interaction vector **r-R'**, of length d. The bare canonical structure constants can be expressed by the simple formula,

$$S_{l'lm} = (-)^{l+m+1}(l+l')!\left[\frac{(2l'+1)(2l+1)}{(l'+m)!(l'-m)!(l+m)!(l-m)!}\right]^{1/2}\left(\frac{\omega}{d}\right)^{l'+l+1} \tag{2.47}$$

With particular elements like

$$S_{ss\sigma} = -2\left(\frac{\omega}{d}\right), S_{sp\sigma} = (2\sqrt{3})\left(\frac{\omega}{d}\right)^2 \tag{2.48}$$

etc. For a general direction of z-axis the structure constant matrix is to be obtained from (2.47) and table I in (Slater and Koster, 1954) or directly from table II of Andersen note[1978]. The envelope function is to be augmented not only inside the atoms at which it is centered but also inside all other atoms. We may therefore use solutions of Laplace's equation which are irregular also at the neighboring sites instead of using (2.44).

In the Bra-ket notation, the unscreened or bare MTO, $K^0_{RL}(r_R)$ and the screened MTO, $K^\alpha_{RL}(r_R)$ are denoted by $|K^0_{RL}\rangle^\infty$ and $|K^\alpha_{RL}\rangle^\infty$. The superscript ∞ indicates that the functions extend throughout all space. Omissions of the superscript ∞, as in $|K^0_{RL}\rangle$, $|J^0_{RL}\rangle$ means that the functions are truncated(cut off) outside the Wigner-Seitz sphere centered around $\boldsymbol{R}$. In this notation the bare

multipole about all sites of the structure are given by, (dropping 0 superscript at times)

$$|K>^{\alpha}=|K>-|J>S \tag{2.49}$$

The onsite elements of S are defined to be zero. The regular solutions $J_{R'L'}$ are modified by adding the amount $-\alpha_{R'L'}$ of the irregular solution

$$|J>^{\alpha}=|J>-|K>\alpha \tag{2.50}$$

Here α is the diagonal matrix $[\alpha_{R'L'}]$. The multipole field screened according to (2.50) is defined in analogy with (2.49) as,

$$|K^{\alpha}>^{\alpha}\equiv|K>-|J>S^{\alpha} \tag{2.51}$$

By inserting (2.50) in (2.51) we find that the screened structure constant matrix is given by,

$$|S^{\alpha}>=S+S\alpha S^{\alpha} \tag{2.52}$$

and the screened multipole field is,

$$\begin{aligned}|K^{\alpha}>&=|K>^{\alpha}(1-\alpha S)^{-1}\\&=|K^{0}>^{\alpha}(1+\alpha S)\end{aligned} \tag{2.53}$$

The so-called screening charge is therefore given by αS^{α}. We now want to determine α such that (2.52)-(2.53) have the shortest range. We furthermore want that the screened structure constant be canonical i.e. independent of the atomic potential and the scale of the structure and therefore choose the elements $[\alpha_{RL}]$ to be site independent constants. In fact we are left with three parameters α_s ,α_p, α_d. By numerical inversion of the 9 X 9 matrix $\alpha_l^{-1}-S_{ll'}^{k}$ on a lattice of block vector **k**

and subsequent Fourier transformation $S^{\alpha}_{RL,R'L'}$ may be obtained. More detail may be obtain about the value of the α's may be obtained in Andersen et. al (1985).

So the function $|K^{\alpha}>^{\alpha}$ outside the spheres and $|K^{\alpha}>$ inside the sphere can be expressed as one-centre angular momentum expansions and hence the augmentation is done by continuous and differentiable matching at the sphere radii (s_R). Each radial function

$$K_L(r) \equiv \left(\frac{r}{\omega}\right)^{-l-1}$$

and

$$J_l^{\alpha}(r) \equiv \left[2(2l+1)\right]^{-1}\left(\frac{r}{\omega}\right)^{l} - \alpha_l (r/\omega)^{-l-1}$$

should be matched by a linear combination of $\phi_l(r)$ and $\dot{\phi}_l(r)$.

The latter two functions were obtained numerically from the radial Schrodinger equation at energies E_ν and E_ν+dE_ν and subsequent normalization in the sphere.

The Wronskian of ϕ and $\dot{\phi}$ may be obtained from the Wronskian and Green's second identity as

$$1 = \langle \phi^2 \rangle = \langle \phi | -\nabla^2 + V - E_\nu | \dot{\phi}^2 \rangle \qquad (2.54)$$

to be

$$W\{\phi, \dot{\phi}\} = 0 \qquad (2.55)$$

For the radial solutions of Laplace's equation we obtain;

$$W\{K, J^{\alpha}\} = W\{K, J\} = \omega/2 \qquad (2.56)$$

The tail of the MTO is expanded in (2.51) in J^{α} functions only, whereas we recall that the functions of the energy independent MTO introduced earlier is expanded in terms of ϕ^{α} functions only. These two radial functions for the same RI must have identical logarithmic derivatives. With a given α, $J^{\alpha}(r)$ is specified by (2.50) whereas ϕ^{α} by (2.34). Since they have same logarithmic derivative from Wronskian, we have

$$W\{J^{\alpha},\ \phi^{\alpha}\}=0 \tag{2.57}$$

also as

$$\phi^{\alpha}(r)-\phi(r)+\phi(r)+\phi(r) \tag{2.58}$$

Hence,

$$0=W\left\{J^{\alpha},\phi^{\alpha}\right\}=W\left\{J^{\alpha},\phi\right\}+o^{\alpha}W\left\{J^{\alpha},\phi\right\} \tag{2.59}$$

Simplifying we get,

$$o^{\alpha}=-\frac{W\left\{J^{\alpha},\phi\right\}}{W\left\{J^{\alpha},\phi\right\}} \tag{2.60}$$

Using the result of equation (2.57) we can obtain an expression for α in terms of logarithmic derivatives of ϕ^{α} as,

$$W\{J^{\alpha},\ \phi^{\alpha}\}=0$$

$$W\{J,\ \phi^{\alpha}\}-\alpha W\{K,\phi^{\alpha}\}=0$$

Hence

$$\alpha_l = \frac{W\{J, \phi^\alpha\}}{W\{K, \phi^\alpha\}}$$

$$= \frac{(s/\omega)^{2l+1}}{2(2l+1)} \frac{D\{\phi^\alpha\} - l}{D\{\phi^\alpha\} + l + 1} \tag{2.61}$$

The last expression in the right hand side had been obtained by expanding the Wronskians in terms of logarithmic derivatives.

Now it can be shown that,

$$J(r) \rightarrow \phi^\alpha(r)\, W\{J^\alpha, \phi\} \tag{2.62}$$

$$K(r) \rightarrow \dot{\phi}^\alpha(r) W\{K, \phi\} - \phi(r) W\{K, \dot{\phi}^\alpha\} \tag{2.63}$$

The augmented multipole field thus has the one-centre expansion,

$$\left|K^\alpha\right\rangle \rightarrow -|\phi\rangle W\{K, \phi^\alpha\} - \left|\phi^\alpha\right\rangle \left[-W\{K, \phi\} + W\{J^\alpha, \phi\} S^\alpha\right] \tag{2.64}$$

Where the W{} are diagonal matrices which also obey a useful relation,

$$W\{K, \dot{\phi}^\alpha\}\, W\{J^\alpha, \phi\} = \omega/2 \tag{2.65}$$

2.5 The Atomic Sphere Approximation

In the Atomic Sphere Approximation (**ASA**) the solid is assumed to be wholly composed of slightly overlapping atomic Wigner-Seitz spheres. As a result there is no interstitial region. The LMTO formalism for the approximation assumes

to have a particularly simple form. In the next subsections we shall present the formalism using the bra-ket notation which was frequently used by the Andersen.

The augmented orbital in bra-ket notation can be given by,

$$\left|\chi^{\alpha}\right\rangle^{\infty} = |\phi\rangle + \left|\phi^{\alpha}\right\rangle h^{\alpha} \tag{2.66}$$

It is mentioned earlier that the $\left|\chi^{\alpha}_{RL}\right\rangle^{\infty}$ are functions spread out over all space, whereas $\left|\chi^{\alpha}_{RL}\right\rangle$ is restricted to its own augmented spheres.

Rewriting equation (2.34) as

$$\left|\phi^{\alpha}\right\rangle = |\phi\rangle + |\phi\rangle o^{\alpha} \tag{2.67}$$

For the Muffin Tin Orbitals o^{α} is a diagonal matrix. We also obtain the interaction between ϕ and ϕ^{α} and their energy derivatives from the following matrix equations

$$\begin{aligned} &\langle\phi|\phi\rangle = \hat{1};\ \langle\phi|\dot{\phi}\rangle = 0 \\ &\left\langle\phi\middle|\phi^{\alpha}\right\rangle = o^{\alpha}\ ,\ \left\langle\phi^{\alpha}\middle|\phi^{\alpha}\right\rangle = p^{\alpha} = (o^{\alpha})^2 + p \end{aligned} \tag{2.68}$$

where p is diagonal element with elements

$$p_{RL} \equiv \left\langle\phi^{\alpha}_{RL}\right\rangle \equiv \int_0^{S_R} \phi^2_{Rl}(E,r) r^2 dr \tag{2.69}$$

we note that $0 \le p_{RL} \le p^{\alpha}_{RL,RL}$. From (2.43) it can be recollected that p^{k2}_{RL} corresponds to the energy window.

The expression for overlap matrix can be given by,

$$O^{\alpha} = {}^{\infty}\left\langle \chi^{\alpha} \middle| \chi^{\alpha} \right\rangle^{\infty} = \hat{1} + o^{\alpha} h^{\alpha} + (o^{\alpha} h^{\alpha})^{+} + h^{\alpha} p^{\alpha} h^{\alpha} \tag{2.70}$$

For calculating the Hamiltonian, we use the following relations,

$$\begin{aligned} &(-\nabla^2 + V)\left|\phi^{\alpha}(E)\right\rangle = E\left|\phi^{\alpha}(E)\right\rangle \\ &(-\nabla^2 + V - E_{\nu})|\phi\rangle = 0 \\ &(-\nabla^2 + V - E_{\nu})|\phi\rangle = |\phi\rangle \end{aligned} \tag{2.71}$$

So

$$\begin{aligned} H^{\alpha} &= {}^{\infty}\left\langle \chi^{\alpha} \middle| -\nabla^2 + V \middle| \chi^{\alpha} \right\rangle^{\infty} \\ &= (\hat{1} + o^{\alpha} h^{\alpha})^{+} h^{\alpha} + (\hat{1} + o^{\alpha} h^{\alpha})^{+} E_{\nu} (\hat{1} + o^{\alpha} h^{\alpha}) + h^{\alpha} E_{\nu} p h^{\alpha} \end{aligned} \tag{2.72}$$

Both equation (2.70)and (2.72) contains the one, two and three centre terms.

Now rewriting equation (2.66) in terms of (2.67) we obtain,

$$\left|\chi^{\alpha}\right\rangle^{\infty} = |\phi\rangle(\hat{1} + o^{\alpha} h^{\alpha}) + |\phi\rangle h^{\alpha} \tag{2.73}$$

Assuming $(\hat{1} + o^{\alpha} h^{\alpha})$ can be inverted we can go back to the unscripted representation defined in terms of ϕ and ϕ originally introduced in (2.19), (2.20) as

$$|\chi\rangle^{\infty} \equiv \left|\chi^{\alpha}\right\rangle^{\infty} \left\{\hat{1} + o^{\alpha} h^{\alpha}\right\}^{-1} = |\phi\rangle + |\phi\rangle h \tag{2.74}$$

where $h = h^{\alpha}(\hat{1} + o^{\alpha} h^{\alpha})$ and the hamiltonian in the new basis is given by

$$H = E_{\nu} + h + hE_{\nu} ph = H^{(2)} + hE_{\nu} ph \tag{2.75}$$

and since H is hermitian, E_ν, p are diagonal matrices h too is a hermitian matrix. In that case the overlap matrix can be written as,

$$O = \hat{1} + hph \tag{2.76}$$

The new set of orbitals is orthogonal to the first order in $h \approx H\text{-}E_\nu$ and it is specified by the vector analog of the scalar first order Taylor series (2.14) for energy dependence of the radial wave functions.

In the terminology of LMTO the associated representation is called the γ representation and the physical quantities (orbitals, Hamiltonian etc.) is given by the superscript γ. Thus we see in the Atomic Sphere Approximation, the matrix **h** alone determines the hamiltonian and the overlap, as well as coefficients in the one-centre expansion(2.13). The matrices Ev and p are the diagonal potential parameters. Utilising the matching conditions we shall now obtain actual expressions for the hamiltonian.

By a comparison with χ_{RL} in (2.75) with (2.73), we see that

$$\left| K^{\alpha}_{RL} \right\rangle^{\infty} \rightarrow -\left| K^{\alpha}_{RL} \right\rangle^{\infty} W\{K, \phi^{\alpha}\} \tag{2.76}$$

Thus,

$$\left| K^{\alpha}_{RL} \right\rangle^{\infty} = |\phi\rangle + |\dot{\phi}\rangle \left[-\frac{W\{K,\phi\}}{W\{K,\dot{\phi}^{\alpha}\}} + \frac{W\{J^{\alpha},\phi}{W\{K,\dot{\phi}^{\alpha}\}} S^{\alpha} \right] \tag{2.77}$$

so that

$$h^{\alpha} = \frac{W\{K,\phi\}}{W\{K,\dot{\phi}^{\alpha}\}} + \frac{W\{J^{\alpha},\phi\}}{W\{K,\dot{\phi}^{\alpha}\}} S^{\alpha} \tag{2.78}$$

From (2.56), (2.62) and (2.63) we get that

$$W\{K,\phi^{\alpha}\}W\{J^{\alpha},\phi\}=\frac{2}{\omega} \tag{2.79}$$

hence,

$$h^{\alpha}=-\frac{W\{K,\phi\}}{W\{K,\phi^{\alpha}\}}+\left(\frac{2}{\omega}\right)^{1/2}W\{J^{\alpha},\phi\}S^{\alpha}W\{J^{\alpha},\phi\}\left(\frac{2}{\omega}\right)^{1/2} \tag{2.80}$$

The approximate Hamiltonian $H^{\alpha,(1)}\equiv E_{\nu}+h^{\alpha}$ is thus obtained as,

$$\begin{aligned}H^{(1)}&\equiv E_{\nu}+h^{\alpha}\\&=E_{\nu}-\frac{W\{K,\phi\}}{W\{K,\phi_{\alpha}\}}+(2/\omega)^{1/2}W\{J^{\alpha},\phi\}S^{\alpha}W\{J^{\alpha},\phi\}(2/\omega)^{1/2}\\&=c^{\alpha}+\left(\Delta^{\alpha}\right)^{1/2}S^{\alpha}\left(\Delta^{\alpha}\right)^{1/2}\end{aligned} \tag{2.81}$$

Here

$$c^{\alpha}\equiv E_{\nu}-\frac{W\{K,\phi\}}{W\{K,\phi_{\alpha}\}} \tag{2.82}$$

and

$$\left(\Delta^{\alpha}\right)^{1/2}\equiv(2/\omega)^{1/2}W\{J^{\alpha},\phi\} \tag{2.83}$$

are both potential parameter of LMTO. It may be noted that both the parameters are diagonal matrices. The formulae (2.82) to (2.83) are valid for any choice of α provided the corresponding S^{α} defined through (2.53) doesn't have any poles. We may thus choose

$$\gamma=\frac{W\{J,\phi\}}{W\{K,\phi\}}\equiv\frac{(s/\omega)^{(2l+1)}}{2(2l+1)}\frac{D\{\phi\}-l}{D\{\phi\}+l-1} \tag{2.84}$$

$o^{\gamma}=0$ from (2.60) and $\phi^{\gamma}(r)=\phi(r)$

The corresponding second order Hamiltonain can be given by,

$$\begin{aligned} H^{(2)} &\equiv E_{\nu}+h \\ &= E_{\nu}-\frac{W\{K,\phi\}}{W\{K,\phi\}}+(2/\omega)^{1/2}W\{J^{\gamma},\phi\}S^{\gamma}W\{J^{\gamma},\phi\}(2/\omega)^{1/2} \\ &= c^{\gamma}+\left(\Delta^{\gamma}\right)^{1/2}S^{\gamma}\left(\Delta^{\gamma}\right)^{1/2} \end{aligned} \tag{2.85}$$

where

$$\left|J^{\gamma}\right\rangle=|J\rangle-|K\rangle\gamma$$

and

$$W\{J^{\gamma},\phi\}=(\omega/2)W\{K,\phi\}^{-1} \tag{2.86}$$

The structure factor matrix in γ-representation can be given by,

$$S^{\gamma}\equiv S^{0}\left|\hat{1}-\gamma S^{0}\right|^{-1}=S^{\alpha}\left|\hat{1}-(\gamma-\alpha)S^{\alpha}\right|^{-1} \tag{2.87}$$

and the first potential parameter,

$$\begin{aligned} c^{\alpha} &\equiv E_{\nu}-W\{K,\phi\}/W\{K,\phi\} \\ &= E_{\nu}-(2/\omega)W\{K,\phi\}W\{J_{\alpha},\phi\} \end{aligned} \tag{2.88}$$

which determines the position of RI band and the screened potential parameters,

$$\left(\Delta^{\alpha}\right)^{1/2}\equiv-(2/\omega)^{1/2}W\{J^{\alpha},\phi\}=-(\omega/2)^{1/2}W\{K,\phi\}^{-1} \tag{2.89}$$

determines the width and the hybridization strongly of the band. That , the definition of c^{α} given in equation (2.88), is equivalent to the earlier definition of c in (2.38) as the band centre can be seen from the following simple argument. Recollecting that

$$K(r) \rightarrow -W\{K,\phi^{\alpha}\}\left[\phi(r)-\phi^{\alpha}(r)\frac{W\{K,\phi\}}{W\{K,\phi^{\alpha}\}}\right]$$
$$=\left(\frac{1/2\omega}{\Delta^{\alpha}}\right)^{1/2}\left|\phi(r)-(c^{\alpha}-E_{\nu})\phi^{\alpha}(r)\right|$$
$$\approx\left[\frac{K(s)}{\phi^{\alpha}(c^{\alpha},S)}\right]\phi(c^{\alpha},r)$$

Thus we see that $c^{\alpha}$is the energy to the first order in the its deviation from E_{ν} for which the radial solution of Schrodinger equation matches onto the K(r), (at r=s in the above) the LMTO envelope, which is the irregular solution of the Laplace equation. Thus c^{α} is the energy for which the logarithmic derivative takes the value -l-1. Thus the definition of c^{α} , is equivalent to what was stated earlier in (2.38). Further $\Delta^{\alpha 1/2}$ is proportional to the amplitude of the corresponding radial wave function at the average Wigner-Seitz radius of the lattice ω. We note that

$$(\Delta^{\alpha})^{1/2}\approx(\omega/2)^{1/2}\frac{\phi^{\alpha}(c^{\alpha},S)}{K(S)}\approx(\omega/2)^{1/2}\phi^{\alpha}(c^{\alpha},\omega) \qquad (2.90)$$

For α's chosen independently of the potential then, $H^{(1)}$, as is evident from (2.82) and (2.83), depends only on φ(S) and D{φ} but not on D{ϕ}, and in this case the information about the energy derivative is carried entirely by o^{α} as is seen from (2.60). When α=γ as in (2.94) it becomes equivalent to D{ϕ}. Also C is the energy for which φ(E,r) has the logarithmic derivative -l-1 at the sphere to the order $(C-E_{\nu})^2$ and $\Delta^{1/2}$ becomes the value $(\omega/2)^{1/2}$ φ(C,ω) to order $(C-E_{\nu})$.

Thus $H^{\alpha(1)}$ is a hamiltonian correct to first order whereas $H^{(2)}$ is correct to second order.

The fourth potential parameter is p defined in (2.69). We have shown earlier in (2.43) that $p^{-1/2}$ is the size of the energy window inside which a linear method is supposed yield realistic results.

For broad, free electron like bands it is customary to use, instead of C, another potential parameter viz. the square-well pseudopotential V. For monatomic solid in the ASA, V_S is the bottom of the s-band, and one may set $E_\nu \approx V_S$. For free electrons all V_{RL}'s are equal and denote the bottom of the band.

The potential parameter V thus equals the energy for which $\phi(V,r)$ matches onto the spherical Bessel function for $\kappa=0$, i.e. the energy for which the logarithmic derivative function equals l. The definition of V^α is therefore,

$$V^\alpha = E_\nu - \frac{W\{J,\phi\}}{W\{J,\phi\}} \tag{2.91}$$

V^α may be obtained from the c^α, Δ^α, α from the relation

$$c^\alpha - V^\alpha = \frac{\Delta^\alpha}{\alpha} \tag{2.92}$$

which may be obtained in a straightforward manner as,

$$\begin{aligned} c^\alpha - V^\alpha &= \frac{W\{J,\phi\}}{W\{J,\phi^\alpha\}} - \frac{W\{K,\phi\}}{W\{K,\phi^\alpha\}} \\ &= \frac{W\{J,\phi\}+W\{K,\phi\}\alpha}{W\{K,\phi^\alpha\}\alpha} - \frac{W\{K,\phi\}}{W\{K,\phi^\alpha\}} \\ &= W\{J^\alpha,\phi\}\left|W\{K,\phi\}\alpha\right|^{-1} \\ &= \frac{\Delta^\alpha}{\alpha} \end{aligned}$$

The width parameter analogous to Δ^{α} is defined by,

$$\begin{aligned}\Gamma^{\alpha 1/2} &\equiv -(\omega/2)^{1/2} W\{J,\phi^{\alpha}\}^{-1} \\ &= -(\omega/2)\left|W\{K,\phi^{\alpha}\}\alpha\right|^{-1} \\ &= \frac{(\Delta^{\alpha})^{1/2}}{\alpha}\end{aligned} \tag{2.93}$$

Then the first and second order Hamiltonian may be written in terms of V^{α}, Γ^{α} as,

$$H^{\alpha(1)} = V^{\alpha} + (\Gamma^{\alpha})^{1/2}(\alpha^{-1} - S^{0})^{-1}(\Gamma^{\alpha})^{1/2} \tag{2.94}$$

or in γ-representation

$$H^{\gamma(2)} = V^{\gamma} + (\Gamma^{\gamma})^{1/2}(\gamma^{-1} - S^{0})^{-1}(\Gamma^{\gamma})^{1/2} \tag{2.95}$$

A more detail may be obtain from the Andersen et. al. (1985). As the γ-representation is more accurate, we can transform any general α-representation to the γ-representation. Let us convert the structure factor matrices to the γ-representation.

For crystal we can use the Bloch representation,

$$S^{\alpha}_{R'L',RL} = \sum_{T} \exp\left|i\vec{k}.\vec{T}\right| S^{\alpha}_{R'L',(R+T)L} \tag{2.96}$$

in which the inversion in (2.97) involves finite matrices only. **T** in 2.106 are the lattice translations and **r, R'** label atoms in the primitive cell.

Alternatively one may expand S^{γ} in equation (2.97) as

$$S^{\gamma} = S^{\alpha} + S^{\alpha}(\alpha-\gamma) + S^{\alpha}(\alpha-\gamma)S^{\alpha}(\alpha-\gamma)S^{\alpha} + \ldots\ldots \tag{2.97}$$

The procedure to obtain S^{γ} doesn't require any translational symmetry. However the series has to be carried to convergence and hence $(\alpha-\gamma)S^{\gamma}$ should be much smaller than unity. So, we require to start from the relation,

$$\begin{aligned} H^{(2)\gamma} &= E_{\nu} + h = E_{\nu} + h^{\alpha}(1 - o^{\alpha}h^{\alpha})^{-1} \\ &= E_{\nu} + h^{\alpha} - h^{\alpha}o^{\alpha}h^{\alpha} + h^{\alpha}o^{\alpha}h^{\alpha}o^{\alpha} - \\ &= H^{\alpha(1)} - h^{\alpha}o^{\alpha}h^{\alpha} + h^{\alpha}o^{\alpha}h^{\alpha}o^{\alpha} \ldots\ldots \end{aligned}$$

This method is very powerful because $H^{\alpha(1)}$ (for $\alpha-\beta$) itself delivers one-electron energies correct to first order in E_j-E_{ν}.

Now we shall introduce the MTO-tail cancellation and obtain the so-called KKR-ASA equations. It is also possible to show the KKR-ASA equations are equivalent to the LMTO-ASA eigenvalues equations introduced earlier. The MTO with the interstitial part included is thus given by,

$$\left|\chi^{\alpha}(E)\right\rangle^{\infty} = \left|\phi(E)\right\rangle + \left|\dot{\phi}^{\alpha}\right\rangle h^{\alpha}(E) + \left|\chi^{\alpha}(E)\right\rangle^{i} \qquad (2.98)$$

and h(E) in analogy with the previous (2.78)-(2.80) is given by,

$$\begin{aligned} h^{\alpha}(E) &= (2/\omega)^{1/2} W\{J^{\alpha}, \phi(E)\}\left[-\frac{W\{K, \phi(E)\}}{W\{J^{\alpha}, \phi(E)\}} + S^{\alpha}\right] W\{J^{\alpha}, \phi(E)\}(2/\omega)^{1/2} \\ &\equiv \left|\dot{P}^{\alpha}(E)\right|^{-1/2}\left|-P^{\alpha}(E) + S\right|\left|\dot{P}^{\alpha}(E)\right|^{-1/2} \end{aligned} \qquad (2.99)$$

Here we have introduced the potential function by defining the screened potential function as,

$$P^{\alpha}(E) = \frac{W\{K,\phi(E)\}}{W\{J^{\alpha},\phi(E)\}} = \frac{W\{K,\phi(E)\}}{W\{J,\phi(E)\} - W\{K,\phi(E)\}\alpha}$$
$$= \frac{P^{0}(E)}{1-\alpha P^{0}(E)} \qquad (2.100)$$

where the bare potential function $P^{0}(E)$ can be redefined as,

$$P^{0}(E) \equiv \frac{W\{K,\phi(E)\}}{W\{J,\phi(E)\}} \qquad (2.101)$$

By actually expanding the Wronskian according to (2.62)-(2.65) we recover the previous definition

$$P^{0}(E) \equiv P(E) = 2(2l+1)(\omega/s)^{2l+1}\frac{D(E)+l+1}{D(E)-l} \qquad (2.102)$$

Further

$$\left|\dot{P}^{\alpha}(E)\right|^{1/2} = -(\omega/2)^{1/2} W\{J^{\alpha},\phi(E)\} = \Delta^{\alpha}(E)^{-1/2} \qquad (2.103)$$

is obtained from,

$$\dot{P}^{\alpha}(E) = \frac{W\{K,\phi^{\alpha}(E)\}W\{J^{\alpha},\phi(E)\} - W\{J^{\alpha},\phi^{\alpha}(E)\}W\{K,\phi(E)\}}{W\{J^{\alpha},\phi(E)\}^{2}}$$
$$= \frac{(\omega/2)}{W\{J^{\alpha},\phi(E)\}^{2}}$$

Now the linear combination of MTO's can given by the form,

$$\left|\chi^{\alpha}(E)\right\rangle^{\infty} u(E) = \left|\phi(E)\right\rangle u(E) + \left|\dot{\phi}(E)\right\rangle h^{\alpha}(E) u(E) + \left|\chi(E)\right\rangle^{i} u(E) \qquad (2.104)$$

whatever the values of u(E) the above is a solution of Schrodinger equation for that particular E. For the ASA the interstitial part drops out and the ϕ(E,r) are exact solutions inside the spheres.

Thus the above equation (2.104) is an exact solution of each spheres and each partial wave if the sum of the tails $|\phi^{\alpha}(E)\rangle h^{\alpha}(E)u(E)$ cancels out and we are left with the one centre expansion

$$\left|\chi^{\alpha}(E)\right\rangle^{\infty} u(E) = |\phi(E)\rangle u(E) = |\psi(E)\rangle \tag{2.105}$$

This is the tail cancellation condition which gives rise to the set of linear homogeneous equations,

$$\left|-P^{\alpha}(E)+S^{\alpha}\right|\left|\dot{P}^{\alpha}(E)\right|^{-1/2} u(E) = 0 \tag{2.106}$$

which are the KKR equations in the ASA with screened (or bare) potential functions and structure constants. The energies for which $P^{\alpha}(E)$-S^{α} vanishes are the exact one-electron energies with eigenvectors normalized according to

$$u^{\dagger}(E)\, u(E)=1$$

The energy band problem is thus reduced to that of finding eigenvalues for a single atomic sphere with its spherically symmetric potential subject to k-dependent boundary conditions imposed by the surroundings. The information about the atomic spheres is carried by the logarithmic derivatives $D_l(E)$ which are functions of E, while the information about the structure is carried by the canonical structure matrix which is a function of **k**. We thus obtain for each **k** vector the allowed values of E(**k**). This is the approximate matching condition of the cellular matching problem realized by Wigner and Seitz(1933).

Chapter Three
The Augmented Space Recursion

3.1 Introduction

In this chapter we shall discuss the augmented space formalism (ASF). The augmented space formalism was first introduced by Mookerjee (1973, 1987) and Kaplan and Gray (1977) and provides a straightforward and convenient way of performing configuration averaging in disordered systems. In this formalism, the problem of a random hamiltonian in real space is transformed into an effective non-random hamiltonian in a larger Hilbert space called the augmented space which is a direct product of the real space and the configuration space and averaging is reduced to determining a particular matrix element in the augmented space. This is the augmented space theorem. A straightforward application of the above formalism is computationally expensive for three dimensional systems. The above theorem is usually applied with some kind of approximation.

The recursion method (Haydock, 1980) provides a convenient way for the calculation of the Green function and the local density of states without having to take recourse to the Bloch's theorem and its consequent **k**-space. The formalism

does not require lattice periodicity and hence can be applied to all types of disordered solids.

3.2 The recursion method

The recursion method was introduced to condensed matter applications by Haydock et. al. (1972). The scheme basically calculates quantities related to the local electronic structure. It is particularly useful where there is a essential lack of periodicity. In the absence of periodicity the conventional Bloch theorem is violated and hence the method of k-space integration over the Brillouin zone is no longer useful.

To determine the local electronic structure, the pertinent physical quantity is the local density of states at a particular point **r** i.e.

$$n(E,r) = \sum_n \left|\psi_n(r)\right|^2 \delta(E - E_n) \tag{3.1}$$

(for each spin direction) where ψ_n, E_n are the energy eigenfunctions and corresponding eigenvalues of the system, and the summation is over all such states. n(E,r) is related to the Green function in real space representation by,

$$n(E,r) = -\pi^{-1}\Im m G(r,r',E) \tag{3.2}$$

where the definition of Green's function can be given by,

$$\begin{aligned} G(r,r',E) &= \sum_n \frac{\psi_n(r)\psi_n(r')}{E + i0^+ - E_n} \\ &= \Re\sum_n \frac{\psi_n(r)\psi_n(r')}{E - E_n} - i\pi \sum_n \psi_n(r)\psi_n(r')\delta(E - E_n) \end{aligned} \tag{3.3}$$

from which eqn. (3.2) follows. The recursion method provides a convenient way to calculate n(E,r) without calculating the eigenfunctions and eigenvalues.

Let $\phi_0(r)$, $\phi_1(r)$, $\phi_2(r)$, $\phi_3(r)$.....$\phi_n(r)$ etc. be the set of countable basis in relation to which n(E,r) is to be calculated. We shall assume that the basis set will be reasonably short ranged and tight-binding like. This is the type of basis set considered in the TB-LMTO formalism. In this countable basis, a state vector can be written as,

$$\begin{pmatrix} u_0 \\ u_1 \\ u_2 \\ . \\ . \\ . \\ u_n \end{pmatrix} \tag{3.4}$$

where the elements $\{u_i\}$ are the projections of the state vectors on the basis i.e.

$$u(r) = \sum_{n=0}^{\infty} u_n \phi_n(r) \tag{3.5}$$

Now we are defining a linear operator A is represented by an infinite square matrix with elements $\{a_{mn}\}$ where

$$a_{mn} = \int \phi_m^*(r) A \phi_n(r) d\tau \tag{3.6}$$

The hamiltonian operator is similarly represented by a matrix H, and the Schrodinger equation assumes the following form in this notation

$$Hu_\alpha = \left\{ \left[-\frac{\hbar^2}{2m} \right] \nabla^2 + V(r) \right\} u_\alpha = E_\alpha u_\alpha \tag{3.7}$$

A state u has an adjoint $u^{\dagger}$ represented by row vector whose elements are complex conjugates of u and the adjoint of the linear operator A is denoted by $A^{\dagger}$ and is A's complex conjugate transpose. The basis set $\{\phi_n(r)\}$ is generally not orthogonal. The overlap matrix is given by

$$S_{mn} = \int \phi_m^*(r)\phi_n(r)d\tau \tag{3.8}$$

The physical overlap or inner product of two states is given by $v^{\dagger}Su$. The hamiltonian matrix utilised in the recursion calculation is introduced as follows: The state resulting when the hamiltonian operator **H** acts on a basis vector $\phi_n(r)$ may be represented as a linear combination of basis states as,

$$\mathbf{H}\phi_n = \sum_{n=0}^{\infty} H_{mn}\phi_m(r) \tag{3.9}$$

where $[H_{mn}]$ is the hamiltonian matrix which is different from the matrix representation of **H** as,

$$H_{mn} = \int \phi_m^* H \phi_n d\tau \tag{3.10}$$

Indeed they are related by,

$$H_{mn} = [S\mathbf{H}]_{mn}$$
$$or,$$
$$\mathbf{H} = S^{-1}H \tag{3.11}$$

In the main step of the recursion method a sequence of orthonormal orbitals $\{u_0, u_1 \ldots\ldots u_n\}$ are introduced along with two sets of real parameters $\{a_0, a_1 \ldots\ldots a_n\}$ and $\{b_0, b_1 \ldots\ldots b_n\}$ by the symmetric three recursion relations,

$$\mathbf{H}u_n = a_n u_n + b_{n+1} u_{n+1} + b_n u_{n-1} \qquad (3.12)$$

The sequence of vectors can be finite or infinite with initial conditions u_{-1} = u_{N+1} =0 (in which N could tend to ∞) for the first and last recurrences with N being the number of recursions. The recurrence is called symmetric because the component of u_{n+1} in Hu_n is the same as the component of u_n in Hu_{n+1}.

The hamiltonian matrix H_{mn} in terms of the introduces orbitals u_0, u_1, ... has a tridigonal representation

$$H = \begin{bmatrix} a_0 & b_1 & 0 & \ldots \\ b_1 & a_1 & b_2 & \ldots \\ 0 & b_2 & a_2 & \ldots \\ . & . & . & \\ . & . & . & \ldots \\ . & . & . & \end{bmatrix} \qquad (3.13)$$

Actually the initial state u_0 is a localized orbitals on an atom or bond of the system. u_0 is a localised orbital or bond of the system. u_1 is a linear combination of orbitals on atoms or bonds neighboring u_0 and thus represents the first nearest neighbour environment of u_0. Similarly u_2 represents the second nearest neighbour environment. Each orbital on the chain thus represents a part of the environment-the one with a higher index being a more distant part and the parameters a_n, b_n specify effect of that environment.

The orbital that donot couple to the initial state do not appear in the chain. Indeed the states on a chain constitute an invariant subspace such that H acting on any state produces another state in the subspace.

Let us now consider the calculations of a_n , b_n . Considering that u_0 is normalised i.e. $u_0^\dagger S u_0 = 1$, the recurrence relation of (3.12) for u_0 gives,

$$Hu_0 = a_0 u_0 + b_1 u_1 \tag{3.14}$$

Left hand side is known, a_0 , b_1 on the right hand side may be determined. Applying orthonormality

$$a_0 = u_0^+ SHu_0 \tag{3.15}$$

Rearranging (3.14), $b_1 u_1 = (H - a_0)u_0$ and again orthonormality gives

$$b_1^2 = \left|(H - a_0)u_0\right|^+ S\left|(H - a_0)u_0\right| \tag{3.16}$$

b_1 is usually taken as the positive root of b_1^2 , the inner product being positive definite. Equation (3.12) represents the general step in the recurrence. a_n is obtained similar to (3.15) as,

$$a_n = u_n^+ SHu_n \tag{3.17}$$

The new state is obtained as,

$$b_{n+1} u_{n+1} = (H - a_n)u_n - b_n u_{n-1} \tag{3.18}$$

with

$$b_{n+1}^2 = \left[\left(H - a_n\right)u_n - b_n u_{n-1}\right]^+ S\left[\left(H - a_n\right)u_n - b_n u_{n-1}\right] \tag{3.19}$$

By construction the u_{n+1} is orthogonal to u_n, u_{n-1}. It can be shown that u_{n+1} is also orthogonal to all the preceding vectors u_{n-2}, ..., u_0. (Haydock, 1980)

For convenience of analysis and calculation two sets of polynomials of energy $\{P_n(E)\}$, $\{Q_n(E)\}$ are introduced in the method. The eigenstate in a chain model are represented in terms of state vectors u_0, u_1,.....u_n as $\sum_{n=0}^{\infty} P_n(E)u_n$. Thus,

$$H\left(\sum_{n=0}^{\infty} P_n(E)u_n\right) = E\left(\sum_{n=0}^{\infty} P_n(E)u_n\right) \tag{3.20}$$

Where (3.20) is a matrix operator, and the energy eigenvalues are the zeroes of the determinant *det(E-H)*. The matrix (E-H) is also a tridiagonal matrix,

$$(E-H) \equiv \begin{bmatrix} E-a_0 & -b_1 & 0 & 0 & \cdots \\ -b_1 & E-a_1 & -b_2 & 0 & \cdots \\ 0 & -b_2 & E-a_2 & -b_3 & \cdots \\ 0 & 0 & -b_3 & E-a_3 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \tag{3.21}$$

Let $\Delta_n(E)$ represent the determinant of the first rows and columns of E-H. Now such determinants are also found to obey a similar recurrence relation

$$\Delta_{n+1}(E) = (E-a_n)\Delta_n(E) + b_n^2\Delta_{n-1}(E) \tag{3.22}$$

where the initial conditions are

$$\Delta_{-1}(E) = 0$$

$$\Delta_0 = 1$$

Let us now find the eigenstates. Operate with **H** on the left-hand side of (3.20) we obtain,

$$\sum_{n=0}^{\infty}(a_n P_n^{(\alpha)} + b_{n+1} P_{n+1}^{(\alpha)} + b_n P_{n-1}^{(\alpha)})\mathbf{u_n} = \sum_{n=0}^{\infty} E_\alpha P_n^{(\alpha)} \mathbf{u_n} \qquad (3.23)$$

where $\{P_n^{\alpha}\}$ are polynomials corresponding to the eigenvalue E_α . From linear dependence of vectors $\{u_n\}$, we see,

$$E_\alpha P_n^\alpha = a_n P_n^\alpha + b_{n+1}^\alpha + b_n P_{n-1}^\alpha \qquad (3.24)$$

that is the polynomial set $\{P_n^{\alpha}\}$ also obey a similar recurrence relation. Further the eigenstates are assumed to have coefficient 1 on u_0. Writing explicitly as polynomials of E, with initial conditions

$$P_{-1}(E)=0$$

$$P_0(E)=0$$

The recurrence relation is obtained

$$EP_n(E) = a_n P_n(E) + b_{n+1} P_{n+1}(E) + b_n P_{n-1}(E) \qquad (3.25)$$

$\{P_n(E)\}$ are related to $\{\Delta_n(E)\}$ by,

$$\Delta_n(E) = b_1 b_2 b_3 \ldots\ldots b_n P_n(E) \qquad (3.26)$$

and for $E=E^{\alpha}$, the eigenvalue, we have for chain of length N steps,

$$\Delta_n(E^\alpha) = 0 \qquad (3.27)$$

and

$$(E^{\alpha} - a_{N-1}(E^{\alpha}) - b_{N-1}P_{N-2}(E^{\alpha}) = 0 \qquad (3.28)$$

For an infinite chain the determinant diverges for energies in between eigenvalues, and thus the eigenvalues are energies for which $P_n(E)^{\alpha}$ are bounded as $n \to \infty$.

The zeroes of successive $\{P_n(E)\}$ form a sturm sequence (Szego, 1957). The polynomial $\{P_n(E)\}$ are orthogonal with a non-negative weight function $n_0(E)$ which is identical to local DOS, i.e.

$$\int_{\infty} P_n(E) P_m(E) n_0(E) dE = \delta_{mn} \qquad (3.29)$$

with the expression for completeness being,

$$n_0(E) \sum_n P_n(E) P_n(E') = \delta(E - E') \qquad (3.30)$$

where E and E' both are eigenvalues.

A set of polynomials result from the initial condition,

$$Q_0(E) = 0$$

$$Q_1(E) = 1.$$

The $\{P_n(E)\}$ and $\{Q_n(E)\}$ are two linearly independent solutions of the three-term recurrence, but with different initial namely, $P_0(E)$ is one and $Q_0(E)$ is zero. In order to second order differential equation, the analog of the Wronskian

$$\omega_n(E) = \left| Q_{n+1}(E) P_n(E) - Q_n(E) P_{n+1}(E) \right| b_{n+1}$$

It is possible to express the Green function in terms of P_n and Q_n by,

$$G_0^{(n)} = [b_{n+1}|P_{n+1}(E)P_n(E^+) - P_n(E)P_{n+1}(E^+)|]^{-1} \tag{3.31}$$

3.3 The green function and Local density of States

The recursion method provides a convenient and numerically efficient way to determine the Green function and the local density of states without calculating the eigenfunctions and eigenvalues earlier. The matrix elements of Green function between two states u , v is

$$G_{uv}(E) = v^+ S(E-H)^{-1}u \tag{3.32}$$

If $\{\omega_\alpha\}$ be the eigenstates and the eigenvalues E_α the spectral decomposition is

$$G(E) = v^+ S\left[\sum_\alpha \omega_\alpha (E-E_\alpha)^{-1}\omega_\alpha^+\right]Su \tag{3.33}$$

ω_α is the eigenvalues of H corresponding to E_α . The diagonal Greenfunction corresponding to the element u_0 is

$$G_0(E) = u_0^+ S(E-H)^{-1}u_0 \tag{3.34}$$

As E goes to infinity in complex plane in any direction G_0 (E) tends to zero as 1/E. Further G_0(E) found to be hermitian from (3.34)

$$G_0(E)^+ = u_0^+(E^+ - H^+)S^+u_0 = G_0(E^+) \tag{3.35}$$

from the hermicity of S and SH.

A function with the above properties may be written as a continued fraction,

$$G_0(E) = \cfrac{1}{E - a_0 - \cfrac{b_1^2}{E - a_1 - \cfrac{b_2^2}{\ddots \cfrac{}{E - a_{N-1} - \cfrac{b_N^2}{E - a_N}}}}} \tag{3.36}$$

This relation can be verified by considering explicitly the matrix form for $G_0(E)$.

$$G_0(E) \equiv \begin{bmatrix} E-a_0 & -b_1 & 0 & 0 & \cdots \\ -b_1 & E-a_1 & -b_2 & 0 & \cdots \\ 0 & -b_2 & E-a_2 & -b_3 & \cdots \\ 0 & 0 & -b_3 & E-a_3 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}^{-1}_{\infty} \tag{3.37}$$

From matrix algebra, the (00)-th element of the inverse of the matrix is the ratio of the cofactor of E-a_0 to the determinant. If the determinant with the first n-rows and first n-columns deleted by $D_n(E)$ then,

$$\begin{aligned} G_0(E) &= \frac{D_1(E)}{D_0(E)} \\ &= \frac{D_1(E)}{\left|(E-a_0)D_1(E) - b_1^2 D_2(E)\right|} \\ &= \frac{D_1(E)}{\left|(E-a_0) - b_1^2 D_2(E)/D_1(E)\right|} \end{aligned} \tag{3.38}$$

continuing in this manner we can obtain (3.36).

The spectrum of $G_0(E)$ or local density of states of u_0 is,

$$n_0(E) = \sum_\alpha p_\alpha \delta(E - E_\alpha) \tag{3.39}$$

We also recollect that,

$$n_0(E) = \lim_{\varepsilon \to 0} -\frac{1}{\pi} \Im m[G_0(E - i\varepsilon)] \tag{3.40}$$

The real part of $G_0(E)$ along the real axis is the Hilbert transform of the local density of states,

$$\Re e[G_0(E)] = p\int_{-\infty}^{\infty} \frac{n_0(E')}{(E - E')} dE' \tag{3.41}$$

and may be related to the resistance of the system to excitation at other than eigenenergies. Alternatively $\Re e[G_0(E)]$ represents the response of the system to being driven at a particular energy. A number of important relations for $G_0(E)$ can be written in terms of $\{P_n(E)\}$ and $\{Q_n(E)\}$.(Haydock, 1980)

3.4 Terminators

The continued fraction expansion of the Green function (3.36) is usually terminated after a certain number of levels by a terminator $T^{(n)}(z)$ as,

$$G_{00}(z) = \cfrac{1}{z - a_0 - \cfrac{b_1^2}{z - a_1 - \cfrac{b_2^2}{\ddots \cfrac{}{z - a_{N-1} - T^{(n)}(z)}}}} \tag{3.42}$$

The physical interpretation of the terminator is to substitute the remaining parts of the chain after the n-th vertex or atom by an effective medium. The task is

of obtain a closed form expression for $T^{(n)}(z)$. It introduced at the n-th level keeps the 2n moments of the local DOS unaffected.

The terminator T(z) is calculated directly by processing the coefficient $\{\alpha_n, \beta_n\}$ n=1,2.....p. This is described in detail by Haydock. The terminator possesses herglotz analytic properties and gives the band edges, band widths and band weights accurately. The procedure is fast accurate and stable.

3.5 Augmented Space Theorem

The basic idea of the formalism originated from the recursion method of Haydock, discussed in the previous sections. A self adjoint hamiltonian in a given basis is transformed in that method to a tridiagonal hamiltonian in a new basis introduced in accordance with some prescription. As a result the local density of states could be expressed as a continued fraction expansion. One should note that,

i) the local DOS is positive definite i.e. $n_0(E) \geq 0$

ii) $\int n_0(E)dE$ is finite.

iii) the convergence of continued fraction expansion for $n_0(E)$ requires that all moments of it converge, i.e. $\int E^n n_0(E)dE < \infty$.

The probability density also possesses the same properties i.e.

i) $P_i(n_i) \geq 0$

ii) $\int P_i(n_i)dn_i$ is finite.

iii) All moments converge for most of the physically acceptable probability densities.

The probability density should therefore be expressible as the imaginary part of a herglotz function and can thus be written as the continued fraction expansion

$$P_i(n_i) = -\frac{1}{\pi}\Im m \cfrac{1}{z_i - a_0 - \cfrac{b_1^2}{z_i - a_1 - \cfrac{b_2^2}{\vdots}}} \tag{3.43}$$

here $z_i = n_i + i\delta$.

With $\delta \to 0$, $P_i(n_i)$ is expressed as the matrix element of suitably chosen self-adjoint operator, $\mathbf{M}^i$ by,

$$P_i(n_i) = -\frac{1}{\pi}\Im m\left\langle v_0^0 \middle| \left(z_i I - \mathbf{M}^i\right)^{-1} \middle| v_0^i \right\rangle \tag{3.44}$$

where $\mathbf{M}^i$ is thus a tridiagonal matrix in the configuration space ϕ_i spanned by the basis $\{|v_j^i\rangle\}$ where j=0 ,1,.....(m-1) with m being the number of possible values n_i can take. The state $|v_o^i\rangle$ so defined that $\langle v_0 | \mathbf{M}^i | v_0^i \rangle = a_0$ the first coefficient in the continued fraction expansion.

The operator $\mathbf{M}^i$ will definitely be of finite rank if $P_i(n_i)$ has finite moments to all orders, i.e.

$$\int P_i(n_i) n_i^{\lambda} dn_i = \text{finite}$$

for λ=0,1,2,3..... Barring the exception of Lorentzian distribution function (Mookerjee, 1973) all physically valid probability distribution function obey this condition. With the help of equation (3.44)

$$\langle A \rangle = \int A(\{n_i\}) \left[\prod_i \left\{-\frac{1}{\pi}\Im m\left\langle v_0^i \middle| (z_i \mathbf{I} - \mathbf{M}^i)^{-1} \middle| v_0^i \right\rangle\right\}\right] dn_j \tag{3.45}$$

The integral can be evaluated by integrating out one variable at a time. If we first integrate out the j-th variable and call in ϑ_j,

$$\vartheta_j = \int A(\{n_i\}) \left[\left\{ -\frac{1}{\pi} \left\langle v_0^j \left| (z_i I - M^j)^{-1} \right| v_0^j \right\rangle \right\} \right] dn_j \tag{3.46}$$

Let $|\mu^j\rangle$ be the eigenvectors of $\mathbf{M^j}$ with eigenvalues μ^j i. e.

$$M^j \left| \mu^j \right\rangle = \mu^j \left| \mu^j \right\rangle \tag{3.47}$$

We shall thus have the completeness condition for the eigenvectors of a self-adjoint operators $\mathbf{M^j}$,

$$\sum_{\mu^j} \left| \mu^j \right\rangle \left\langle \mu^j \right| = 1$$
$$\left\langle \mu^j \middle| \mu^j \right\rangle = \delta_{12} \tag{3.48}$$

Rewriting (3.46) as

$$\vartheta_j = \left\langle v_0^j \right| \int A(\{n_i\}) \left[\left\{ -\frac{1}{\pi} \Im m \left\{ \sum_{\mu_1^j} \sum_{\mu_2^j} \left| \mu_1^j \right\rangle \left\langle \mu_1^j \right| \mathbf{X}\left(n_j - \mathbf{M}^j\right)^{-1} \left| \mu_2^j \right\rangle \left\langle \mu_2^j \right| \right\} \right\} \right] dn_j \left| v_0^j \right\rangle$$

$$= \left\langle v_0^j \right| \int A(\{n_i\}) \left[\left\{ -\frac{1}{\pi} \left\{ \sum_{\mu_1^j} \sum_{\mu_2^j} \left| \mu_1^j \right\rangle \frac{\delta_{12}}{\left(n_j - \mu_1^j\right)} \left\langle \mu_2^j \right| \right\} \right\} \right] dn_j \left| v_0^j \right\rangle$$

$$= \left\langle v_0^j \right| \int A(\{n_i\}) \left[\left\{ -\frac{\Im m}{\pi} \left\{ \sum_{\mu_1^j} \left| \mu^j \right\rangle \frac{1}{\left(n_j - \mu_1^j\right)} \left\langle \mu_j \right| \right\} \right\} \right] dn_j \left| v_0^j \right\rangle$$

With the identity $\lim_{\varepsilon \to 0} (1/\pi) \Im m \frac{1}{x + i0^+ - a} = \delta(x - a)$ we obtain,

$$\vartheta_j = \left\langle v_0^j \right| \int A(\{n_i\}) \left[\sum_{\mu^j} \left| \mu^j \right\rangle \delta\left(n_j - \mu_j\right) \left\langle \mu_j \right| \right] dn_j \left| v_0^j \right\rangle$$
$$= \left\langle v_0^j \middle| \sum_{\mu^j} \left| \mu^j \right\rangle A(\{n_i, i \neq j\} \mu_j) \left\langle \mu^j \middle| v_0^j \right\rangle \right. \tag{3.49}$$

As $|\mu_j\rangle$'s are eigenvectors of $\mathbf{M}^j$,

$$\vartheta_j = \left\langle v_0^j \middle| \tilde{A}(\{n_i, i \neq j\}, \mathbf{M}^j) \middle| v_0^j \right\rangle$$

We note that the operator $\mathbf{A}$ ($\{n_i, i \neq j\}$), $\mathbf{M}^j$) is the same function of $\mathbf{M}^j$ as $A(\{n_i, i \neq j\}, n_j)$ is of n_j. By integrating out all the variables above all the n's will be replaced by the corresponding **M**'s, thus giving us the theorem,

$$\langle A(\{n_i\})\rangle = \langle f | \tilde{A}(\{\mathbf{M}\}) | f \rangle \tag{3.50}$$

where $|f\rangle = |v_0^1 v_0^2 v_0^3 \ldots\ldots\rangle = \prod_i^{\otimes} |v_0^j\rangle$ is the ground state configuration in the product space $\Phi = \prod^{\otimes}_i \varphi_i$ containing the information about all possible configuration of the system. $\mathbf{A}(\{\mathbf{M}^i\})$ is an operator functional in the configuration space Φ. This is the augmented space theorem (Mookerjee 1973, 1987). A general configuration state spinning Φ is given by,

$$\left| v_{m_1}^1 v_{m_2}^2 \ldots\ldots v_{m_i}^i \ldots\ldots \right\rangle \tag{3.51}$$

Such a state may also be defined by a sequence of points $\sigma = \{j: m_j \neq 0\}$ called the cardinality sequence at which there are excitations and cardinality C is the number of such excitation. For a binary alloy the value is 1 for each excitation. The ground state configuration in this notation is, $|f\rangle = |\varnothing\rangle$ with $\varnothing$ being the nullset. For any operator **B** in the configuration space $\langle\sigma|\tilde{B}|\sigma'\rangle \equiv B^{\sigma\sigma'}$ is a concise notation. The statement of augmented space theorem in this notation is

$$\langle A(\{n_i\})\rangle = |\tilde{A}(\{\mathbf{M}\})|^{00} \tag{3.52}$$

3.6 Application to disordered Solid

Now shall discuss the application of this formalism to binary random alloys. Let us suppose that the alloy is described by a random tight-binding hamiltonian

$$H = \sum_i \varepsilon_i |i\rangle\langle i| + \sum_i \sum_{j \neq i} V_{ij} |i\rangle\langle j| \tag{3.53}$$

By simple algebra the Green function

$$\begin{aligned} G(z) &= \left(z\hat{I} - \hat{H}\right)^{-1} \\ &= \frac{1}{z} + \frac{\hat{H}}{z^2} + \frac{\hat{H}^2}{z^3} + \ldots\ldots\ldots \\ &= \sum_{n=0}^{\infty} \frac{1}{z^{n+1}} \hat{H}^n \end{aligned} \tag{3.54}$$

and any element $G_{ij}(z)$ is given as,

$$\begin{aligned} G_{ij}(z) &= \sum_{n=0}^{\infty} \frac{1}{z^{n+1}} \langle i | \hat{H}^n | j \rangle \\ &= \frac{\delta_{ij}}{z} + \frac{H_{ij}}{z^2} + \sum_k \frac{H_{ik} H_{kj}}{z^3} + \ldots\ldots \end{aligned} \tag{3.55}$$

G_{ij} (z) has all its singularities on the real axis and is analytic in $\Im mz \neq 0$ plane. Further for the expansion (3.55)

$$G_{ij}(z) \approx \frac{\delta_{ij}}{z} \; as \quad z \to \infty$$

also,

$$\Im m\langle G(z)\rangle = -G^+(z) G(z) \Im mz \tag{3.56}$$

implying that $\Im mG(z) < 0$ for $\Im mz > 0$ in the upper half of the complex plane. The above shows that as **H** is bounded and self-adjoint, G(z) is herglotz. Taking the configuration average of the (3.56) we get

$$\Im m\langle G(z)\rangle = -\langle G^{+}(z)G(z)\rangle \Im mz \tag{3.57}$$

The average Green function thus retains the herglotizity of the exact Green function. If we define an effective medium by a translational invariant effective hamiltonian Σ than the corresponding Green function is,

$$G(z) = (z\hat{I} - \Sigma)^{-1} \tag{3.58}$$

and hence,

$$\Im mG(z) = -G(z)\Im m(zI - \Sigma)G^{+}(z) \tag{3.59}$$

As $G(z)$ is herglotz so is $\Sigma(z)$ and converse is also true, i.e. if $\Sigma(z)$ is herglotz so is $G(z)$. Now applying the augmented space theorem to find the configuration averaged Green function for the random hamiltonian (3.53) for a random binary alloy system, A_xB_{1-x}. The occupation of a site can be described by a random variable n_i defined by,

$$n_i = \begin{cases} 1 & \text{if site i is occupied by A} \\ 0 & \text{if site i is occupied by B} \end{cases} \tag{3.60}$$

The hamiltonian **H** is a function of a set $\{n_i\}$. The random parameters ε_i and V_{ij} may be expressed as,

$$\begin{aligned} \varepsilon_i &= \varepsilon_B + (\varepsilon_A - \varepsilon_B)n_i \\ V_{ij} &= V_{BB} + (V_{AA} + V_{BB} - V_{AB} - V_{BA})n_i n_j \\ &\quad + (V_{AB} - V_{BB})n_i + (V_{BA} - V_{BB})n_j \end{aligned} \tag{3.61}$$

The Green function corresponding to $H(\{n_i\})$

$$G(\{n_i\}) = [zI - H(\{n_i\})]^{-1} \tag{3.62}$$

is also a random function. The probability density $P_i(n_i)$ can be written as,

$$P_i(n_i) = x\delta(n_i - 1) + (1 - x)\delta(n_i) \tag{3.63}$$

The continued fraction expansion of $P_i(n_i)$ is given by,

$$\begin{aligned} P_i(n_i) &= -\frac{1}{\pi}\Im m\left[\frac{x}{n_i^+ - 1} + \frac{y}{n_i^+}\right] \\ &= -\frac{1}{\pi}\Im m\left[\frac{1}{n_i^+ - x - \dfrac{xy}{n_i^+ - y}}\right] \end{aligned} \tag{3.64}$$

The operator $\mathbf{M^i}$ for a binary alloy is a tridiagonal matrix of rank 2 and is given by (Mookerjee, 1987)

$$M^i = \begin{pmatrix} x & \sqrt{xy} \\ \sqrt{xy} & y \end{pmatrix} \tag{3.65}$$

Thus,

$$\begin{aligned} M^i\left|v_0^i\right\rangle &= x\left|v_0^i\right\rangle + \sqrt{xy}\left|v_1^i\right\rangle \\ M^i\left|v_1^i\right\rangle &= y\left|v_1^i\right\rangle + \sqrt{xy}\left|v_0^i\right\rangle \end{aligned}$$

A general state in the total configuration space $\Phi = \prod_i^{\oplus} \phi_i$ can be written as, $\left|f_\sigma\right\rangle = \prod_i \left|v_{mi}^i\right\rangle$

$$n_i = \begin{cases} 0 \text{ for } i \notin \sigma \\ 1 \text{ for } i \in \sigma \end{cases}$$

Thus by augmented space theorem the configuration averaged Green function is given by,

$$\langle G(\{n_i\})\rangle = \langle \phi \| z\hat{I} - \tilde{H}(\{\mathbf{M}^i\}) \| \phi \rangle \tag{3.66}$$

where $\tilde{H}(\{\mathbf{M}^i\})$ is obtained by replacing $\{n_i\}$ in $H(\{n_i\})$ by $\{\mathbf{M}^i\}$.

The rank of the basis vectors $\{|i, \sigma\rangle\}$ spanning the augmented space is $N \times M^N$. For a macroscopic system $N \sim 10^{23}$ and it is not computationally feasible to directly determine the configuration averaged quantities from the augmented space theorem.

The recursion method in Augmented Space

The methodology

The hamiltonian for the binary alloys system is represented in the tight-binding form as,

$$H = \sum_i \varepsilon_i a_i^+ a_i + \sum_i \sum_j V_{ij} (a_i^+ a_j + a_j^+ a_i) \tag{3.67}$$

The hamiltonian is an operator in real space $\boldsymbol{H}$ spanned by the countable tight-binding basis $\{|i\rangle\}$. For computational feasibility within the recursion method the hamiltonian should be short-ranged. In the TB-LMTO formalism the basis set is chosen in such way.

The random hamiltonian elements are expressed in terms of a set of random occupation variables $\{n_i\}$ which take the value 1 if the i-th site is occupied by an A atom and 0 if occupied by a B atom. Thus the diagonal element in (3.67) is

$$\varepsilon_i = \varepsilon_A n_i + \varepsilon_B(1-n_i) = \varepsilon_B + \delta n_i \tag{3.68}$$

where $\delta = \varepsilon_A - \varepsilon_B$. The off-diagonal element V_{ij} for a LCAO type approach is given by,

$$V_{ij} = n_i V_{AA} n_j + (1-n_i) V_{AB} n_j + n_i V_{BA}(1-n_j) + (1-n_i) V_{BB}(1-n_j) \tag{3.69}$$

The element $V_{CC'}$ is the overlap between the sites for occupation by C, C' type of atoms in which C, C' may be either A or B. For the TB-LMTO

$$V_{ij} = (\nabla_B^{1/2} + \delta \nabla n_i) S_{ij} (\nabla_B^{1/2} + \delta \nabla n_j) \tag{3.70}$$

where $\delta V = \nabla_A^{1/2} - \nabla_B^{1/2}$. Here $\nabla_C^{1/2}$ is the LMTO parameter for a C type of atom and S_{ij} is the TB-LMTO structure factor matrix. Within the TB-LMTO formalism S_{ij} can be chosen to be short ranged i. e. of appreciable value only upto second nearest neighbours. In either case the off-diagonal term may be written as,

$$V_{ij} = V_{BB} + V_1(n_i + n_j) + V_2 n_i n_j \tag{3.71}$$

For a spatially homogeneous disorder, and in the absence of short-ranged order the probability distribution for n_i is independent of i and as shown in previously

$$P(n_i) = x_A \delta(n_i - 1) + x_B \delta(n_i) \tag{3.72}$$

which may be written in ASF as the resolvent of a self-adjoint operator $\mathbf{M}^i \in \phi_i$, a space of rank two

$$P(n_i) = -\frac{1}{\pi} \Im m \left\langle v_0^i \middle| (n_i I - \mathbf{M}^i)^{-1} \middle| v_0^i \right\rangle \tag{3.73}$$

with $\mathbf{M^i}$ being an operator in a Hilbert space of rank two which may be written explicitly as,

$$M^i = x_A b_0^{i+} b_0^i + x_B b_1^{i+} b_1^i + \sqrt{x_A x_B}(b_0^{i+} b_0^i + b_1^{i+} b_1^i) \qquad (3.74)$$

here $b_{ik}^{\dagger}$ is a creation operator for a configuration "k" labeled 0 and 1 or $\uparrow$ and $\downarrow$ at the site of R_i. By the augmented space theorem the configuration averaged Green function is given by

$$\langle G(z)\rangle = \langle \phi \mid G \mid \phi \rangle$$

where $G(z) = (zI - H)^{-1}$

Here H is obtained by replacing n_i in *H* by $\mathbf{M^i}$ in the form

$$\hat{H} = \sum_i \varepsilon_{i\lambda} a_i^+ a_i + \sum_i \sum_{j\neq i} V_{DD} a_i^+ a_j + \delta \sum_i M_{\lambda\mu}^i a_i^+ a_i b_{i\lambda}^+ b_{j\mu} + \sum_i \sum_j \sum_\lambda \sum_\mu V_1 a_i^+ a_j \left[M_{\lambda\mu}^i b_{i\lambda}^+ b_{j\mu} + M_{\lambda\mu}^j b_{i\lambda}^+ b_{j\mu} \right]$$
$$+ \sum_i \sum_j \sum_\lambda \sum_\mu \sum_{\lambda'} \sum_{\mu'} V_2 a_i^+ a_j M_{\lambda\mu}^i M_{\lambda'\mu'}^j b_{i\lambda}^+ b_{j\mu} b_{i\lambda'}^+ b_{j\mu'} \qquad (3.75)$$

The operator ***H*** acts on the enlarged Hilbert space which is the direct product of real space spanned by the countable TB-type basis set in *H* and the configuration space $\Phi = \Pi \otimes \phi_i$ spanned by the various configurations of the model alloy. The enlarged hamiltonian doesn't involve any random variables and at the same time incorporates within itself the full information about the distribution of random variables.

The recursion for the calculation of the Green function $G_{LL'}(R_{i'}, R_i, z)$ now proceeds as follows:

The starting state may be chosen as

$$|\varsigma_1\rangle = |R_i, L\rangle \otimes |\varnothing\rangle \tag{3.76}$$

and the recursion coefficients were calculated as,

$$\beta_{n+1}^{+(L)}|\varsigma_{n+1}\rangle = \hat{H}|\varsigma_n\rangle - \alpha_n^{(L)}|\varsigma_n\rangle - \beta_n^{2(L)}|\varsigma_{n-1}\rangle \tag{3.77}$$

where

$$\begin{aligned} \alpha_n^{(L)} &= \langle \varsigma_n | \Theta \hat{H} | \varsigma_n \rangle \\ \beta_n^{(L)} &= \langle \varsigma_{n-1} | \Theta \hat{H} | \varsigma_n \rangle \end{aligned} \tag{3.78}$$

The calculation was carried out to certain number of levels N and the regular and irregular set of polynomials $\{P_n(E)\}$ and $\{Q_n(E)\}$ were introduced with proper initial condition as discussed before. The method of computing the Green function from the finite number of generated coefficients using terminator has been discussed before in Section 2.3 and a more detail may be obtained in Nex (1978), Haydock (1980), Haydock and Nex (1984).

A model Greenian was chosen

$$F(z) = \sum_{k=1}^{b} \frac{8\omega_k}{(\beta_k - \alpha_k)^2} \left[z - \frac{(\alpha_k + \beta_k)}{2} - (z - \alpha_k)^{1/2} (e - \beta_k)^{1/2} \right] \tag{3.79}$$

where α_k, β_k as explained before in Section 2.3 are the left and right band-edges and ω_k is the weight of the subband.

The terminator as we discussed before is given by,

$$T(z) = \frac{S_{n-2}(z) - F(z)R_{n-1}(z)}{\delta_n^2[S_{n-3}(z) - F(z)R_{n-2}(z)]} \tag{3.80}$$

and the Green function by,

$$G(z) = \frac{Q_{n-2}(z) - \beta_{n-1}^2 T(z)Q_{n-3}(z)}{P_{n-1}(z) - \beta_{n-1}^2 T(z)P_{n-2}(z)} \tag{3.81}$$

The terminator procedure clearly retains the herglotz properties. The configuration averaged density of states is given by,

$$\langle n(E)\rangle = \left(-\frac{1}{\pi}\right)\Im m\sum_L \langle \mathbf{R}_i, L\oplus\varnothing | G_0(E+i\delta) | \mathbf{R}_i, L\otimes\varnothing\rangle \tag{3.82}$$

Chapter Four
Spin Glasses

It was found that atomic disorder can lead to magnetic behaviour qualitatively different from that found in pure materials. The new state was termed as the spin glass (Anderson 1974). Spin glasses are random magnetic systems that exhibit several exotic properties as a consequence of frustration caused by competing ferromagnetic and antiferromagnetic exchange interactions (Adkins et. al., 1974; Tanaka, 1980). The anomalously slow relaxation observed in spin glasses is also observed in (Nagi; Weissman, 1988) many other complex systems like glasses, polymers etc.

One of the earliest attempts to formulate the theory of spin glasses was made by Edwards and Andersen (1976). They consider a classical Heisenberg model and to simplify the calculation, they replace random distribution of magnetic impurities on the lattice sites with RKKY exchange interaction by a random bond distribution, $P(J_{ij})$ between nearest neighbours with spins S_i on all lattice sites. They propose a new type of "order" parameter, which replaces, long-range spatial spin correlations, with long-time correlations

$$q(T) = \lim_{t\to\infty} << S_i(t)S_j(o) >_T >_J \neq 0$$

Here $<.....>_J$ means the configuration averaging over the distribution $P(J_{ij})$ for all pairs i, j and $<.....>_T$ means thermal averaging. The spin glass parameter q(T) is defined either for an Ising or a Heisenberg model. In both cases, a simple

mean field approximation leads to $q \neq 0$ below a chracteristic temperature T_f and to a second order phase transition at T_f (Klein et. al. 1963, 1968). However, the solution turned out to be metastable. Analytically, the most important contribution in this case was made by Shrrington and Kirkpatrick (1978) . They considered an Ising model with infinite number of interactions. I this model, a given spin interacts with all other spins with same distribution, $P(J_{ij})$. In Ideal systems similar models with the number of nearest neighbour interaction $Z \rightarrow \infty$ is exactly solvable and exhibit mean field properties. Surprisingly, the calculations of thermal properties in the Sherrington Kirkpatrick (1978) model turned out to be extremely difficult. The simplest solution has unphysical properties such as a negative entropy at T=0 and negative "Staggered" susceptiblity. Improved solutions were obtained either by fairly complicated mathematical methods, symmetry breaking schemes or by solving mean field equations derived for a fixed distribution of bonds (Thouless et. al., 1977).

Experimental studies also revealed many interesting phenomena in Spin Glass alloys (Palmer, 1984; Mookerjee,1980; Binder, 1986; Walker, 1980; Ford 1979). One of the most intensively studied systems of this type is AuFe. The transition to long-range magnetic ordering occurs at a concentration of 16% of Fe. The concentration around this has been intensively studied by means of magnetic measurements such as magnetization, ac and dc susceptibility, EPR, magnetoresistance, Mossbaur and neutron scattering (Mookerjee, 1983; Mulder, 1982; Murani, 1980). These measurements indicate that for concentration 16 to 18 at % of Fe, a low temperature ferromagnetic state appears which shows both long-range as well as spin glass like behaviour. It has now become clear that the observed properties of spin glasses are due to the large number of metastable states, the

system has at low temperatures and the fascinating properties of the system arise due to the long relaxation times required for the system to pass from one metastable states are those which are stable against flipping a single spin, i.e. the states in which each spin is parallel to its internal 'weiss' field. It was shown that (Rammal) every metastable state corresponds to a solution of the mean field equation of Thouless, Anderson and Palmer, in the cooperative phase transition model of Edwards and Anderson.

At low temperature, the system gets trapped in one of the low lying metastable states at least for a short time. The excitation corresponds to spin waves and reflects charactersitics of metastable states. At high temperatures, thermally activated or quantum mechanical tunneling, commonly known as Spin glass relaxation, become more prominent at higher temperatures or longer time scales. This phenomenon arises due to the flipping of single spins or clusters of spins as a result of which the system 'hops' or relaxes from one metastable state to another or to the global ground state. This gives rise to the irreversible or nonergodic properties of spin glass (Souletee, 1978).

Chapter Five
Results and Discussion

It is found that the atomic disorder can lead to magnetic behaviour qualitatively different from that found in pure materials. The new states goes under the name 'Spin Glass'. In this work we have calculated the density of states for the spin glass alloys.

We use the TB-LMTO programs developed at the Max-Planck institut fur Feskoerper for Schung at Stuttgart by T. A. Paxton, O. Jepsen and O. K. Andersen later redevoloped by Professor A. Mookerjee and his group. Professor Mookerjee introduced the augmented space recursion in this program. A flow diagram of the computational process is given in the table below:

Step 1	We have to transfer the unbarred potential parmeters(from Varena notes of O. K. Andersen) into the barred ones (in Ryd. units)
Step 2	We then generat the real space map for a FCC lattice for both surface and bulk.
Step 3	After generating the real space map, this step then generate the augmented space map for a FCC lattice. This is with only diagonal type of disorder.
Step 4	We now generate the hamiltonian. We run the recursion on the Augemented space map and obtain recursion on the the augmented space map and obtain recursion coefficients upto the n-th step. We process the recursion coefficients and obtain the DOS.

We have calculated the density of states for the spin glass alloys i.e. the alloys made of the transition metals and rare earth metals. We have calculated the density of states with different combination of them such as 25% of transition metals with 75% of rare earth metals, 50% of the former and 50% of the latter, and similarly 75% and 25% combination. Fig. 1 shows the density of states of AgCo for different combinations of concentrations. The transition metals have magnetization in two possible directions- up or down. There are up and down parameters given in details by Andersen. There are two sets of parameters corresponding to Co-up and Co-down. Hence we obtain two DOS of Co-alloys for up and down orientations. At the same time, we observe changes in the corresponding noble metals. The changes are small but nevertheless could be taken into account through alloying with up and down parameters of transition metals.

In the similar fashion we presented the density of states of AgFe(fig. 2), AgNi(fig. 3),AuCo(fig. 4), AuFe (fig. 5), AuNi(fig. 6), CuCo(fig. 7), CuFe (fig. 8) and CuNi (fig. 9).

Using the density of states of the above figure we have calculated the Fermi Energies, Magnetic Moments and Total Energies of the Alloys. The magnetic moments for Ag-based alloys in different concentrations are presented in the Fig. 10, and the Au-based and Cu-based alloys are presented in the fig. 11 and fig. 12 respectively. In all cases the magnetic moments XFe > XCo > XNi (where X=Ag, Au, Cu). This is because the d-band filling increases from Fe to Co to Ni and in any environment Mag. Mom. (Fe) > Mag. Mom. (Co) > Mag. Mom (Ni).

For low concentration of Fe, Co and Ni in Ag and Au, the magnetic moments are almost same in Ag and Au. If we consider the density of states for low concentration of Ag and Au with Fe, Co and Ni (Fig 1(a), Fig2(a), Fig 3(a), Fig 4(a), Fig 5(a), Fig 6(a)), the bands of the two constituents donot overlap to any extent. For example, the density of states of Fe-up and Fe-dn in 25-75 AuFe and 25-75 AgFe are quite alike, which leads to the almost similar magnetic moments. Thus, in all cases, for low concentration of Fe, Co and Ni in Au or Ag, the magnetic moments are almost same.

With increasing concentration of Fe, Co and Ni in Ag and Au, there is now slightly larger overlap between the Ag(or Au) bands and bands of Fe, Co or Ni. So the magnetic moments at higher concentrations (of Fe, Co or Ni) are slightly different for the Ag or Au based alloys.

In all cases, the magnetic moment decreases almost linearly with concentration of non-magnetic component. This is seen in experimental results prior to the spin-glass regime.

The cases of Cu based alloys are slightly different. The density of states show that for all three Fe, Co and Ni the bands of Cu overlap (Fig 7, 8 and 9) with the magnetic constituents bands. There are strong hybridization in the bands. Comparing with Au-based alloys let us consider the case of AuFe alloy. The magnetic moment of AuFe decreases from 1.6 μ_B/atom at 25-75 (25% of Au and 75% of Fe) to 0.78 μ_B/atom at 75-25 , which means a decrease of 51.25%. Similarly for AgFe, the same decrease is 50.6%. For CuFe, the change is from 1.6μ_B/atom to 0.6μ_B/atom represents a change of 62.5%. The reason of this larger change is as

follows:- the strong hybridization of the Cu and Fe bands results (at higher concentrations) in an increase of the Fe band-width. From the Stoner Criterion this leads to a decrease of magnetic moment. The same argument hold for CuCo and CuNi alloys. For CuNi the magnetic moment almost vanishes at 75-25. The spin glass regime takes over before this and our argument donot hold.

Fig, 13, Fig 14 and Fig 15 represents the Total Energy per atom calculated from the density of states given in the Fig. 1-9 for Ag, Au and Cu based alloys. We obtained a linear variation with component A energy and component B with concentration. This result is expected if there are no short range ordering or clustering effects. These figures depicted that such effects are not present in the alloys discussed above. Any strong deviation from linearity will indicate such effects and then we have to modify our calculations to include short ranged ordering (SRO).

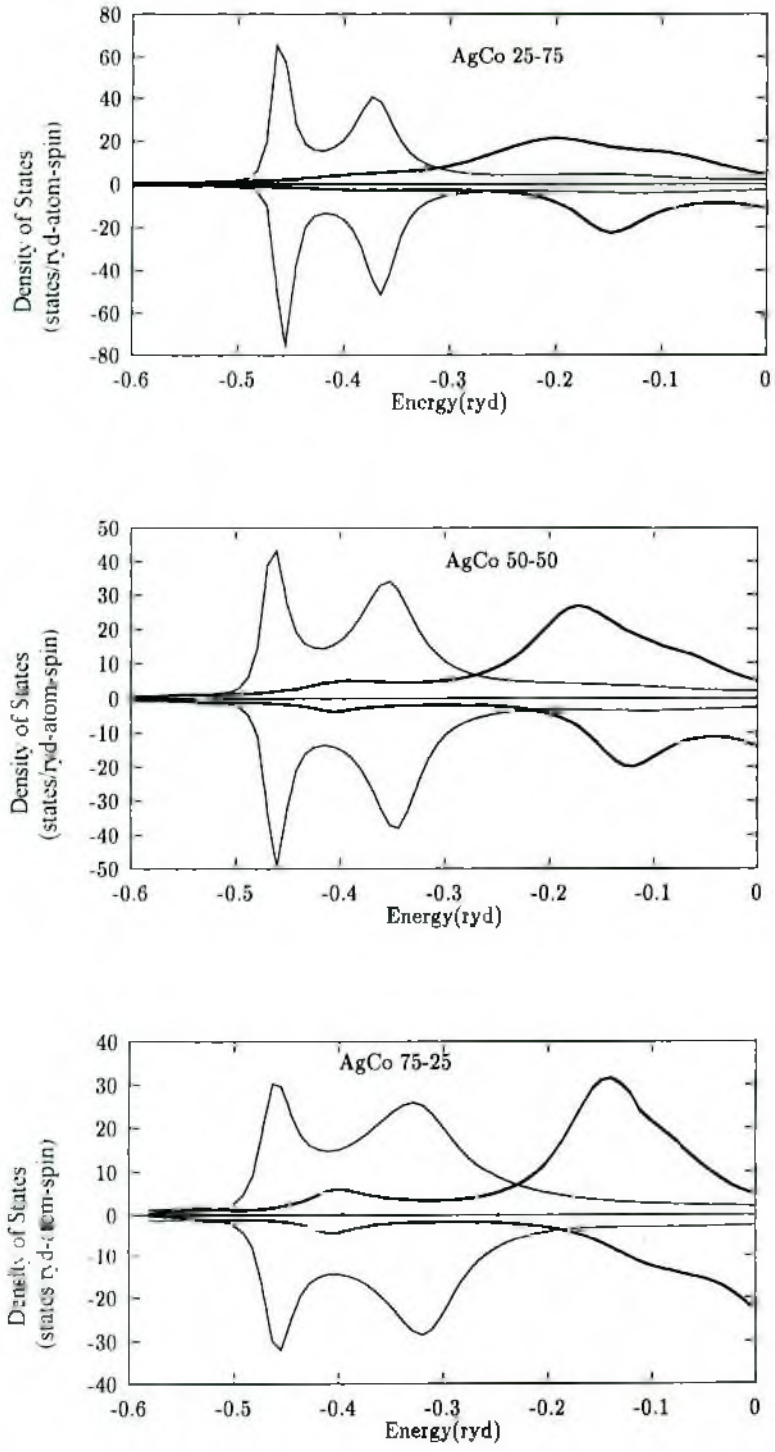

Fig1. Density of States (States/ryd-atom-spin) of AgCo alloys against energy for a) Ag 25%, Co 75%,b) Ag50%, Co50% and c) Ag75%, Co25%

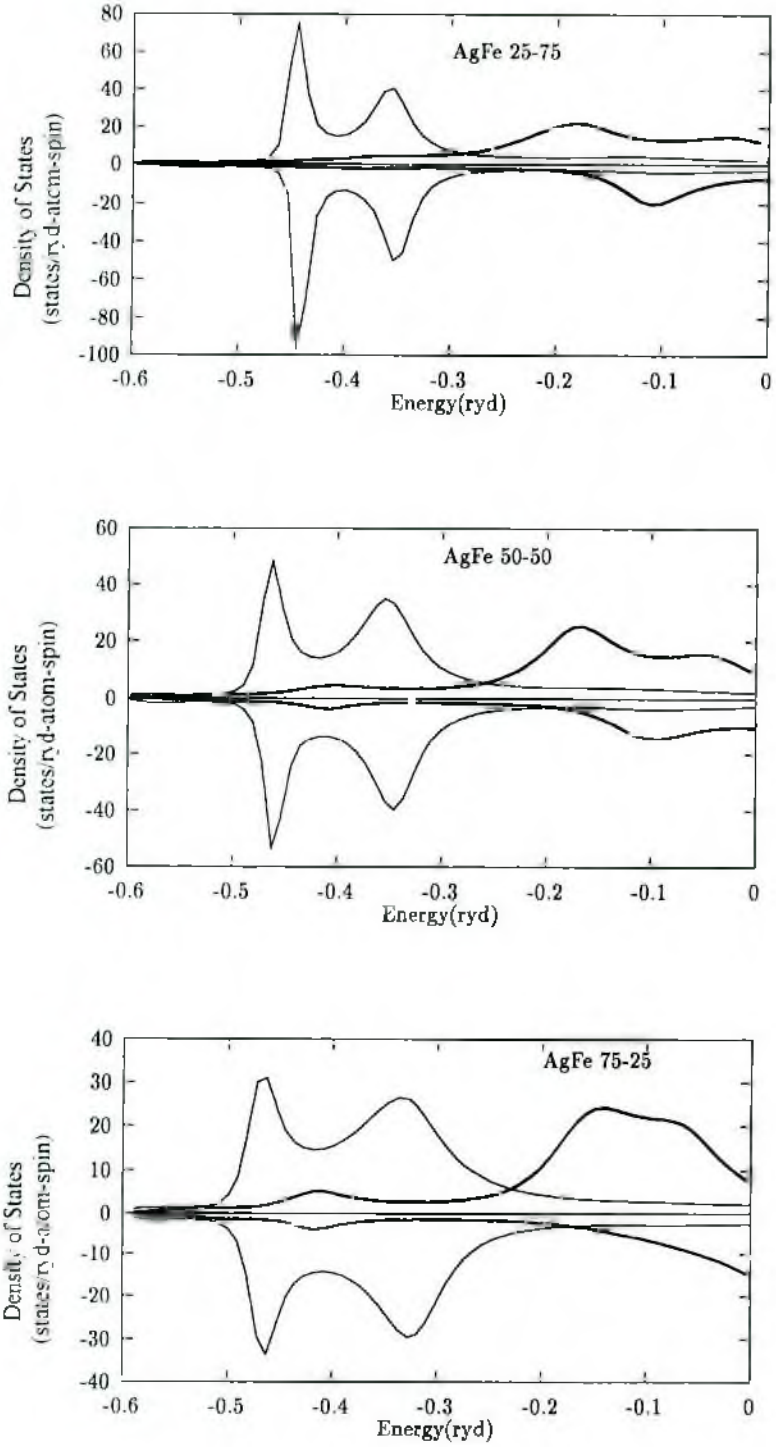

Fig2. Density of States (States/ryd-atom-spin) of AgFe alloys against energy for a) Ag 25%, Fe 75%,b) Ag50%, Fe 50% and c) Ag75%, Fe25%

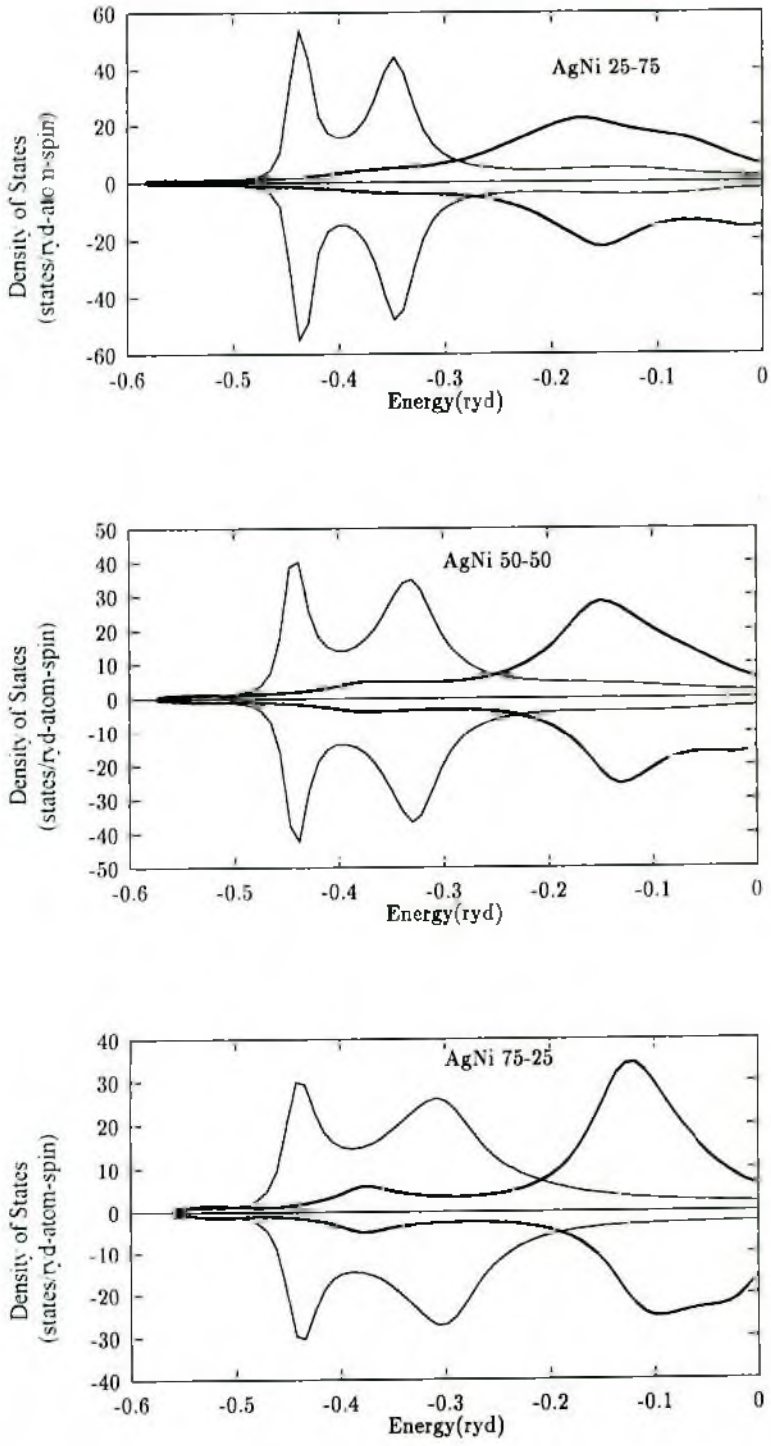

Fig3. Density of States (States/ryd-atom-spin) of AgNi alloys against energy for a) Ag25%, Ni75%,b) Ag50%, Ni50% and c) Ag75%, Ni25%

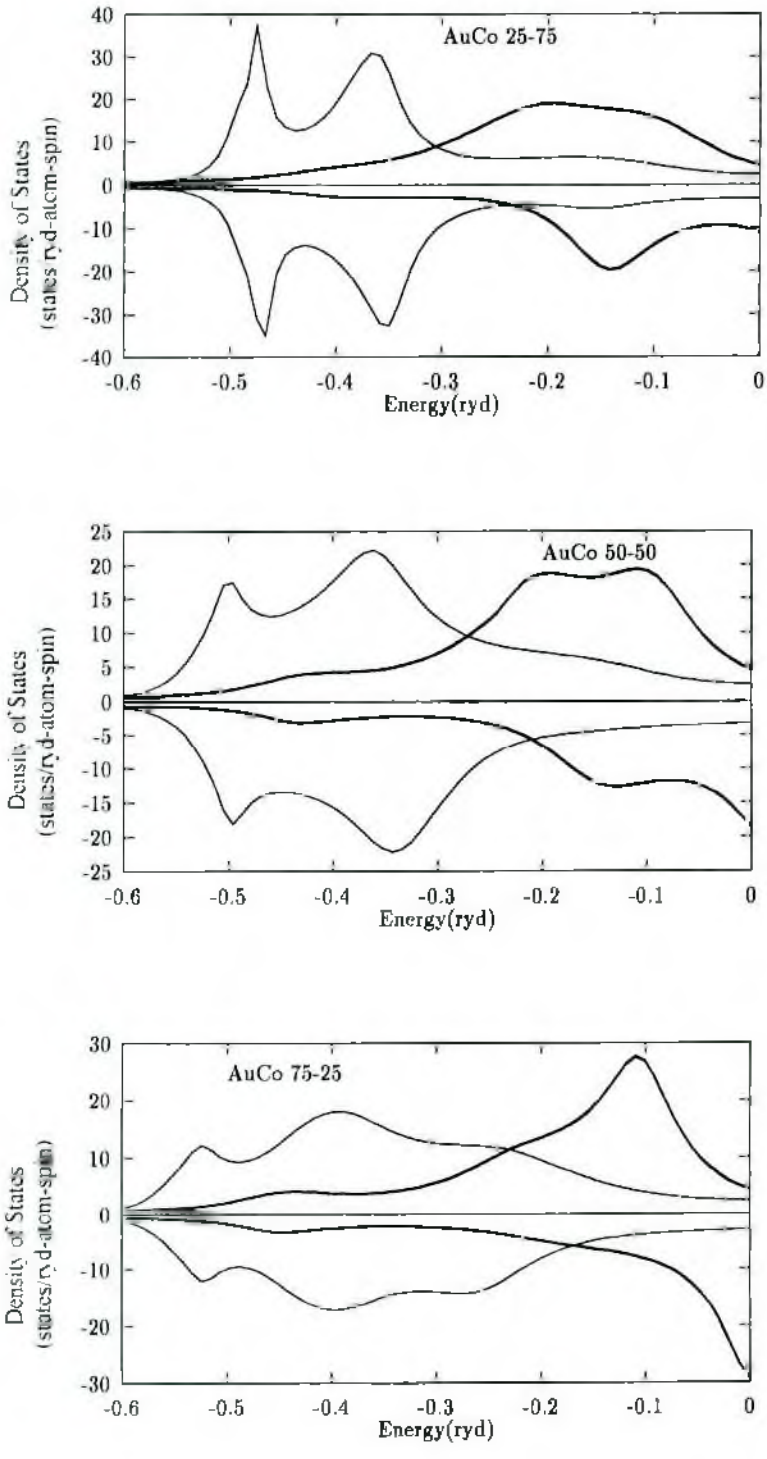

Fig4. Density of States (States/ryd-atom-spin) of AuCo alloys against energy for a) Au 25%, Co 75%,b) Au50%, Co50% and c) Au75%, Co25%

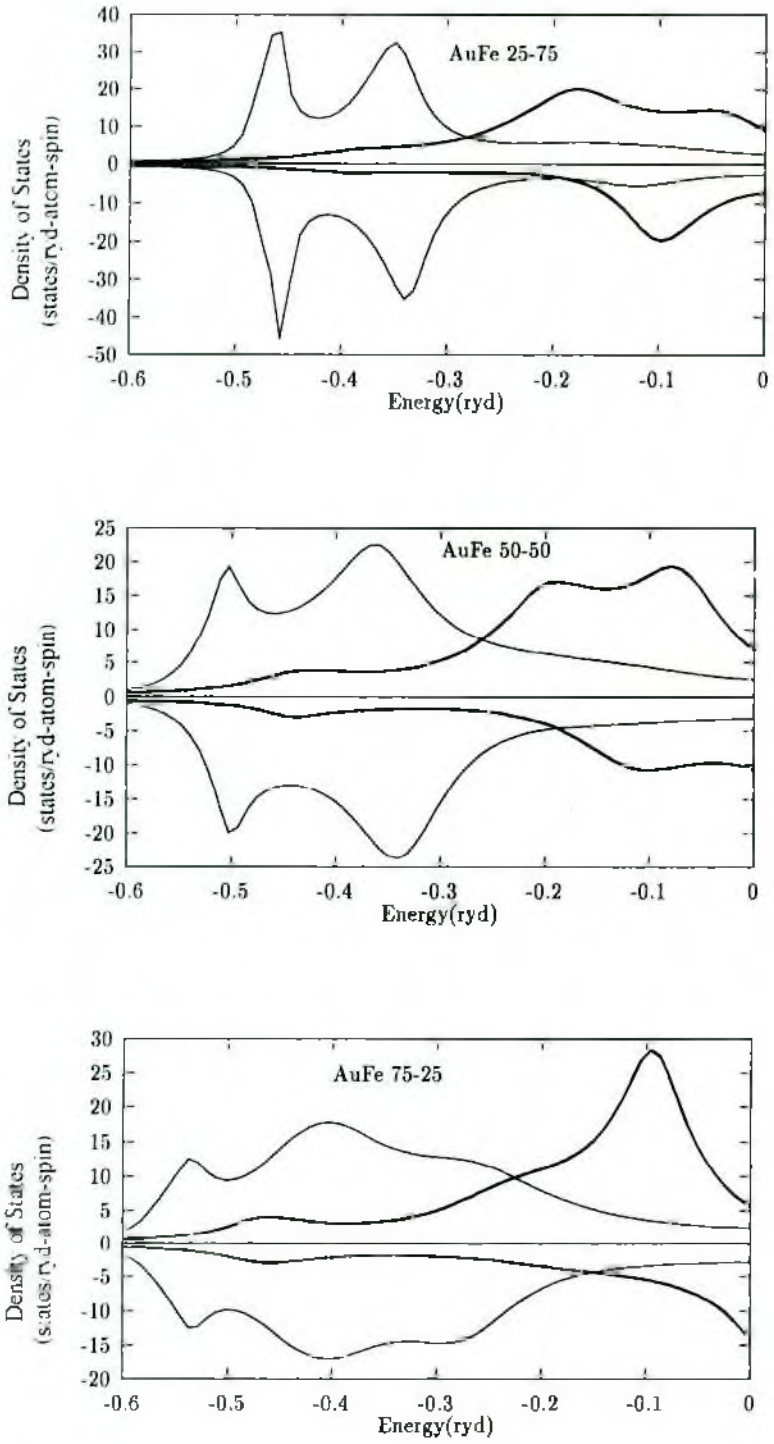

Fig5. Density of States (States/ryd-atom-spin) of AuFe alloys against energy for a) Au25%, Fe75%,b) Au50%, Fe50% and c) Au75%, Fe25%

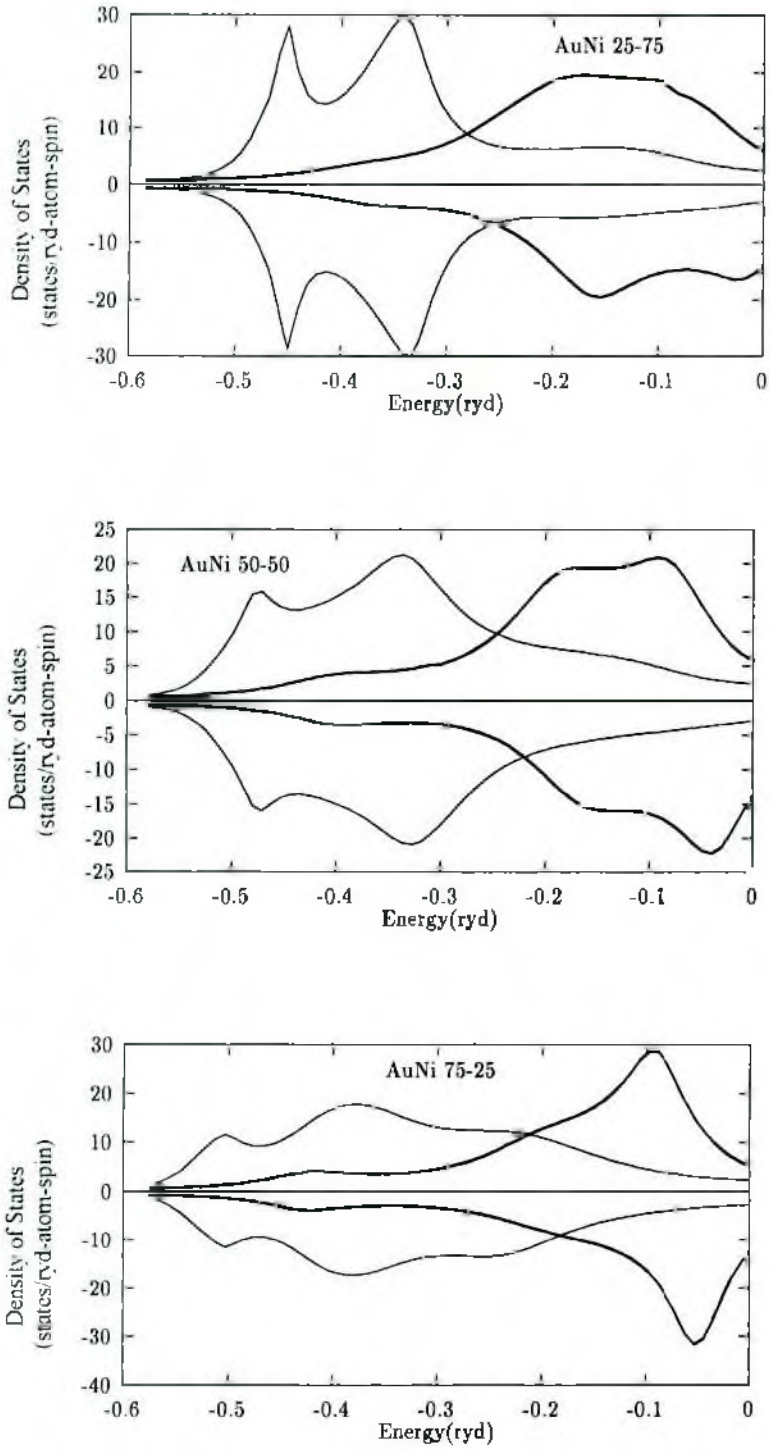

Fig6. Density of States (States/ryd-atom-spin) of AuNi alloys against energy for a) Au25%, Ni75%,b) Au50%, Ni50% and c) Au75%, Ni25%

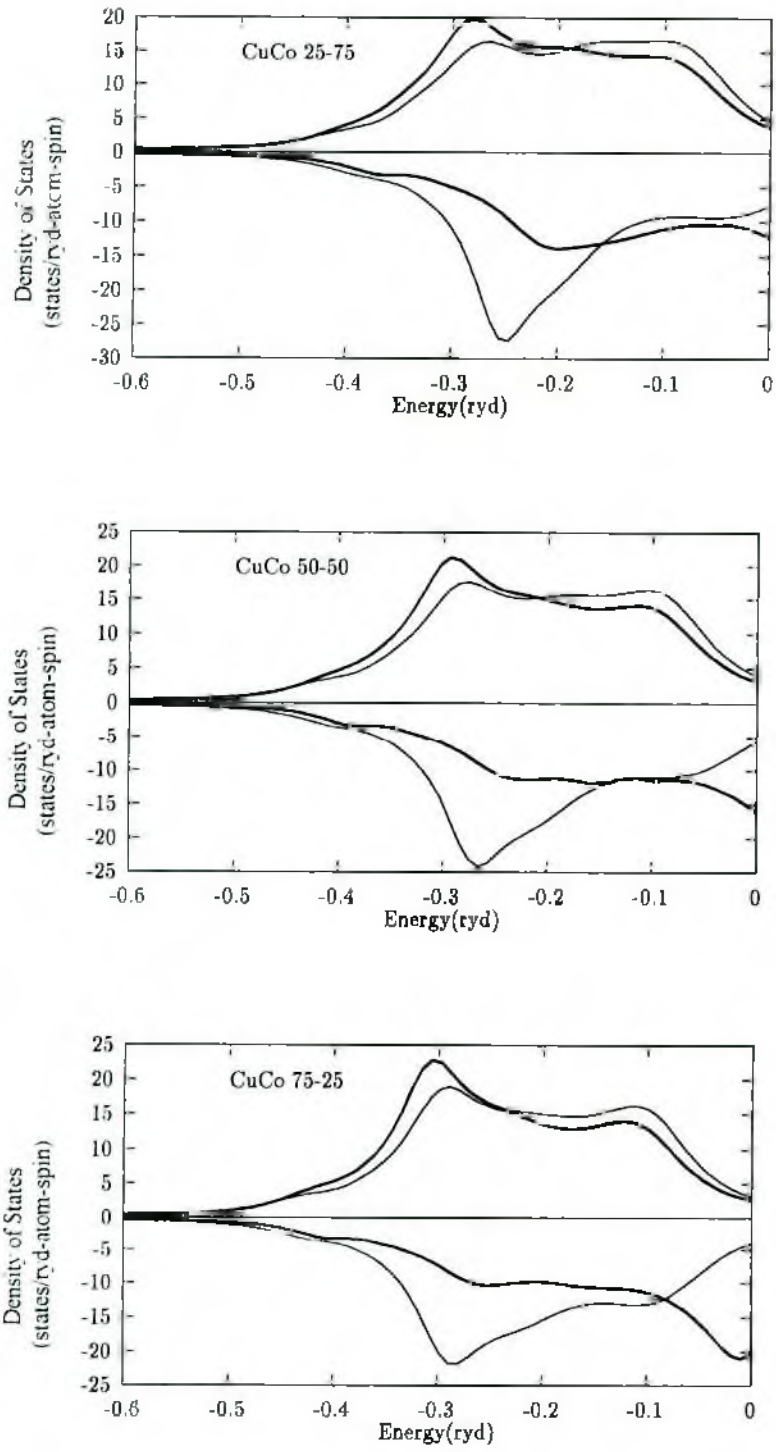

Fig7. Density of States (States/ryd-atom-spin) of CuCo alloys against energy for a) Cu25%, Co75%,b) Cu50%, Co50% and c) Cu75%, Co25%

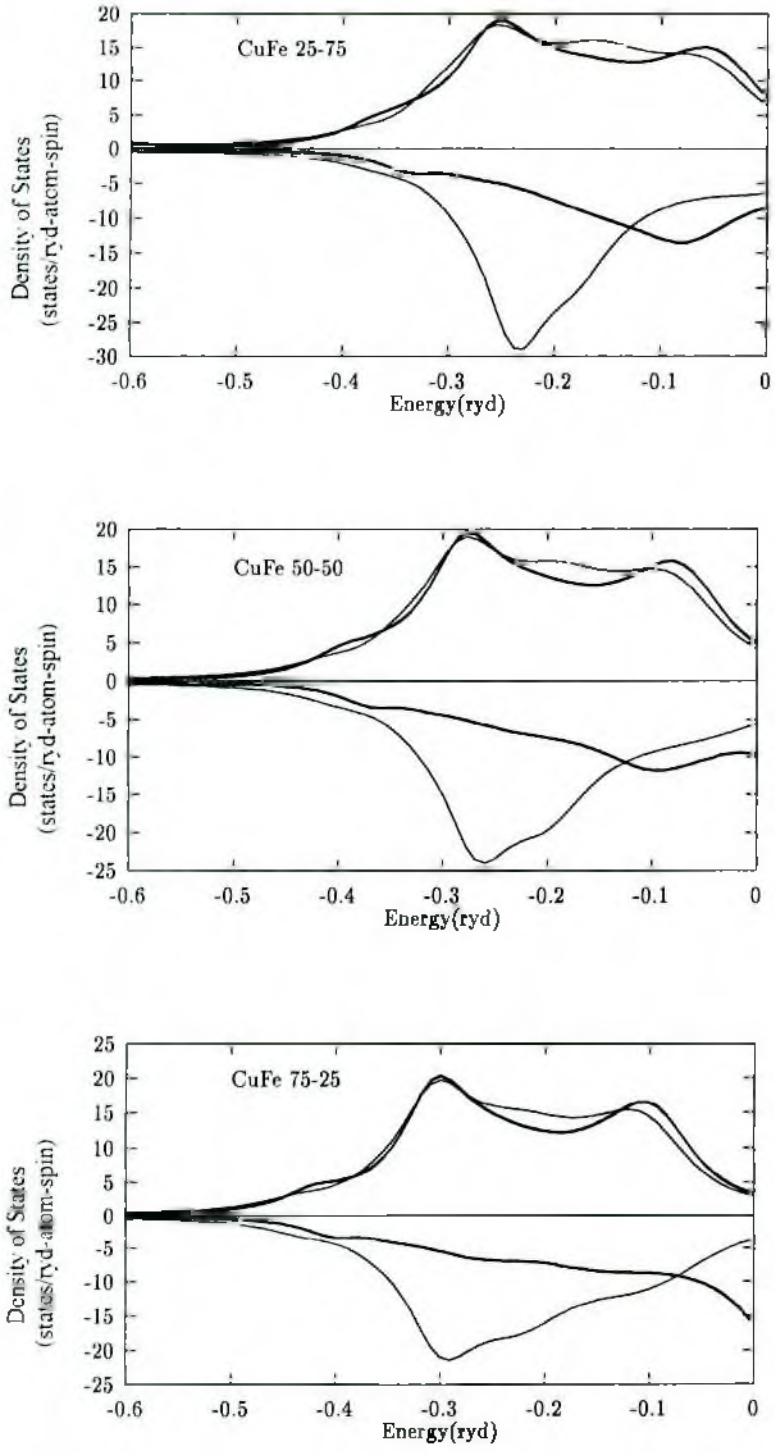

Fig8. Density of States (States/ryd-atom-spin) of CuFe alloys against energy for a) Cu25%, Fe75%,b) Cu50%, Fe50% and c) Cu75%, Fe25%

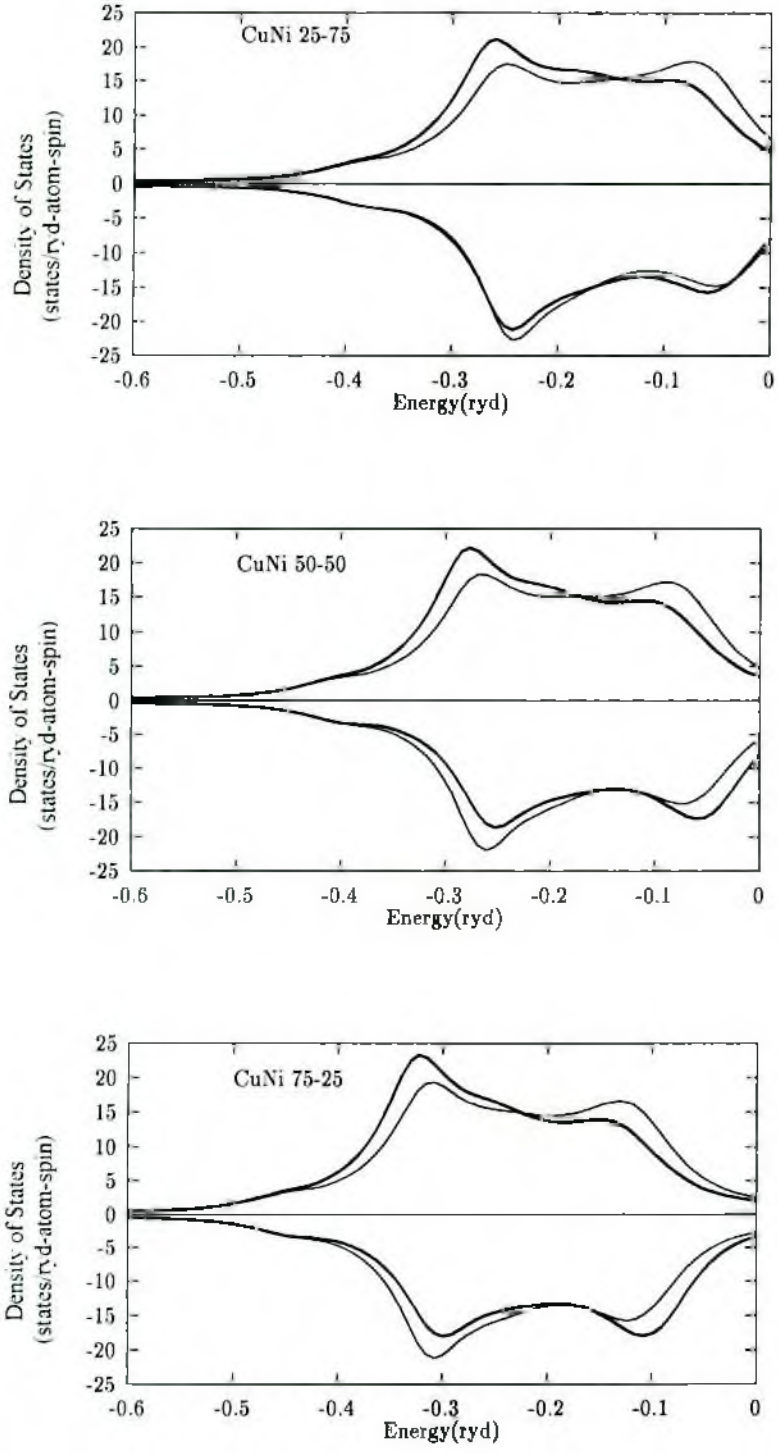

Fig9. Density of States (States/ryd-atom-spin) of CuFe alloys against energy for a) Cu25%, Ni75%,b) Cu50%, Ni50% and c) Cu75%, Ni25%

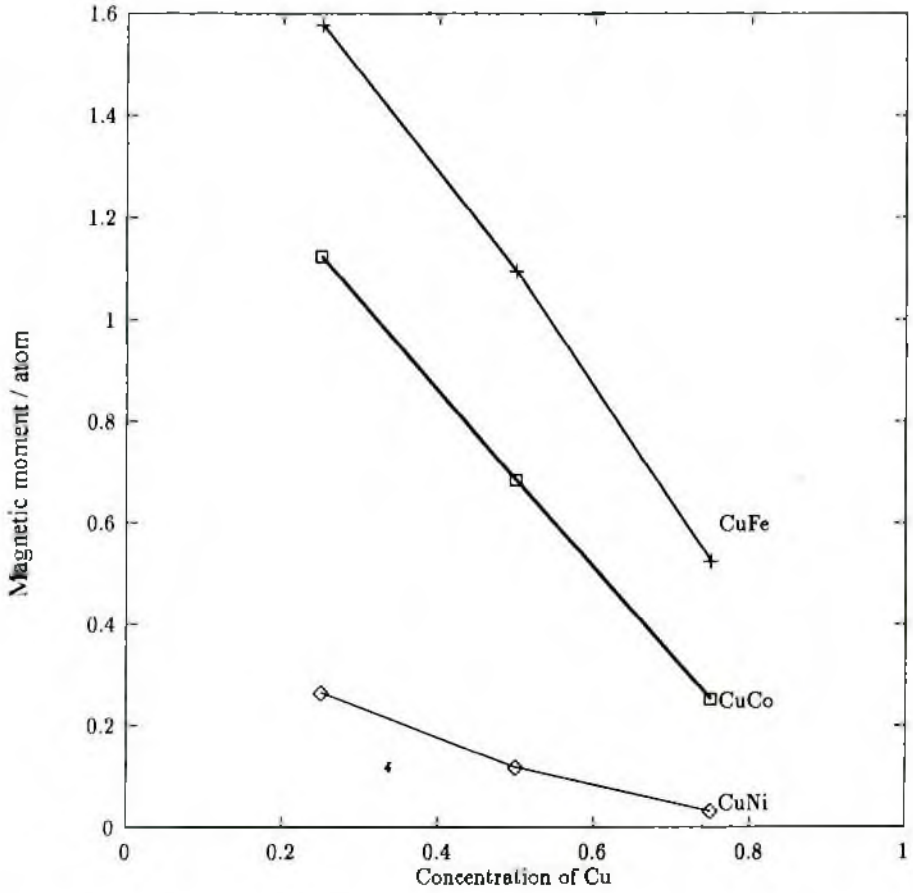

Fig10. Magnetic moment per atom of CuFe, CuNi and CuCo against concentration of Cu

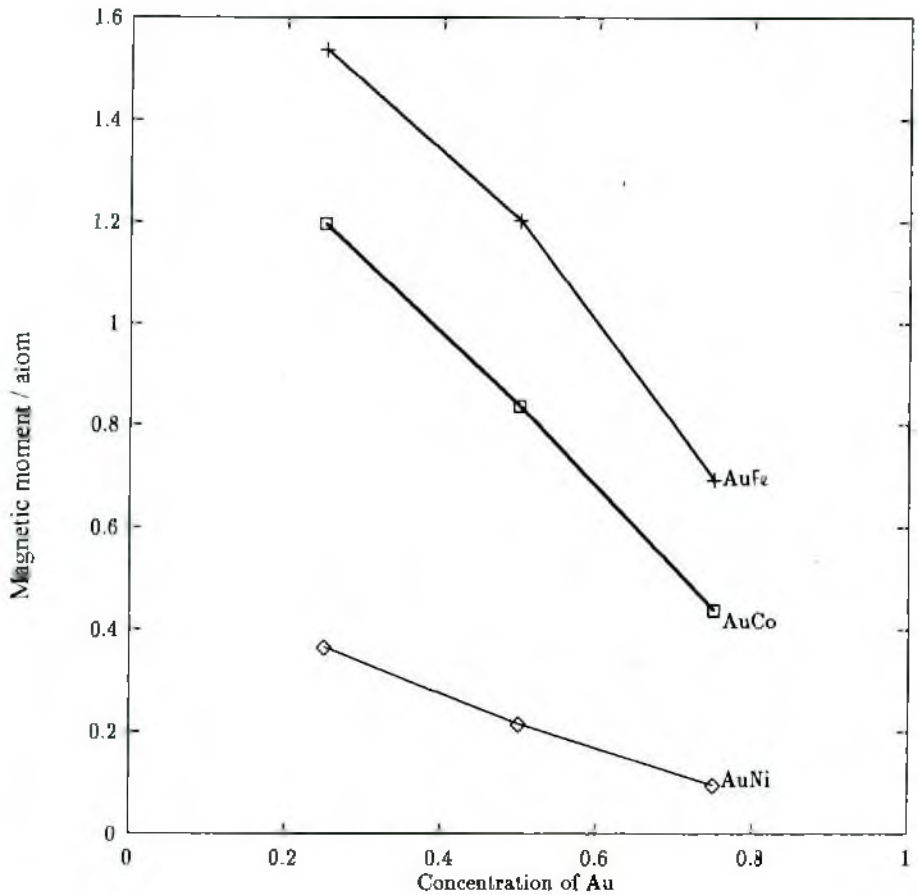

Fig11. Magnetic moment per atom of AuFe, AuNi and AuCo against concentration of Au

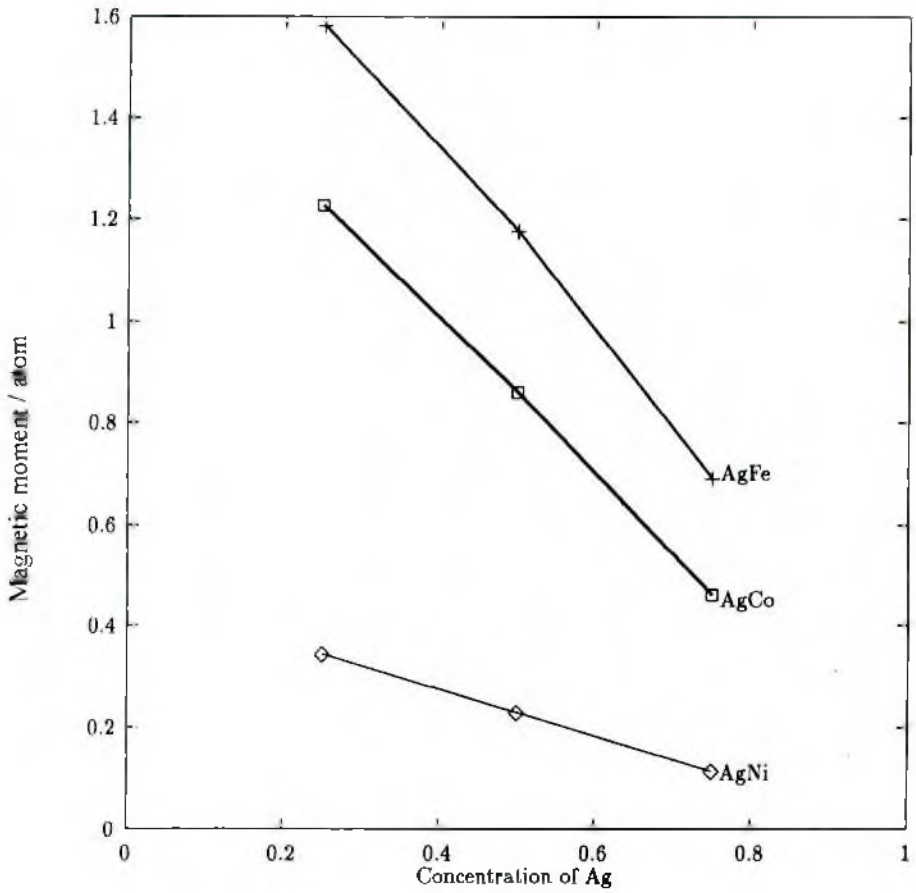

Fig12. Magnetic moment per atom of AgFe, AgNi and AgCo against concentration of Ag

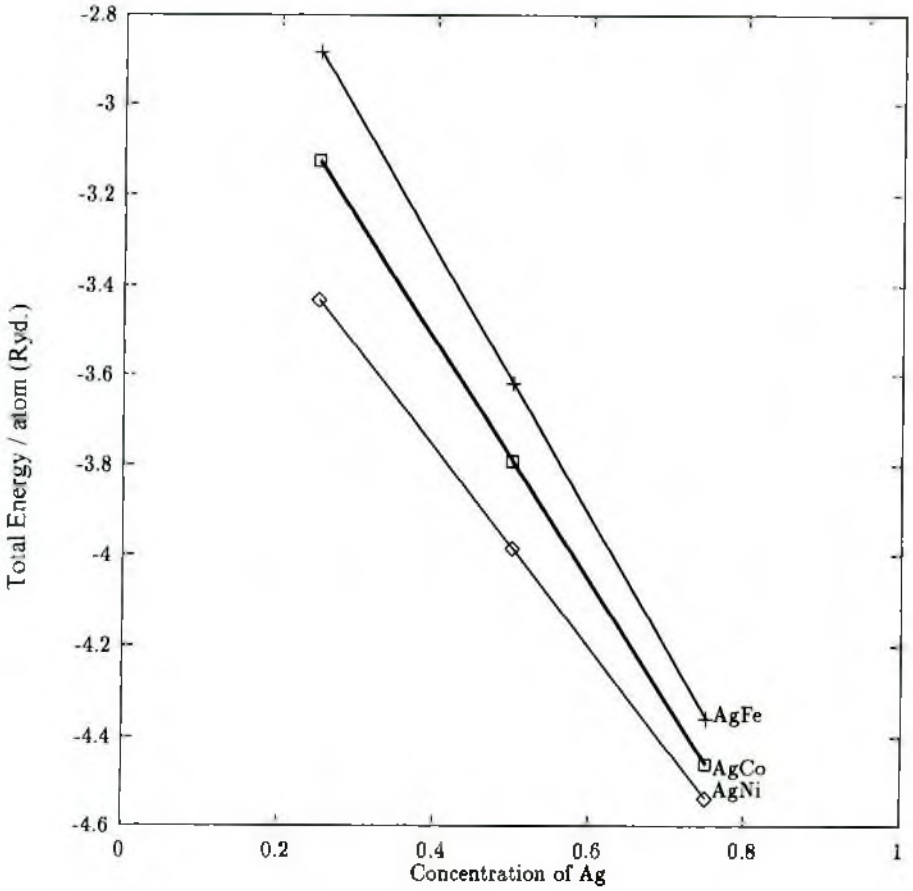

Fig13. The total energy of AgFe, AgNi and AgCo against concentration of Ag

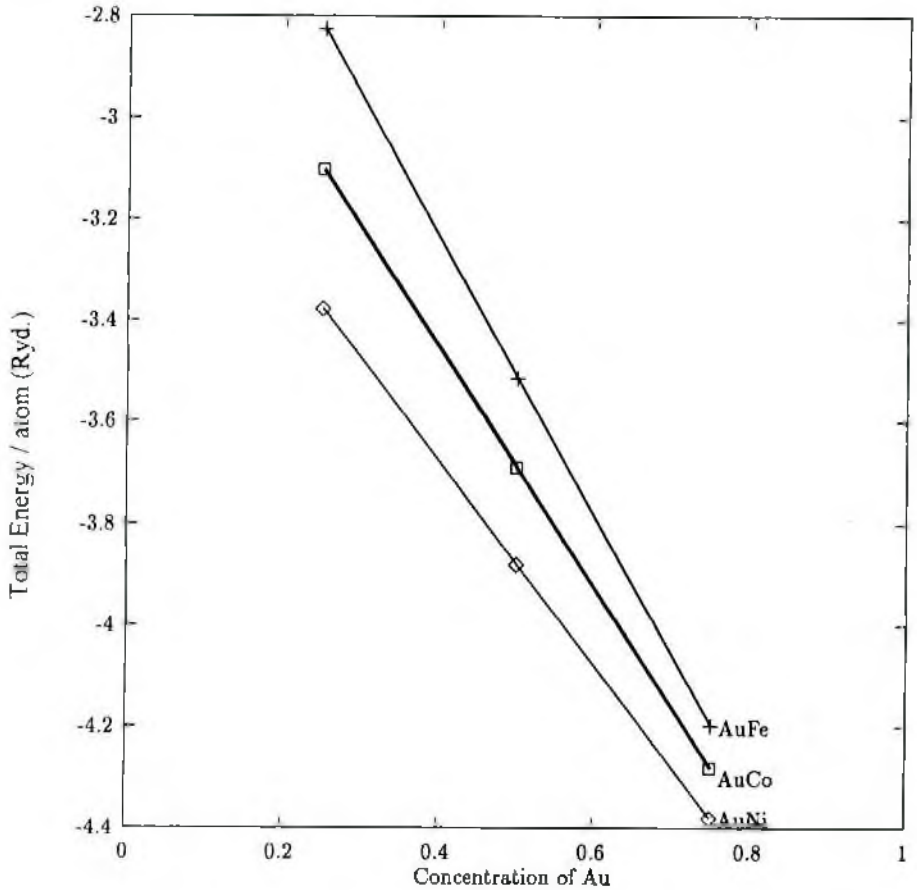

Fig14. The total energy/atom of AuFe, AuNi and AuCo against concentration of Au

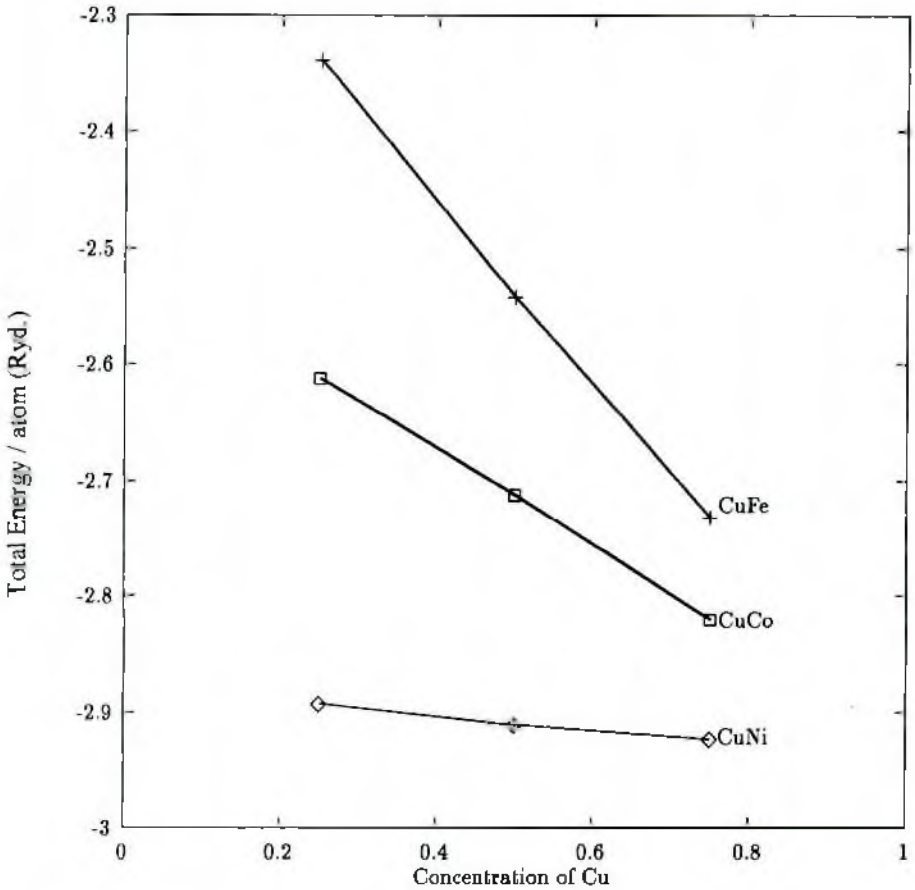

Fig15. The total energy/atom of CuFe, CuNi and CuCo against concentration of Cu

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