Chapter 2

ELECTRONIC STRUCTURE OF DISORDERED ALLOYS WITH UNCORRELATED DISORDER *

2.1 INTRODUCTION AND MOTIVATION

Tailoring materials with a desirable set of properties for intended applications, is one of the important aspects in the present day materials research. Atomistic simulations of physical properties from first principles has become matured with the advent of powerful computers, and can be exploited for predicting the behaviour of materials without actually synthesizing them. Progress in electronic structure methodologies has made it possible today to get estimates (with accuracy $\sim 0.01$ ev/atom) of ground state properties like bulk and shear moduli, cohesive energy, heat of formation etc. as well as other mechanical, electronic, optical, magnetic and superconducting properties of bulk solids, surfaces and interfaces. The recent advances in the first principles calculations of material properties may be attributed to the following developments: (a) The Hohenberg-Kohn-Sham density functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) which rigorously proved, that the complicated and unmanageable many electron problem can be transformed into an effective one-electron problem, which in turn can be solved within the so called local density approximation. (b) The linearized band structure methods, introduced by Andersen (1975) for solving the electronic structure of solids. The linearized augmented plane wave (LAPW) and the linearized muffin tin orbital method (LMTO) (Andersen, 1975), the linearized version of the augmented plane wave (APW) (Slater, 1937) and Korringa Kohn and Rostoker (KKR) (Korringa, 1947; Kohn and

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Rostoker 1954) respectively, are most widely used today for *ab initio* (i.e. without any a priori assumptions regarding inter-atomic interactions) investigation of materials. In particular the tight-binding (TB) LMTO method (Andersen and Jepsen, 1984) which combines the simplicity of empirical tight binding (TB) method with the accuracy and rigour of a first principles approach, has turned out to be an ideal tool for handling both ordered as well as disordered solids.

The theoretical development sketched in the preceding paragraph yields reasonable results for ordered solids, but it has to be supplemented with other considerations for the study of electronic structure of disordered solids. In the recent times the disordered metallic alloys are used in an enormous variety of applications. The reasons for this ubiquitous use revolve around the possibility of modifying their properties—strength, ductility, corrosion, resistance, thermal and electrical properties etc., to meet specific engineering requirements. The design of alloys with specific properties demands, at the microscopic level, first principles parameter free calculations of the electronic structure.

In contrast to ordered solids, the calculation of any physical properties of disordered alloys requires configuration averaging over all realizations of the random variables characterizing the disorder. Most experiments measure configurationally averaged properties. The configuration averaging is usually achieved in the framework of the coherent potential approximation (CPA) (Soven 1967, Taylor 1967). The essence of the CPA is to replace the array of random potentials by an effective energy dependent coherent potential \( \Sigma(z) \). The scattering properties of \( \Sigma(z) \) are then determined self-consistently (in a single site mean-field sense), from the requirement that an electron travelling in an infinite array of \( \Sigma(z) \) undergoes on average, no further scattering upon replacement of any \( \Sigma(z) \) with the actual potential. So CPA is a self-consistent prescription which allows one to obtain an effective non-random Hamiltonian. CPA coupled with first principles band structure methods in the framework of LDA provides a starting point for the *ab initio* calculation of the electronic structure of disordered alloys. This has been achieved both in the framework of KKR (Stocks et. al., 1977) and TB-LMTO (Kudronovský and Drchal, 1990) for the description of the electronic structure of disordered alloys. Though CPA provides reliable results, there are many situations where the single site approximation inherent in CPA begins to fail: as in cases where clustering effects become important (e.g. in the impurity bands of split band alloys, like Zn band in Cu rich CuZn alloy), where short range order dominates leading to ordering or segregation, where local lattice distortion because of size mismatch of the constituents leads to essential off diagonal disorder (as in CuPd and CuBe alloys). Some of these lead to true off-diagonal disorder in the Hamiltonian which cannot be treated in either an additive or multiplicative form, which reduces it to an equivalent diagonal disorder problem.

The preceding discussion suggests that there is a growing need for an alternative scheme for configuration averaging which could take into account some of the effects which could not be studied within CPA. In this respect we have proposed and implemented a new method for configuration averaging based on the recursion method of Haydock et. al (1972) and the augmented space theorem of Mookerjee (1973a). The coupling to the recursion method is
intrinsically multisite so the method does not involve any single site approximation. As a result both diagonal as well as off diagonal disorder can be treated on an equal footing. This method, coupled with the first principles linearized band structure methods like TB-LMTO, constitutes a promising method for the first principles description of the electronic structure of disordered alloys. This method retains the Herglotz analytic properties of the configuration averaged Green function \( G(z) \) i.e.:

1. \( G(z) \) is analytic everywhere except for parts of the real axis.
2. its spectrum is bounded and \( G(z) \) behaves like \( 1/\mathbb{z} \) as \( z \to \pm\infty \) on the real \( z \) axis.
3. \( \text{Sgn}\{\Im G(z)\} = -\text{Sgn}\{\Im m(z)\} \)

Further, we have used the local point group symmetries of the underlying lattice and the larger symmetries in the full augmented space arising out of homogeneity of disorder. This allows us to work on a small irreducible subspace of the augmented space, greatly reducing our computational effort. The description of the augmented space recursion method together with its application to specific alloy systems is the main objective of this chapter.

The remainder of this chapter is organised as follows: In section 2.2 we shall review the various one electron band structure methods, in section 2.3 we shall discuss the TB-LMTO method in some details. This will be the basis of our future work on disordered alloys. Section 2.4 will be devoted to the description of configuration averaging. In section 2.5 we will examine the various mean-field approximations proposed for configuration averaging based on the single site approximation. Section 2.6 will constitute the cluster generalizations of CPA and their applications. In section 2.7 we shall examine the recursion method as an alternative to band structure calculations. In section 2.8 we shall discuss the augmented space theorem. Section 2.9 will constitute the detailed description of the augmented space recursion. In section 2.10 we shall discuss the computational details and in section 2.11 we shall present our results. We will present our conclusions in section 2.12.

2.2 THE ONE ELECTRON PROBLEM

Our present day fundamental understanding of materials and material properties are associated with our increasing ability to apply the principles of quantum mechanics to study the material world at a microscopic level. In particular it is the stationary Schrödinger equation:

\[
[-\nabla^2 + V] \psi = E \psi
\]

(2.1)

(along with appropriate boundary conditions), which allows us to take into account the interactions among the various sets of particles, that form the cornerstone of such studies. The potential \( V \) in general stands for all possible interactions between the particles comprising a
given system: the interactions among the electrons, among the nuclei and between the electrons and the nuclei. It is not hard to realize that the solution of the Schrödinger equation under an all inclusive form of $V$ is by no means an easy task. One has to invoke approximations in the form of $V$, to get approximate solutions. This at first glance appears as a rather restrictive set of affairs, but can be a blessing in disguise. The exact wavefunctions containing the interactions and motions of say Avogadro's number of particles could hardly be presented in a recognizable form to yield any useful information. On the other hand the wavefunction associated with a judiciously chosen albeit approximate interaction $V$, can reveal a great deal about the physical properties of a system.

One of the approaches which is usually adopted in the present day first principles electronic structure calculations is the so called one-electron or single-particle picture. Here one assumes that it is meaningful to study the behaviour of a single electron in an average field $V(r)$, produced by other electrons and the nuclei. The Hohenberg Kohn Sham density functional formalism provides a self-consistent prescription of calculating the one electron potential $V(r)$. In practice, one uses the local density approximation (LDA), where the coulomb interaction is written as a sum of direct potential $V_Q$ as seen by a given electron due to the charge distribution in the system and the exchange correlation part $V_{xc}$, which at a given position depends only on the local charge and spin-charge densities. One solves equation (2.1) for one electron in a local potential $V(r)$ characteristic for a system of atoms, to obtain the charge density:

$$\rho(r) = \sum_{j \in occ} |\Psi_j|^2$$  \hfill (2.2)

and subsequently uses it to find the potential $V(r)$ for the next iteration towards charge (and spin) self-consistency by solving Poisson's equation for the Hartree part and by using the density functional description for the exchange-correlation part. 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 electronic structure reduces to the self-consistent solution of the Hohenberg-Kohn-Sham equations. For crystalline solids 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, $E(\vec{k})$ for a $\vec{k}$ vector in the first Brillouin zone of the reciprocal lattice. Pseudopotentials (Pickett, 1989) as well as all electron methods have been used to solve the Hohenberg Kohn Sham equations for a large number of solids. First principles pseudopotentials with plane wave bases are extremely successful for s-p band materials in particular. The only restriction is that the pseudopotentials should be sufficiently weak to allow expansion of the pseudo-wavefunctions as plane waves. This automatically eliminates a large class of materials from consideration. In particular for materials containing less broad bands, such as transition metals, rare-earths, actinides and many oxides and halides, the pseudopotential becomes quite deep, making the use of plane wave basis set tedious and rather impractical. In order to treat s,p,d and f electrons on the same footing it is necessary to use the full one-electron potential from all the electrons in the presence of nuclei.
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 waves, Gaussian orbitals etc. (Callaway, 1964)

(b) Partial wave methods: here the wavefunction is expanded in a set of energy and potential dependent partial waves like the Wigner-Seitz cellular method (Callaway, 1964) the augmented plane wave method (APW) and the Korringa-Kohn-Rostoker (KKR) method.

The essential disadvantage of the fixed basis sets is that they must be large inorder to be reasonably complete, but for the methods based on partial waves this requirement is minimal, only s,p,d and perhaps f orbitals are required for the description of the electronic structure. Further , in a self-consistent calculation, the partial waves form a dynamical basis set always adapted to the potential and energy in question. Most importantly, the partial waves apply equally well to any atom in the periodic table. The main drawback of the methods based on partial waves is that, for the evaluation of the one-electron energies , it involves the solution of a secular equation which, in contrast to fixed basis set, has a complicated non-linear energy dependence. Even for moderately sized matrices this requires orders of magnitude more computation in the solution of an eigenvalue problem with the same matrix size.

An important breakthrough in this direction, where the effort of computation is reduced but the accuracy is preserved, is the introduction of the linearized band-structure methods by Andersen. These methods combine all the desirable features of the classical methods using the fixed basis functions and those of the partial waves. As a result LAPW and LMTO, the linearized versions of APW and KKR respectively, have emerged as powerful tools for the first principles calculation of electronic structure. The most recent advance in the linearized methods, is the tight-binding version of LMTO, proposed by Andersen and Jepsen (1984). The TB-LMTO not only combines the simplicity of the empirical TB-method and the accuracy and rigour of a first-principles approach but also gives a short ranged basis set. This short ranged basis set results in a sparse representation of the Hamiltonian. This is ideal for the study of the disordered systems. In contrast to empirical tight-binding methods , the TB-LMTO Hamiltonian is parametrized by a set of potential parameters (to be discussed later in the text) which are derived self-consistently from a first-principles theory and are not fitted quantities. In our subsequent calculations we shall employ the TB-LMTO for the description of the electronic structure of disordered alloys. This is discussed in detail in the next section.

2.3 THE METHOD OF LINEARIZED MUFFIN TIN ORBITALS

The method using partial waves and the muffin-tin approximation, is based on the assumption that inside the atoms where the kinetic energy $| \epsilon - V(r) |$ is numerically large and the...
wavefunctions varies rapidly, the potential is essentially spherically symmetric. The muffin-tin approximation (MTA) retains only this part of the potential inside atom-centered muffin-tin spheres. As a consequence, the Schrödinger's equation becomes separable in this part of space. The potential in the interstitial region between the spheres is weakly varying and is taken to be flat in the muffin-tin approximation. The LMTO is based on the MTA and the notable features (Andersen et. al., 1985) of the formalism are:

1. The description of metals, including transition metals, as well as semiconductors and insulators are treated on an equal footing.
2. The LMTO basis set is minimal, orbitals at most upto the f-levels only are needed for an accurate description of electronic structure in solids.
3. The LMTO orbitals centered at a given site may be expanded about other sites in terms of radial functions, spherical harmonics and structure constants. Within the atomic sphere approximation (ASA), the Wigner-Seitz (WS) cells are substituted by slightly overlapping Wigner-Seitz spheres. This leads to factorization of the matrix elements of a given operator into products of structure constants and radial integrals.
4. The original long ranged LMTO $\chi_{RL}(r)$ basis set can be transformed exactly into new basis sets, with varying degree of localization in real space.
5. The LMTO set is complete for the muffin-tin potential used in its definition, but it can be used also to treat potentials other than muffin tin ones where there is no shape assumption in the charge density or the potential.

2.3.1 Muffin-Tin Orbitals (MTO) And Their Representation

In the LMTO method, an energy independent basis set $\chi_{RL}(r)$ is derived from the energy dependent partial waves in the form of muffin-tin orbitals (MTO). The set is constructed in such a way that it has the following characteristics:

(a) it is appropriate to the one electron effective potential $V(r)$ of the solid
(b) it is a minimal basis set
(c) it is continuous and singly differentiable in all space.

As a first step in the LMTO method, the space is partitioned into two regions, viz. the muffin tin spheres centered at various atomic (if necessary, also interstitial ) sites $R$ and the interstitial region. In the atomic sphere approximation (ASA) the touching muffin tin spheres are substituted by overlapping Wigner-Seitz spheres, thereby dispensing with the interstitial component. The ASA is a reasonable approximation (Andersen et.al., 1985) provided that
there are few electrons in the interstitial region or the overlap between the Wigner-Seitz (WS) spheres is less than 30%. The ASA is possible for closely packed materials, as well as for those open structures which, through addition of interstitial *empty spheres*, can be made to be closed packed. All the calculations presented in this thesis are based on the ASA.

The energy-independent muffin-tin orbitals (MTO) $\chi_{RL}^\alpha (r_R)$, with collective angular momentum index $L=(\ell\, m)$ centered at the lattice site $R$ corresponding to a general MTO representation $\alpha$ in the ASA are:

$$\chi_{RL}^\alpha (r_R) = \phi_{RL} (r_R) + \sum_{R'L'} \phi_{RL'}^\alpha h_{RL,R'L'}$$  \hfill (2.3)

$$\phi_{RL} (r_R) = \phi_{R}(r_R) + \phi_{RL}(r_R) \phi_{RL}^\alpha$$  \hfill (2.4)

$$\phi_{RL}(r_R) = \phi_{R}(r_R) Y_L(r_R)$$

where $r_R = r - R$, $r_R = r_R | r_R |$ and $Y_L$'s are the spherical harmonics. The function $\phi_R$ is the solution of the radial scalar-relativistic Schrödinger equation for the spherically averaged one-electron LDA potential $V_R(r_R)$ at some reference energy $E_{\nu,RL}$ and is normalized to unity within the sphere of radius $s_R$ at $R$. The energy $E_{\nu,RL}$ is usually chosen to be in the middle of the energy interval of interest (e.g. centre of gravity of the occupied part of the band). The quantity $\phi_{RL}^\alpha = \langle \phi_{RL} | \phi_{RL} \rangle$ is the overlap. The expansion coefficients $h^\alpha$ in equation (2.3) are determined in such a way that the wavefunction is continuous and differentiable at the sphere boundary at each sphere. Its explicit form is:

$$h_{RL,R'L'}^\alpha = (C_{RL}^\alpha - E_{\nu,RL}) \delta_{RR'} \delta_{LL'} + (\Delta_{RL}^\alpha)^{1/2} S_{RL,R'L'}^\alpha (\Delta_{R'L'}^\alpha)^{1/2}$$  \hfill (2.5)

where $C_{RL}^\alpha$ and $\Delta_{RL}^\alpha$ are the potential parameters, $S_{RL,R'L'}^\alpha$ is the structure matrix in the MTO representation $\alpha$.

The potential parameters as well as the overlap $\phi^\alpha$ can be expressed in terms of the potential function $P_{RL}^\alpha$ and its first and second derivatives evaluated at the energy $E_{\nu,RL}$, with the aid of the relations:

(i) The Band Centre Parameter:

$$C_{RL}^\alpha = E_{\nu,RL} - P_{RL}^\alpha(E_{\nu,RL})[P_{RL}^\alpha(E_{\nu,RL})]^{-1}$$

(ii) The Band Width Parameter:

$$(\Delta_{RL}^\alpha)^{1/2} = [P_{RL}^\alpha(E_{\nu,RL})]^{-1}$$

(iii) The Orbital overlap:

$$\phi^\alpha = \tilde{P}_{RL}^\alpha(E_{\nu,RL})[2P_{RL}^\alpha(E_{\nu,RL})]^{-1}$$
The structure constant $S^\alpha$ and the potential function $P^\alpha$ (indices RL are dropped for brevity) which enter the definition of the muffin tin orbitals play a central role in the LMTO theory. The potential functions $P^\alpha_{RL}(E)$ are expressed in terms of the conventional potential functions $P^0_{RL}(E)$ and the elements $\alpha_{RL}$ of the diagonal matrix $\alpha$ defining the muffin tin representation ($\alpha$)

$$P^\alpha_{RL}(E) = P^0_{RL}(E)[1 - \alpha_{RL}P^0_{RL}(E)]^{-1}$$

The quantities $P^\alpha_{RL}(E)$ have the direct physical meaning: they are proportional to the cotangents of the phase-shifts related to the solid state potential $V_R(r_R)$ in a sphere at $R$. So the potential parameters entering the Hamiltonian, through $P^\alpha$ and $P^0$, characterize the scattering properties of atoms placed at lattice sites.

The geometry of the lattice sites enters the theory via, the structure constant $S^\alpha$. This is expressed in terms of the conventional structure matrix $S^0$:

$$S_{RL,R'L'}^\alpha = [S^0(1 - \alpha S^0)^{-1}]_{RL,R'L'}$$

(2.6)

The elements $S_{RL,R'L'}^\alpha$ depend only on $R/w$ and $R'/w$ where $R$ and $R'$ are the atomic positions, and $w$ is the average Wigner-Seitz radius of a solid. The structure constant $S^0$ depends only on the geometrical arrangement of the lattice sites, and not on the type of atoms occupying them. The quantities $S_{RL,R'L'}^\alpha$ behave like $(w/d)^{l+l'+1}$ where $d=|R-R'|$. For low orbital indices $\ell = 0,1$, $S^0$ is long ranged in the real space. However the elements of $S_{RL,R'L'}^\alpha$ in the most tight binding representation $\alpha = \beta$ behaves like $\exp[-\lambda_{RL}^0 d/w]$. The values of the parameter $\lambda_{RL}^0$ depends on the choice of the screening (whether it is sp screening or spd). These set of parameters which yields the most localized representation are unique (independent of $R$) for closely packed structures. The following two site-independent sets of screening constants:

$$\alpha = \{\alpha_s, \alpha_p, \alpha_{d>1}\} = \{0.28723, 0.02582, 0.0\}$$

$$\alpha = \{\alpha_s, \alpha_p, \alpha_d, \alpha_{d>2}\} = \{0.34850, 0.05303, 0.01071, 0.0\}$$

for sp and spd screening respectively, have been found numerically to give short ranged envelope functions for all reasonably homogeneous three-dimensional structures. The band distortion parameter $\alpha$ which relates the physical quantities in the two representation may be expressed as:

$$\alpha = (P^0)^{-1} - (P^\alpha)^{-1} = (S^0)^{-1} - (S^\alpha)^{-1}$$

### 2.3.2 The Hamiltonian And The Overlap Matrices

The scalar relativistic Schrödinger equation for a solid is solved by seeking the wavefunction $\Psi^\alpha(r)$ as a linear combination $\sum_{RL} \chi^\alpha_{RL} (r_R) U_{RL}^\alpha$ of the MTO which form the basis set of the
conventional variational principles. The eigenvectors \( U^\alpha_{RL} \) and the eigen energies \( E \) are found to be a solution of the eigen value problem:

\[
\sum_{RL}(H_0^\alpha_{RL},RL - E_0^\alpha_{RL},RL)U_0^\alpha_{RL} = 0 \tag{2.7}
\]

the overlap \( O_{RL',RL}^\alpha = \langle \Psi_{RL}^\alpha | \Psi_{RL'}^\alpha \rangle \) and the Hamiltonian \( \langle \Psi_{RL}^\alpha [-\nabla^2 + V(t)] | \Psi_{RL'}^\alpha \rangle \) matrices are evaluated straightforwardly to yield:

\[
O^\alpha = (I + h^\alpha \sigma^\alpha)(\sigma^\alpha h^\alpha + I) + h^\alpha p h^\alpha \tag{2.8}
\]

\[
H^\alpha = h^\alpha (I + \sigma^\alpha h^\alpha) + (I + h^\alpha \sigma^\alpha)E_\nu(\sigma^\alpha h^\alpha + I) + h^\alpha E_\nu p h^\alpha \tag{2.9}
\]

The matrices \( h^\alpha \), \( E_\nu \) and \( \sigma^\alpha \) are already defined and \( p = \langle \phi_{RL} | \phi_{RL} \rangle \) turns out to be a small parameter in the linear method and is usually neglected in ASA (resulting in error not exceeding 1% of the band width i.e. approximately 5 mRyd for d bands)

In the so called orthogonal representation \( \alpha = \gamma \), \( O_{RL}^\alpha = 0 \) and the Hamiltonian and the overlap matrices become:

\[
H'_{RL,RL'} = C_{RL}^\gamma \delta_{RR'} \delta_{LL'} + (\Delta_{RL}^\gamma)^{1/2} S_{RL,RL'}^\gamma (\Delta_{RL'}^\gamma)^{1/2} \tag{2.10}
\]

\[
O'_{RL,RL'} = \delta_{RR'} \delta_{LL'} \tag{2.11}
\]

\[
S_{RL,RL'}^\gamma = [S^0(1 - \gamma S^0)^{-1}]_{RL,RL'} \tag{2.12}
\]

Rather than transforming between the structure matrices one can directly transform between the two-centre Hamiltonians. The transformation between an arbitrary (\( \alpha \)) and the nearly orthonormal representation (\( \gamma \)) is given by:

\[
h^\gamma = h^\alpha (1 + \sigma^\alpha h^\alpha)^{-1}
\]

the above expression can be expanded to yield:

\[
H^\gamma = H^\alpha - h^\alpha \sigma^\alpha h^\alpha + \ldots \tag{2.13}
\]

where

\[
H^\alpha = h^\alpha + E_\nu
\]
Usually the Hamiltonian in the nearly orthonormal representation $\gamma$ is expressed in terms of the Hamiltonian in the most localized representation $\alpha = \beta$, where the basis functions are short ranged and Hamiltonian is sparse to facilitate calculation in real space. This form of the TB-LMTO Hamiltonian Eqn. (2.13) will be used by us in our subsequent calculations based on the recursion method.

### 2.3.3 A Practical Scheme For Self-Consistency

In the previous sections we have seen how to set up the Hamiltonian and overlap matrices in nearly orthonormal as well as most localized representation, in the framework of atomic sphere approximation. In order to perform charge self-consistency in the ASA, one merely needs the electron density $\rho_R(r)$, spherically averaged in each sphere of radius $s_R$. The spherically averaged valence electron density $\rho_R^v(r)$ can be expressed in terms of the energy moments $m_{RL}^2$ of the projected density of states $\rho_{RL}^v(E)$ given by:

$$n_{RL}(E) = -1/\pi^3 m [(EI + i0^+ - H^0)]^{-1}_{RL,RL} \tag{2.14}$$

Here $m^0$ determines the number of electrons, $m^1$ and $m^2$ determine the radial redistribution of the charge and for the correct choice of the $E_{v,RL}$ (i.e. in the centre of gravity of the occupied part of the band) $m^1$ should be zero. $\rho_R^v(r)$ is only the valence electron density, to which one has to add the spherically symmetric core electron (atomic) contribution, in order to obtain the total spheridized electron density $\rho_R(r)$. The output one electron ASA potential in the sphere at $R$ (radius $S_R$) is:

$$V_R(r) = V_{sphere} + V_{made}$$

where

$$V_{sphere} = \int_0^{S_R} \frac{2\rho_R(r')}{|r - r'|} 4\pi r'^2 dr' - \frac{2Z_R}{r} + \mu_{xc}(\rho_R(r))$$

and

$$V_{made} = \sum_{R'} 2q_{R'} \sum_T |R - R' - T|^{-1}$$

Here $Z_R$ is the nuclear charge and $q_{R} = Z_R - \int_0^{S_R} \rho_R(r) r^2 dr$ is the excess charge in the atomic sphere at $R$, $\mu_{xc}$ is the local density exchange-correlation potential obtained in the framework of the density functional theory.

Thus $V_{sphere}$ is the total intrasphere contribution (both electron-electron and electron-nucleus) to the potential and $V_{made}$ is the electrostatic Madelung potential (due to neighbouring spheres) spherically averaged within the sphere. In each iteration, after obtaining the
the charge density and the potential one has to solve the radial Schrödinger equation (or Dirac-Pauli equation) to obtain $\phi_{RL}$, $\phi_{RL}$, $\phi_{RL}$ and the potential parameters $C_{RL}$, $\Delta_{RL}$ and $\gamma_{RL}$ to construct the Hamiltonian, the density of states and the charge-density and repeat the process till self-consistency.

### 2.4 CONFIGURATION AVERAGING

In a study of disordered systems, the configuration averaging is a necessary requirement. The potentials describing a disordered solid are characterized by random variables: random in space as in quenched disordered solids or random in time as in annealed disordered systems. A particular realization of the random variable describing a disordered system constitutes a particular configuration of a system in question. In statistical mechanics, it is assumed that for large enough time all microscopic states (ensembles) of a system consistent with specific macroscopic constraints are realized and therefore time averages may be replaced by ensemble averages. This is the so called *ergodic theorem*. Similarly for a disordered system, in the limit of infinite size, all possible environments (configurations) may be achieved in a single sample. A global probe samples all possible environments in the samples weighted with appropriate probabilities. A global property is thus automatically configurationally averaged, even if it refers to a single sample. Invoking spatial ergodicity one may argue that configuration average provides information about the spatial averaging of a physical quantity in a disordered system.

So in a measurement (a global probe) of a physical observable one determines the average trend among the samples and not the variation among the various realizations of the samples. In the corresponding theoretical formulation, if the fluctuations among the configurations is negligible compared to their mean, then it is the configuration average which should be compared with the experimentally determined quantities. Also it has been emphasized by Anderson (1969) that only the physically measured quantities should be configurationally averaged: the density of states or the response functions rather than the Hamiltonian or self-energies; the diffusion probabilities rather the wavefunctions. This is one of the reasons why the methods based on the Green function are favoured for the study of disordered systems rather than the Schrödinger equation and wavefunction approach. Further, configuration averaging is a valid procedure only when the mean dominates over the higher moments. In other words the property under cosideration is *self-averaging*. The density of states, total energies, effective cluster interactions to be studied in the present and some of the following chapters of this thesis are all self-averaging, and therefore require configuration averaging. On the other hand, it has been demonstrated (Kumar and Jayannavar, 1985) that the variance of the resistance of a disordered chain diverges much faster than its mean as the length of the chain increases. In such a situation configuration averaged resistance has no meaning and one needs to define a proper measure which makes such quantities self-averaging. The study of some of these properties will be undertaken in chapter 6.
2.5 MEAN FIELD THEORIES:

In this section we will briefly review the single site mean-field approximations proposed for configuration averaging in disordered solids. In order to understand these theories we will briefly recapitulate the Green function formalism for disordered alloys.

The Green function is a representation of the resolvent of the Hamiltonian, defined by the relation:

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

(2.15)

This provides a starting point for the analysis of the disordered system. Since most of the electronic properties of systems and their response to perturbations caused by externally applied forces are related directly to the single or many particle Green functions, one of the major tasks of the study of disordered systems is the evaluation of the configuration average of the corresponding Green function. For example, a knowledge of the density of states (DOS) is sufficient to yield all physical information regarding the single particle properties of a disordered material. Since the DOS is related to the diagonal elements of the Green function:

$$G(z) = (l/N)Tr<n(zI - H)^{-1}|n>$$

(2.16)

so it is necessary to develop methods for the evaluation of \( \langle G \rangle \), the average of \( G \) over the configurations of the disordered material.

In the multiple scattering approach, we consider the Hamiltonian \( H \) of a disordered system to be the sum of the Hamiltonian \( H_0 \) of a translationally invariant material and a perturbing part \( V \) (not necessarily small) which includes disorder. The resolvent \( G \), corresponding to the full Hamiltonian \( H \) can be expressed in terms of the unperturbed resolvent \( G_0 = (zI - H_0)^{-1} \), which is assumed to be known and the perturbation \( V \) as:

$$G = (zI - H)^{-1} = (zI - H_0 - V)^{-1}$$

$$G = G_0 + G_0TG_0$$

(2.17)

where the scattering matrix or the t-matrix is given by

$$T = V(I - G_0V)^{-1} = (I - VG_0)^{-1}V$$

(2.18)

The same series may also be expanded to yield:

$$G = G_0 + G_0VG_0 + G_0VG_0VG_0 + \ldots$$

(2.19)
This operator expansion represents the propagation of an excitation, in the perfect lattice, represented by $H_0$ with scattering taking place at the various defects (impurities) represented by $V$. An expression for the ensemble averaged $\langle G \rangle$ in the site representation takes the form:

$$\langle G_{ij} \rangle = G^{ij}_0 + \sum_n G^{in}_0 \langle V_n \rangle G^{nj}_0 + \sum_n \sum_m G^{in}_0 \langle V_n G^{nm}_0 V_m \rangle G^{nj}_0 + \ldots \tag{2.20}$$

where $\langle \ldots \rangle$ denotes a complete average over all configurations of the system. The unperturbed propagators $G^{ij}_0$ are independent of configurations, leaving only the the average of the products of the form $\langle V_i V_j \ldots V_n \rangle$. These averages are rather complicated quantities depending on the distances between the sites, concentration gradient and other characters of the material under study. The usual method to solve the problem is to perform an approximate decoupling of various terms in the series and resum it in such a way so as to avoid divergences. In practice one seeks approximations to the exact self-energy which is such that the ensemble averaged resolvent can be written in the form of the Dyson's equation:

$$\langle G \rangle = G_0 + G_0 \Sigma(G) = (G^{-1}_0 - \Sigma)^{-1} \tag{2.21}$$

The self-energy $\Sigma$ is a function of the energy $z$, and must be translationally invariant corresponding to the equivalent property for $\langle G \rangle$ and we can therefore write:

$$\langle G(\bar{k}) \rangle = [z - E(\bar{k}) - \Sigma(\bar{k}, z)]^{-1} \tag{2.22}$$

The study of disordered system now reduces to the approximate evaluation of the self-energy $\Sigma$, and most of the methods attempt to replace the true, disordered material by a translationally invariant medium characterized by a self-energy $\Sigma$ determined in some approximate way and then calculate $\langle G \rangle$ by equation [2.22].

### 2.5.1 The rigid band model (RBM)

The conceptually simplest way of introducing order into the problem is to neglect entirely the differences between the potentials of the alloy constituents, as is done in the rigid band model (RBM) (Mott and Jones, 1958). The only difference between the systems is the number of electrons per atom (and the position of the bands), which in turn should account for the differences in the physical properties between the constituents and their alloys. Obviously these approximations are too drastic to yield any useful results.

### 2.5.2 Virtual crystal approximation (VCA)

In the VCA (Nordheim, 1931) one assumes that in the weak scattering limit, the alloy potential is periodic with the same potential $\langle \ V \rangle$ associated with any site. The resulting
Green function is then a Green function of a pure system with a simple shift $\langle V \rangle$. This approximation gets reflected in the self-energy $\Sigma$, where VCA yields the lowest order term $\Sigma_{VCA} = \langle V \rangle$, which is real, energy independent and has no dependence on the wave-vector $\vec{k}$. The VCA is convergent at the band edges and is exact for small enough perturbations. It has been fairly successful in explaining the properties of weak scattering alloys in which the wavefunctions are extended over many lattice spacings and each particle sees nearly the same average perturbation. However $\Sigma_{VCA}$ is real, therefore the lifetime of the $k$-state is infinite as in pure systems, contrary to the expectation that in a disordered system the states should be decaying as a result of scattering off the impurities. So the method does not work for larger disorders. Further VCA fails to reproduce the gap in an alloy with split bands.

2.5.3 The Average T-matrix approximation (ATA)

For small concentrations one may neglect the intersite scattering and concentrate on evaluating the terms which involves only scattering off the same site. The Green function can be expressed in terms of the scattering-matrix or the $t$-matrix. The average $t$-matrix approximation (Korringa, 1958; Beeby, 1964) calculates the configuration averaged $t$-matrix in the single site approximation. The effect of the disorder in the local environment is neglected.

In the single site approximation, the $t$-matrix may be written as:

$$ t_i = V_i + V_i G_0^{ii} V_i + \ldots $$

(2.23)

and in the average $t$-matrix approximation the self-energy $\Sigma_{ATA}$ takes the form:

$$ \Sigma_{ATA} = \frac{\langle t \rangle}{[1 + G_0^{ii}(t)]} $$

(2.24)

where $\langle t \rangle = \langle t_i \rangle$ and,

$$ \langle t \rangle_{ATA} = \frac{V_i}{(1 - V_i G_0^{ii})} $$

(2.25)

$G_0^{ii}$ is usually chosen to be $G_0^{VCA}$.

In contrast to the VCA, the ATA yields impurity bands and $\vec{k}$ labelled states with finite life times. Its main limitation is that the self-energy is not determined self-consistently and its inability to reproduce correctly the band edges of the alloy DOS. This is due to the use of the VCA unperturbed Green function $G_0^{VCA}$ in eqn.[2.25] As a consequence, the self-energy, has the analytic structure of the host lattice Green function plus a simple pole. The pole produces the impurity bands but cannot move the unperturbed band-edges from their values in the host (VCA) material.
2.5.4 The Coherent Potential Approximation (CPA)

The CPA (Soven, 1967; Taylor, 1967) belongs to the class of mean field theories analogous to the Weiss-molecular field theory of magnetism. In such theories the properties of the entire material are determined from the behaviour at a localized region, usually taken to be a single site (cell) in the material. In the multiple scattering description (MST) of a disordered system, one considers the propagation of an electron through a disordered medium as a succession of elementary scatterings at the random atomic (point) scatterers. In the single site approximation one considers only the independent scattering off different sites and finally takes the average over all configurations of the disordered system consisting of these scatterers. For a system with homogeneous disorder, the configuration average of any physical quantity over all configurations is independent of position (site) in the lattice. One may then consider any single site in a specific configuration and replace the surrounding material by a translationally invariant medium, constructed to reflect the ensemble average over all configurations. In the CPA this medium is chosen in a self-consistent way. One assumes that averages over the occupation of a site embedded in the effective medium should yield quantities indistinguishable from those associated with a site of the medium itself. Because a translationally invariant medium produces no scattering of a wave, it is assumed that the scattering off a real atom embedded in a CPA medium, averaged over the possible configurations of a single site, should equal the corresponding Green function of the medium itself. This self-consistency condition yields an effective Hamiltonian describing the medium, called the coherent-potential Hamiltonian. The averages one performs in the CPA involve only the occupation of a single site and consequently the CPA is a single site approximation.

The CPA self-consistency demands that if any of the effective potentials $\Sigma(z)$ (coherent potential) is replaced by an exact potential $\epsilon_i$, there would be no extra scattering on the average. Mathematically this is equivalent to saying that average of the single site scattering $t$ matrix values [eqn. 2.23]:

$$\langle t[\epsilon_i, \Sigma(z)] \rangle = 0$$

$$\langle \frac{(\epsilon_i - \Sigma(z))}{1 - (\epsilon_i - \Sigma(z))(G(z))} \rangle = 0 \quad (2.26)$$

where $\Sigma(z)$ is the coherent potential. It is translationally symmetric, complex and energy dependent but is independent of the wave-vector $\mathbf{k}$. $\langle G(z) \rangle$ is the configuration averaged diagonal element of the Green function for the alloy, which by definition is the Green function for the coherent potential.

$$\langle G(z) \rangle = G_0(z - \Sigma(z)) \quad (2.27)$$

Equations [2.26] and [2.27] constitutes the self-consistent CPA equations.
The single site CPA has been combined with the band-structure methods like KKR and TB-LMTO to yield a first principles description of the electronic structure of disordered alloys. The Hamiltonian on which KKR-CPA (Stocks et al., 1977) is based consists of a random array of non-overlapping muffin-tin potentials \( V_\alpha(r - R_i) \) centered on the lattice sites \( R_i \). There are as many different muffin tin potentials as there are atomic species \( \alpha \). The essence of the CPA is to replace this random array of real muffin tin potentials \( V_\alpha \) by a ordered array of effective coherent potentials \( V_c \). The scattering properties of \( V_c \) are then determined self-consistently in a single site mean field sense, from the requirement that an electron travelling in an infinite array of \( V_c \)'s undergoes on average no further scattering upon replacement of a single site \( V_c \) potential with the \( V_\alpha \) potentials. Once the scattering properties of a single \( V_c \) are known, the quantities such as species decomposed average density of states and charge density can be obtained in a straightforward manner.

The TB-LMTO Hamiltonian for a disordered system, (in the nearly orthogonal representation) has randomness in the potential parameters \( C \), \( \Delta \) and \( \gamma \). Due to random \( \Delta \) and \( \gamma \), the \( H^\gamma \) have a complicated off-diagonal randomness, which cannot be treated within CPA. In order to facilitate the calculation, the Green function \( G(z) \) in the general MTO representation \( \alpha \) is expressed in terms of an auxiliary Green function \( g(z) \) as:

\[
G_{RL,RL'}(z) = \lambda_{RL}^\alpha(z)\delta_{RR'}\delta_{LL'} + \mu_{RL}^\alpha(z)g_{RL,RL'}^\alpha(z)\mu_{RL'}^\alpha(z)
\]

where

\[
g_{RL,RL'}^\alpha(z) = \left\{ [P^\alpha(z) - S^\alpha]^{-1} \right\}_{RL,RL'}
\]

\[
\lambda_{RL}^\alpha(z) = (\gamma_{RL} - \alpha_{RL})\mu_{RL}^\alpha(z)/\Delta_{RL}^{1/2}
\]

\[
\mu_{RL}^\alpha(z) = \left[ \hat{P}_{RL}^\alpha(z) \right]^{1/2} = \Delta_{RL}^{1/2}/(\Delta_{RL} + (\gamma_{RL} - \alpha_{RL})(z - C_{RL}))
\]

where

\[
P^\alpha(z) = \frac{z - C^\alpha}{\Delta^\alpha}
\]

In the most tight binding representation \( \alpha = \beta \), \( S^\alpha \) are nonrandom. As a consequence, the original problem with both diagonal and off-diagonal disorder gets mapped onto an equivalent problem where all random quantities \( g^\alpha \), \( \lambda^\alpha \) and \( \mu^\alpha \) are site diagonal and CPA (Kudmovský and Drchal, 1990) can be employed to calculate configuration averaged resolvent \( \langle G \rangle \).
Both KKR-CPA and TB-LMTO CPA have been widely used to study the electronic structure of various disordered alloys to be discussed later in the text.

The self-consistent CPA possesses a large number of desirable features which unambiguously classify it as the unique, fully self-consistent single site theory of substitutionally disordered alloys. Like the ATA and other single site theories based on perturbative calculations the CPA is exact up to (not including) order $Z^{-1}$ to all orders in the concentration $c$. The leading errors in the CPA is of the order of $Z^{-1} c^2$, where $Z$ is the nearest neighbour co-ordination number. Unlike ATA and other single site theories the CPA is exact both in the weak scattering and narrow band limits and also provides a good interpolation between these two limits. The CPA yields self-energies and Green-functions which are analytic everywhere in the complex energy plane except for a branch-cut along the real axis inside the host and impurity bands. A formal measure of accuracy of the CPA and other alloy theories is given the by an examination of the moments of the densities of states and spectral weight functions $\langle \mathcal{G}(k) \rangle$. The single site CPA gives a larger number of such moments exactly than do other single site theories. For a tight-binding binary alloy, with only diagonal disorder CPA gives a significantly larger number of moments (8) than do the ATA(4), the VCA(3) and the RBM(2).

In spite of its many desirable properties the CPA does not provide a fully satisfactory theory for calculating the properties of disordered alloys. This motivates a search for better theories for configuration averaging in alloys. All the drawbacks of the CPA stem from its single site nature. As a single site mean field theory, the CPA fails to account for the statistical fluctuations in the chemical environment (local or long-ranged) of a site in a disordered material. The local environment of a site affects the charge density on the site and consequently potential on the site. The neglect of such charge transfer effects in treating the electronic structure of alloys is inherent in any single site approximation, and constitutes a violation of the Friedel sum rule, and may lead to in specific cases inaccuracies in the calculated physical properties. Further, such fluctuations are responsible for band-tailing and sharp structures in the density of states, and can strongly affect the physical properties, such as the formation of the magnetic moments. The local environment of a site also affects the value of the transfer integrals which link that site to the surrounding sites in a real medium. The effect of surrounding medium manifests itself as cluster effects and also local lattice distortion in non-isochoric alloys leading to predominantly off diagonal disorder which cannot be taken into account in a single site theory. Furthermore, as a single site theory the CPA yields $k$ independent momentum state life times and in general is incapable of treating rigorously the transport properties and localization of states in disordered systems (although it can give accurate results in some cases). Finally the effect of short range order is beyond the scope of the CPA. In principle, the limitations of the CPA could be overcome to a large extent within the framework of a many-site or cluster generalizations.
2.5.5 The Method Of Blackman, Esterling and Berk (BEB)

The single site self-consistent approximation of Blackman, Esterling and Berk (1971) takes exact account of the correlation between diagonal and off-diagonal disorder. It treats both the diagonal and the off-diagonal disorder on the same footing. Like the original CPA, it is a completely self-consistent theory which preserves all the desirable properties of the CPA including analyticity and correct behaviour in various limits. Furthermore it reduces to CPA in the limit of vanishing off diagonal disorder.

In order to understand the method of BEB, let us consider a single band tight-binding Hamiltonian for a binary alloy \( \text{A}_x\text{B}_{1-x} \) with both diagonal and off diagonal disorder. In site representation it is given by:

\[
H_{ij} = \epsilon_i \delta_{ij} + W_{ij}(1 - \delta_{ij})
\]

The site diagonal energies \( \epsilon_i \) are assumed to take only the values \( \epsilon_A \) and \( \epsilon_B \), depending on whether an atom of type A or type B occupies site \( i \). In addition the transfer integrals \( W_{ij} \) are allowed to assume the independent values \( W_{ij}^{AA} \), \( W_{ij}^{BB} \) and \( W_{ij}^{AB} \), depending on the chemical occupation of the sites \( i \) and \( j \). In order to facilitate the calculation of the configuration averaged green function \( \langle G(z) \rangle \), the Green function expansion is written in terms of the locaters \( g_i \) as:

\[
G_{ij} = g_i \delta_{ij} + g_i \sum_{k \neq i} W_{ik} G_{kj}
\]

(2.28)

corresponding to any given alloy configuration, where

\[
g_i = (E - \epsilon_i)^{-1}
\]

We note that in contrast to the case of only diagonal disorder the values of \( g_i \) and \( W_{ik} \) on the right hand side of eqn( 2.28) are correlated with one another; \( g^i = g^A \) implies that \( W_{ik} \) can be \( W_{ik}^{AA} \) or \( W_{ik}^{AB} \) but not \( W_{ik}^{BA} \) or \( W_{ik}^{BB} \). The method of BEB, now consists of a scheme to decouple the diagonal and off diagonal disorder, using the projection techniques. The following projection operators are introduced such that the operator index \( x_i \) is defined to be equal to 1(0) if the atom occupying site \( i \) is A(B). Similarly \( y_i = (1 - x_i) \). In the projection operator space, it was demonstrated by BEB that the equation of motion eqn. (2.28) reduces to an matrix equation given by:

\[
G_{ij} = g_i \delta_{ij} + g_i \sum_{k \neq i} W_{ik} G_{kj}
\]

For a binary alloy the matrices \( g_i \), \( G_{ij} \) and \( W_{ij} \) are 2x2 matrices. Further the operator \( W_{ij} \) does not involve projection operators, so the disorder is confined to matrices \( g_i \) and thus is purely diagonal. As a consequence we can employ the single site approximations discussed in the preceding section for the purpose of configuration averaging.

Recently the method has been used in the framework of TB-LMTO (Sluiter and Singh, 1994) for the first principles calculation of electronic structure of disordered alloys.
2.6 CLUSTER GENERALIZATIONS:

The generalization of the CPA, to a fully satisfactory cluster theory has several important requirements other than the overall numerical accuracy. First of all, such an extension should take rigorous account of the local environment fluctuations in a self-consistent way and should yield an effective medium Green function that is uniquely defined and becomes exact in the limit of large cluster sizes. Secondly, the resultant effective medium should possess the full symmetry of the empty lattice, in particular its translational invariance. Thirdly, the self energy and the Green function of the effective medium should be unique, analytic functions of complex energy \( z \) in the entire upper (or lower) complex energy plane. The analytic and the Herglotz property are of vital importance as their failure leads to the violation of causality and the fundamental sum rules leading to unphysical properties. Several methods have been put forward as cluster generalisations of CPA, and we shall discuss some of these briefly:

2.6.1 The Embedded Cluster Method (ECM)

In the ECM (Gonis and Garland, 1977), a cluster of real atoms is embedded in an effective medium usually obtained in the single site CPA. The Green function corresponding to each configuration \( J, G^J(E) \), of the real cluster is computed and finally the density of states of the material is obtained by the configuration average over all cluster configurations of the Hamiltonian.

\[
n(E) = \sum_J P_J n^J(E)
\]

where \( P_J \) is the probability of occurrence of the configuration \( J \). For a given analytic effective medium the ECM yields analytic, well defined and physically meaningful results. The main disadvantage of the method is that it is non self consistent and therefore it does not yield a new effective medium or improved momentum spectral weight functions \( G(k) \).

2.6.2 The Molecular CPA (MCPA)

In deriving the MCPA (Tsukada, 1977) one considers the disordered material as a collection of non-overlapping cluster of sites (or molecules). The clusters are arranged on the sites of a translationally invariant superlattice and are such that their translation through the superlattice vectors generates all the points of a given original lattice. Similar to CPA one invokes a self-consistency criterion, generalized to clusters, to obtain the cluster self energy self-consistently. The resulting MCPA selfconsistency requires the solution of a matrix equation and yields an effective medium consisting of repeating supercells (clusters) and are characterized by a cluster diagonal self energy. So in the process, the cluster onsite terms as well as the intra-cluster hoppings get renormalised but the inter-cluster hoppings remain unaltered.
Like the CPA, MCPA yields analytic, unique and physically meaningful results. It accomplishes the self-consistent incorporation of local environment fluctuations into the effective medium self-energy. In particular, the MCPA yields DOS's associated with specific cluster configurations. However, the MCPA possesses two severe drawbacks that preclude its application to all but simplest cases. Firstly, the MCPA is computationally very difficult, requiring the solution of matrix self-consistent equations. Secondly, the MCPA yields a superlattice effective medium which violates the single site translational invariance of the given lattice. Such a medium would not affect greatly the DOS calculated in the MCPA but may yield spurious gaps in the band structure at the boundary of the superlattice Brillouin zone which could affect the calculation of transport properties.

2.6.3 The Cluster CPA By Augmented Space Formalism

The augmented space formalism (to be discussed later in the text) is an exact prescription for obtaining configuration averages. In this method, a random Hamiltonian defined on a Hilbert space is mapped onto an ordered Hamiltonian in an enlarged space, namely the augmented space. The configuration average by ASF, reduces to the evaluation of a particular matrix element in this augmented space. Though the method is exact, but because of its huge rank ($N \times 2^N$, for a binary alloy with $N$ sites) one has to invoke approximations to reduce the rank of this space. In practice one retains the fluctuations due to disorder, confined to a cluster, and replaces the rest of the system by an effective medium. Finally, the effective medium is determined (Kumar et al., 1982) self-consistently, with the prescription that the chosen cluster does not produce any extra scattering when embedded in this medium. In contrast to MCPA, this method yields a translationally invariant medium characterized by self-energies which renormalizes the onsite terms in a cluster as well as the inter and intra cluster hopping terms and thereby don't produce artificial zone boundary effects. Though the method yields Herglotz Green function, but it becomes computationally difficult as the number of coupled self-consistent equations increases with the size of the chosen cluster. The method has been implemented both in the framework of KKR (Razee et al., 1990) and TB-LMTO (Datta et al., 1993), but its application till date has been confined to model systems.

2.6.4 The Diagrammatic Technique And The Travelling Cluster Approximation (TCA)

The basic idea behind the diagrammatic technique (Nickel and Butler, 1973) is to expand the Green function or the self-energy in powers of the density of scatterers and sum the selected set of diagrams, properly weighted, to account for the multiple scatterings of the same set of sites. These n-site theories collectively called CPAn, do improve upon the the original CPA and also take into account the local environment effects. However, the earlier works in this direction yielded non-analytic and hence non-physical results. In particular, they have been found to lead
to negative densities of states for certain range of relevant alloy parameters.

A major breakthrough in this direction is the travelling cluster approximation proposed by Mills and Ratanavararaka (1978). This method is also based on the augmented space formalism. The method relies on the fact that instead of attempting to sum all possible diagrams necessary for a consistent treatment of scattering events one should sum a certain type of diagrams so that the corresponding self-energy satisfies the condition:

$$\Im m \Sigma \leq 0 \text{ for } \Im m z > 0$$

which is necessary (although not sufficient) for analyticity. The travelling cluster formalism provides a consistent rule for summing such classes of diagrams so that the self energy and Green function with proper analytic properties can be obtained. Further the diagrammatic consistency generates all higher order graphs associated with a given type of scattering and includes such scattering throughout the material.

Inspite of its advantages over CPA, TCA suffers from several drawbacks. Firstly the method is exceedingly difficult computationally making its application to realistic systems nearly impossible. Secondly it gives no precise guidance as to which diagrams should be summed. In the TCA diagrams are neglected which apriori appear to be at least as important to those retained. Thirdly the TCA does not treat individual cluster of atoms exactly and does not appear to take short range ordering effects properly into account.

2.7 THE RECURSION METHOD

In simple metals, the interactions between the electrons and the atoms is weak, and the electronic structure is determined by the long range periodicity of the atomic potentials. As a consequence the electronic property of a solid manifests itself as a coherent superposition of the electronic properties of all atoms, as demonstrated by the band theory of solids. When the electrons interact strongly with the atoms, like the d electrons in transition metals, this picture breaks down, and the physical properties no longer depend on the long range periodicity, rather on the local environment of each atom. Though band theory is still valid, but the physics is better understood by means of a solution that explicitly accounts for the role of the local environment. The recursion method (Haydock, 1980) provides such a solution of the Schrödinger equation.

The recursion method offers an alternative to the band structure method. The main difference between these approaches is that the mathematics of the recursion method is cast in terms of the diagonal element of the resolvent rather than the eigen-functions of the Hamiltonian. The recursion method is suitable for computing the local properties which are related to the diagonal elements of the resolvent, where it offers a large computational advantage over the band structure methods. The recursion method is more robust, compared to the methods based on the evaluation of the wavefunction because the resolvent of the Hamiltonian or the projected density of states is exponentially insensitive to changes in Hamiltonian far from the orbital of
projection. This property is embodied in the quantum analogue of the electromagnetic black body theorem: namely, the density of states inside a cavity is exponentially insensitive to the shape of the cavity. As a result the radiation from a black-body cavity has a spectrum which is independent of its shape or the material from which it is made. Since quantum mechanics is a wave phenomena, the quantum analogue is obvious. Further, the recursion method is based on real space so it does not require lattice periodicity for its operation, in contrast to the band structure methods. As a result, both ordered, disordered and systems with broken translational symmetry (such as surfaces) can be treated within the recursion method.

The representation of the tight-binding Hamiltonian is usually sparse. In a tight-binding approximation the local orbital in a solid interacts only with near neighbours. This is true of the TB-LMTO Hamiltonian. In the recursion method one exploits this sparseness and performs a unitary transformation on the local orbital basis to produce a tridiagonal representation of the Hamiltonian. A new basis function is defined iteratively so as to ensure that each new member interacts only with its preceding and following members. The first orbital in the new basis is chosen to be the one whose local density is sought.

If \( | u_1 \rangle \) denotes the starting vector, the recursion procedure generates a new set of vectors which are mutually orthogonal to each other, with the aid of the following relations:

\[
b_{n+1} | u_{n+1} \rangle = H | u_n \rangle - a_n | u_n \rangle - b_n | u_{n-1} \rangle
\]

with \( | u_0 \rangle = 0 \). The \( a_n \) and \( b_n \) are the coefficients chosen so as to orthogonalize \( | u_{n+1} \rangle \) to the preceding vectors \( | u_n \rangle \) and \( | u_{n-1} \rangle \) and \( b_{n+1} \) is chosen to normalize \( | u_{n+1} \rangle \). The recursion coefficients are given by:

\[
a_n = \langle u_n | H | u_n \rangle
\]

\[
b_n = \langle u_{n+1} | H | u_n \rangle
\]

The recursion coefficients describe the higher moments of the orbital projected density of states for the initial orbital and represent the influence of increasingly remote orbitals. In the process of recursion a new basis is generated by repeated operation of \( H \), with each operation allowing the electrons to hop further from the initial orbital. This procedure is very easy to implement numerically, because we need to perform only matrix multiplications. However, some care has to be taken. There may be round-off errors due to finite precision of computers resulting in new vectors after some iterations which are not orthogonal to all the preceding ones. In the new orthogonal basis the Hamiltonian has the tridiagonal form and the recursion coefficients \( a_n \) and \( b_n \) are respectively the diagonal and off-diagonal elements of the tridiagonal Hamiltonian matrix in the new representation. The method also yields an explicit continued fraction form for the diagonal elements of the Green function:
G_{11} = \langle u_1 | (zI - H)^{-1} | u_1 \rangle = \frac{b_0^2}{E - a_1 - \frac{b_1^2}{E - a_2 - \ldots}} \tag{2.30}

In practice the continued fraction is evaluated to a finite number of steps. Haydock (1972) has mapped the contributions of the continued fraction coefficients \( (a_n, b_n) \) to self-avoiding walks on the underlying lattice, where \( a_n \) and \( b_n \) contain information about only the irreducible paths of length \((2n-1)\) and \(2n\) respectively, i.e. those closed paths that do not return to the initial orbital at any intermediate stage. He has shown that the dominant contribution comes from the paths that wind round the initial starting state. This allows one to work only on the finite part of the Hilbert space: a particular sized cluster around the initial starting state.

Thus if one tries to model an infinitely extended system, the recursion algorithm after \( n \) steps contains contributions only from a central cluster consisting of \( O(n^3) \) atoms. For numerical purposes this limits the number of atoms that can be modelled, and also implies that one is always studying a finite system. The terminating continued fraction obtained in the process yields a number of isolated bound states, appropriate for a finite cluster. For most purposes this is an unphysical approximation to the problem under investigation and one needs to overcome these finite size effects by embedding the cluster in an infinite medium. Mathematically a suitable terminator should be appended to the continued fraction, so as to obtain a Green function with a branch cut, rather than a set of simple poles. Several terminators are available in the literature, which reflects the asymptotic properties of the continued fraction expansion of the Green function accurately. The advantage of such a termination procedure is that the approximate resolvent retains the Herglotz properties. It preserves the first \( 2N \) moments of the density of states exactly. This represents the effect of a cluster at a distance \( N \) from the starting state. It also maintains the correct band-widths, band-weights and the correct singularity at the band edges.

2.7.1 Terminating Schemes

Once a set of \( \{ a_n, b_n \} \) \( n = 1, N \) has been calculated, there are several ways of appending a terminator to the continued fraction expansion of the diagonal element of the resolvent to yield the density of states. For applying the termination scheme to approximate the tail of the continued fraction, we have to ensure that the approximate resolvent \( R \) (which replaces \( G \)) should be such that the corresponding approximate Hamiltonian should have a similar energy spectrum, as the original Hamiltonian \( H \). In other words the resulting approximate density of states should preserve the singularities (singularities at the band edges and Van-Hove singularities) of the density of states of the system one is examining.

In early applications to systems with a single band of states, \( \{ a_n, b_n \} \) were found to be rapidly convergent to some \( (a, b) \). So if for \( n \geq N \) we set \( a_n = a \) and \( b_n = b \), we can sum the remainder of the infinite continued fraction analytically.
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\[
t(E) = \frac{b_n^2}{E - a_n - \frac{b_n^2}{b_{n+1}}}
\]

is replaced by

\[
t(E) = \frac{b^2}{E - a - \frac{b^2}{E - a - \ldots}}
\]

we can solve for

\[
t(E) = 1/2 \{(E - a) - [(E - a)^2 - 4b^2]^{1/2}\}
\]

The quadratic termination (Haydock, 1972) produces a cut on the real axis of the complex $E$ plane between $(a-2b)$ and $(a+2b)$ with the correct analytic character for the three dimensional spectra i.e. $(|E - E_{edge}|)^{1/2}$, near the edges. The original \{ $a_n$, $b_n$ \} to whose continued fraction expansion the $t(E)$ is appended, then modulate the semielliptical spectrum of $t(E)$ with the particular local information extracted from $H$.

In more complex systems involving a number of isolated bands (for example semiconductors and transition metal compounds), it is found that the \{ $a_n$, $b_n$ \} are not at all rapidly convergent, as they now incorporate the detailed information of internal band edges and singularities. For this purpose the quadratic terminator is not suitable, and the quadrature method proposed by Nex(1978) is found to be more useful. In this approach it is the indefinite integral $N(E)$ of the density of states $n(E)$ that is approximated and the result is then differentiated to yield the local density of states. The quadrature approach does not generate the terminator $t(E)$ explicitly and requires no information other than the truncated continued fraction.

It has been found that given the band-edges and the truncated continued fraction, the analytic terminator proposed by Haydock and Nex(1984; 1985) and later improved by Lucini and Nex (1987) produces much better results as compared to the quadrature method. Here we shall outline the salient features of the analytic terminator schemes for a solid with single band.

A set of coefficients \{ $a_n$, $b_n$ \} is first generated recursively from the three term recurrence relation given by eqn(2.29). We generate such coefficients up to $n = n_2$ steps. We now generate orthogonal polynomials of the first and second kinds: $P_n(z)$ and $Q_n(z)$ for the above recurrence relation. These are the solutions of:

\[
P_{n+1}(z) = (z - a_n)P_n(z) - b_n^2 P_{n-1}(z)
\]

(2.31)
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\[ Q_n(z) = (z - a_n)Q_{n-1}(z) - b_n^2Q_{n-2}(z) \]  

(2.32)

with \( P_{-1} = Q_{-1} = 0 \), \( P_0 = Q_0 = 1 \)

The next step is to locate accurately, from the generated continued fraction coefficients (\( n < n_2 \)), the lower (left) band edge \( a \), the band width \( r \) and the weight \( w \). From this we construct a model Herglotz function with square-root band edge singularities:

\[ F(z) = 8w \left[ z - (a + r/2) - \sqrt{(z - a)(z - a - r)} \right] / r^2 \]

We now run the recursion again with the Hamiltonian replaced by \( z \), the state vectors by polynomials described by eqn (2.31) and eqn (2.32). The inner product by a union of Gauss-Chebyshev quadrature:

\[ f(z) \odot g(z) = \sum_{i=1}^{n} \Omega_i f(\alpha_i') g(\alpha_i') \]

where

\[ \Omega_i = \frac{\pi w}{(n + 1) \sin^2 \theta_i} \]

\[ \alpha_i' = a + (1 - \cos \theta_i) r/2 \]

\[ \theta_i = \frac{i \pi}{n + 1} \]

This will generate a set of recursion coefficients \( \{ c_n, d_n \} \) and a set of mutually orthogonal polynomials \( \{ R_n(z) \} \) and \( \{ S_n(z) \} \). The terminator is then given by:

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

Again from the fact that \( R_n \) and \( S_n \) are polynomials of order \( n \) and \( F(z) \) is a Herglotz function, it follows immediately that the terminator is itself Herglotz.

The Green function is given by:

\[ G(z) = \frac{Q_{n-2}(z) - b_{n-1}^2T(z)Q_{n-3}}{P_{n-1}(z) - b_{n-1}^2T(z)P_{n-2}} \]

Using very similar arguments as before, the Green function is Herglotz if \( T(z) \) is Herglotz.
This method of analytic termination of Haydock and Nex (1984; 1985) was further improved by Lucini and Nex (1987). It is easy to understand that in a chain with constant parameters suppose one appends a constant terminator with infinite band-width then the spectrum will consist of delta functions. When the band edge mismatch is reduced these delta-functions broaden into Lorentzians and finally only show up as oscillations superimposed on the semi-elliptic local DOS resulting from such constant coefficients. In such a simple picture one can consider the chain parameters \( a_n \) and \( b_n \) to represent the potentials on the one dimensional chain and one can regard the eigenstates of the computed chain as being initially unable to tunnel out through the potential barrier of the terminator. As the height of the barrier is reduced they become resonances superposed on the local density of states. The situation is analogous to the coherent reflection of the eigenstates by the step function in the potential represented by the discontinuous join to the terminator. The method of Lucini and Nex suggests linear interpolation between the computed and the analytic terminator coefficients to reduce the spurious oscillations arising out of this coherent reflection. The method is analogous to splicing as opposed to butt-joining pieces of wood.

We start with computed continued fraction coefficients \( a_n \), \( b_n \) upto \( n \) levels and with terminator coefficients \( a^t_n \) and \( b^t_n \). The method of Lucini and Nex now suggests to linearly interpolate between the computed coefficients and that of the analytic terminator in the following manner:

\[
\begin{align*}
\tilde{a}_n &= \begin{cases} 
\frac{1}{n_2 - n_1} 
\end{cases} \left\{ \begin{array}{l}
\frac{a_n(n_1-n) + a^t_n(n-n_2)}{(n_1-n_2)}, \quad n \leq n_2 \\
\frac{a^t_n}{n_1 - n}, \quad n_2 \leq n \leq n_1
\end{array} \right.
\end{align*}
\]

where \( n_1 \) is the start and \( n_2 \) is the end of the interpolation. Similarly \( \tilde{b}_n \) can be obtained by replacing \( a_n \) with \( b_n \) in the above expression. Again such a termination procedure retains the Herglotz properties of the Green function.

### 2.8 THE AUGMENTED SPACE FORMALISM:

The augmented space formalism, introduced by Mookerjee (1973a) is a novel and conceptually attractive method for the calculation of the configuration averaged Green function of a disordered material. In this method one transforms the Hamiltonian describing a given disordered system to an ordered Hamiltonian whose Green function matrix elements correspond to appropriate configurational averages of the Green function of the original disordered system! The new ordered Hamiltonian is said to be in an augmented space which can be described as the direct product of the Hilbert space \( \mathcal{H} \) spanned by the original Hamiltonian with a configuration or disorder space \( \Phi \) which spans all possible configurations of the system. As a result, configuration averages in real space are mapped onto inner products in the augmented space.

Let us suppose that the Hamiltonian describing a disordered system is characterized by a set of independent random variables \( \{ n_i \} \). Each random variable \( n_i \) take the values \( m_1, m_2, \ldots \). ...
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... m_γ and one can decompose the joint probability distribution of the random variables \( \{ n_i \} \) as:

\[
P(\{n_i\}) = \prod_i p_i(n_i)
\]

where \( p_i(n_i) \) is the probability density of the individual variables. We assume that the probability density satisfy the following properties like the density of states corresponding to the Green function:

\[
p_i(n_i) \geq 0
\]

\[
\int_{-\infty}^{+\infty} p_i(n_i) n_i^m dn_i = \text{finite}
\]

So it suggests that, analogous to the density of states the probability density could be expressed as the imaginary part of a Herglotz function, and this Herglotz function in turn is related to the resolvent of a self-adjoint operator. So for each density \( p_i(n_i) \), we construct a space \( \phi_i \), spanned by the states of \( n_i \) such that the system configuration space is defined as \( \Phi = \bigotimes \phi_i \). To each random variable \( n_i \) a self-adjoint operator \( M^{(i)} \in \phi_i \) is associated, such that:

\[
p(n_i) = -\frac{1}{\pi} \Im \langle \gamma_0^i | (n_i + i\delta) I - M^{(i)} \rangle^{-1} | \gamma_0^i \rangle
\]  

(2.33)

where \( | \gamma_0^i \rangle = \sqrt{\frac{1}{\alpha}} \sum_{j=1}^{\infty} | m_j^i \rangle \) is a specific member of \( \phi_i \). The form of \( p_i(n_i) \) suggests, that \( M^{(i)} \) can be extracted by performing a sequence of steps which is just reverse of the recursion method described in section \( 2.7 \). So if one can express the probability density as a continued fraction, then \( M^{(i)} \) can be written as a tridiagonal matrix analogous to the Hamiltonian in the recursion method.

Let us consider the average of any function \( f \) of \( n_i \), which may be written as:

\[
\langle f \rangle_{\text{ave}} = \int_{-\infty}^{+\infty} f(n_i) p(n_i) dn_i
\]

\[
\langle f \rangle_{\text{ave}} = -\frac{1}{\pi} \Im \int_{-\infty}^{+\infty} f(n_i) \langle \gamma_0^i | (n_i I - M^{(i)}) | \gamma_0^i \rangle dn_i
\]  

(2.34)

Inserting the eigen states of \( M^{(i)} \), \( \mu_i \) and \( \mu_i' \) in equation (2.34), which also forms a complete set of basis states we have:
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\[ \langle f \rangle_{\text{ave}} = -\frac{1}{\pi} \Im \sum_{\mu_i} f(n_i) |\mu_i\rangle \langle \mu_i| (n_i I - M^{(i)})^{-1} |\mu_i\rangle \langle \mu_i| \langle \gamma_0 | dn_i \]

\[ = \langle \gamma_0 | \sum_{\mu_i} f(n_i) |\mu_i\rangle \delta(n_i - \mu_i) \langle \mu_i| \langle \gamma_0 | \]

\[ = \langle \gamma_0 | \sum_{\mu_i} f(\mu_i) |\mu_i\rangle \langle \mu_i| \langle \gamma_0 | \]

\[ = \langle \gamma_0 | \tilde{f}(M^{(i)}) |\gamma_0 \rangle \]  \hspace{1cm} (2.35)

where \( \tilde{f} \) is the same functional operator of \( \{ M^{(i)} \} \) as \( f \) was a function of \( \{ n_i \} \). This is the Augmented space theorem.

The above prescription can easily be generalized to find the configuration averaged resolvent
\[ \langle G \rangle = \langle (z I - H)^{-1} \rangle \] of the random Hamiltonian \[ H(n_1, n_2, \ldots, n_i, \ldots) \]. We define the
configuration ground state as \[ |\gamma_0 \rangle \] in the product space as \[ |\gamma_0 \rangle = |\gamma_0 \rangle \otimes |\gamma_0 \rangle \otimes \ldots |\gamma_0 \rangle \ldots \]. The
augmented space theorem then states that the configuration average:

\[ \langle G_{ii} \rangle = \int G_{ii}(n_1, n_2, \ldots, n_i, \ldots) \prod p(n_i) dn_i \]

\[ = \langle \gamma_0 | \tilde{G}_{ii}(M^{(i)}, \tilde{M}^{(i)} \ldots M^{(i)}) \rangle |\gamma_0 \rangle \]

\[ = \langle \gamma_0 \otimes i | \tilde{G}(M^{(i)}, \tilde{M}^{(i)} \ldots M^{(i)}) \rangle |\gamma_0 \rangle \] \hspace{1cm} (2.36)

where \( \tilde{M}^{(i)} = I \otimes \ldots \otimes M^{(i)} \otimes I \). Again \( \tilde{G} \) is the same function of \( \tilde{M}^{(i)} \) as \( G \) was of \( n_i \). The
calculation of \( \langle G_{ii} \rangle \) then reduces to the problem of the ground state matrix element in the
augmented space \[ \Psi = \mathcal{H} \otimes \Phi \] where \( H \in \mathcal{H} \) and \( \Phi = \prod \phi^i \) , an idea familiar in quantum
mechanical averaging.

For a binary probability distribution,

\[ p_i(n_i) = x \delta(n_i - 1) + (1 - x) \delta(n_i) \]  \hspace{1cm} (2.37)

where

\[ n_i = \begin{cases} 1, & \text{for } i = A \\ 0, & \text{for } i = B \end{cases} \]

This probability distribution (2.37) can easily be recast into a continued fraction expansion:

\[ p(n_i) = -\frac{1}{\pi} \Im \sum \frac{1}{n_i - x - \frac{x(1 - x)}{n_i - (1 - x)}} \] \hspace{1cm} (2.38)
The matrix $M^{(i)}$ has the form:

$$M^{(i)} = \begin{pmatrix}
  x & \sqrt{x(1-x)} \\
  \sqrt{x(1-x)} & (1-x)
\end{pmatrix}$$

So for a binary probability distribution $M^{(i)}$ is an operator on a Hilbert space of rank two spanned by $|\gamma_0^i\rangle$ and $|\gamma_1^i\rangle$. This operator has eigenvalue $m_1 = 0$ and $m_2 = 1$ with the eigen-vectors $|0\rangle$ and $|1\rangle$. The basis $|\gamma_0^i\rangle$, $|\gamma_1^i\rangle$, where $M^{(i)}$ has a tridiagonal representation may be expressed in terms of the eigen basis as:

$$|\gamma_0^i\rangle = \sqrt{x}|0\rangle + \sqrt{1-x}|1\rangle$$
$$|\gamma_1^i\rangle = \sqrt{1-x}|0\rangle - \sqrt{x}|1\rangle$$

The above expressions derived for the binary probability distribution will be useful in our subsequent discussion.

### 2.9 AUGMENTED SPACE RECURSION

The recursion method provides an efficient algorithm to calculate the diagonal elements of the resolvent of a sparse Hamiltonian. For a disordered system the augmented space theorem maps a disordered Hamiltonian described in a Hilbert space $\mathcal{H}$ onto an ordered Hamiltonian in the augmented space $\Psi$, and configuration average of the Green function reduces to the evaluation of a particular matrix element in this augmented space. So if one performs a recursion method in the augmented space one can obtain the matrix element required by equation (2.36) to obtain the configuration average of a Green function directly. Though the idea was conceived long time back (Mookerjee, 1973b), but it cannot be realized into practice because of the large rank of the augmented space, namely $(N \times 2^N)$ for a binary alloy described on a tight-binding Hamiltonian with $N$ sites. The usual approach as described in section (2.6) was to systematically reduce the rank of the augmented space. In practice the fluctuations in the augmented space are confined to a cluster and the rest of the system in the augmented space is approximated by an effective medium. The effective medium is then determined self-consistently, leading to the cluster generalizations of the CPA. Though the method yields Herglotz Green function but the number of coupled self-consistent equations to determine the effective medium increases rapidly as the size of the chosen cluster. This computational intractability of the method results in its application restricted to model systems.

The direct recursion in the augmented space does not possess this restriction. The advantage of the method is that it does not involve single site approximation or the solution of self-consistent equations to determine the effective medium. It can treat both diagonal as well as off-diagonal disorder on an equal footing, and preserves all the essential features of the recursive
solution of the Schrödinger equation. The work-load of the recursion method is proportional to
the size of the system. It can be further reduced if one exploits the symmetry of the Hamiltonian
both in the real space as well as in the augmented space arising as a result of homogeneity of
disorder. The rank of the irreducible subspace of the augmented space on which the recursion
is effectively carried out is drastically reduced. The implementation of the augmented space
recursion exploiting the symmetry of the augmented space, in the TB-LMTO framework forms
one of the major contributions of the present thesis.

The starting point for the augmented space recursion is the most localized sparse tight-
binding Hamiltonian derived systematically from the LMTO-ASA theory and generalized to
substitutionally disordered random binary alloys:

\begin{align}
H_{RL,R'L'}^0 &= \hat{C}_{RL} \delta_{RR'} \delta_{LL'} + \hat{\Delta}_{RL} S_{RL,R'L'}^0 \hat{\Delta}_{R'L'} \\
\hat{C}_{RL} &= C_{RL}^A n_R + C_{RL}^B (1 - n_R) \\
\hat{\Delta}_{RL} &= (\Delta_{RL}^A)^{1/2} n_R + (\Delta_{RL}^B)^{1/2} (1 - n_R)
\end{align}

Here R denotes the lattice sites and L = (\ell m) are the orbital indices (for transition metal \ell \leq 2) C_{RL}^A, C_{RL}^B and (\Delta_{RL}^A)^{1/2}, (\Delta_{RL}^B)^{1/2} are the potential parameters of the constituents
A and B (in the most tight-binding representation of \alpha = \beta) of the alloy. \(n_R\) are the local
site occupation variables which randomly take values 1 and 0 according to whether the site
is occupied by an A atom or not. From the discussion in section [2.8], it is clear that the
representation of the Hamiltonian in the augmented space \(\hat{H}\) consists of replacing the local site occupation variables \(\{n_R\}\) by \(\{\hat{M}^R\}\), and is given by:

\begin{align}
\hat{H} &= \sum_{RL} \left( C_{RL}^B \hat{I} + \delta C_{RL} \hat{M}^R \right) \otimes a_R^\dagger a_R + \cdots \\
&+ \sum_{RL} \sum_{R'L'} \left( (\Delta_{RL}^B)^{1/2} \hat{I} + \delta \Delta_{RL} \hat{M}^R \right) S_{RL,R'L'}^0 \left( (\Delta_{R'L'}^B)^{1/2} \hat{I} + \delta \Delta_{R'L'} \hat{M}^R \right) \cdots \\
&\otimes a_R^\dagger a_{R'}
\end{align}

where,

\begin{align}
\delta C_{RL} &= [C_{RL}^A - C_{RL}^B] \\
\delta \Delta_{RL} &= [(\Delta_{RL}^A)^{1/2} - (\Delta_{RL}^B)^{1/2}]
\end{align}

Other parameters have their usual meaning and \(\hat{I}\) is the identity operator defined in the
augmented space. \(\hat{M}^R\) in the second quantized notation is given by:
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\[ \tilde{M}^R = xb^\dagger_{R_0}b_{R_0} + (1 - x)b^\dagger_{R_1}b_{R_1} + \sqrt{x(1 - x)} \left( b^\dagger_{R_0}b_{R_1} + b^\dagger_{R_1}b_{R_0} \right) \]  \hspace{1cm} (2.43)

\((b^\dagger_{R_0},b_{R_0})\) and \((b^\dagger_{R_1},b_{R_1})\) are the creation and annihilation operators in the augmented space, where each site is characterized by two states \((0,1)\) which may be identified with the up and down states of an Ising system. So a particular configuration in a binary alloy is characterized by a collection of 0's and 1's in a particular sequence and these configuration states are stored extremely efficiently in bits of words and the algebra of the Hamiltonian in the configuration space mirrors the multi-spin coding techniques (Chowdhury et al., 1986; Datta and Mookerjee, 1992) used in numerical works with the Ising model. The multi-spin coding technique will be discussed in details later in the text.

The Hamiltonian is now an operator in a much enlarged space \(\Psi = \mathcal{H} \otimes \prod \phi_R\) (the augmented space), where \(\mathcal{H}\) is the Hilbert space spanned by the countable basis set \(|\{R,L\}\rangle\). The enlarged Hamiltonian does not involve any random variables but incorporates within itself the full information about the random occupation variables. If we substitute eqn.\[2.43\] for \(M^R\) in eqn.\[2.42\], then the augmented space Hamiltonian takes the form:

\[ \tilde{H} = \left( \sum_{RL} C^B_{RL} \hat{I} \otimes a^\dagger_R a_R + \sum_{RL,R'L'} (\Delta^B_{RL})^{1/2} S^\theta_{RL,R'L'} (\Delta^B_{RL})^{1/2} \hat{I} \otimes a^\dagger_R a_{R'} \right) + \ldots \\
\sum_R \sum_{\lambda,\mu} \delta C_{RL} \tilde{M}^{(R)}_{\lambda,\mu} \otimes a^\dagger_R a_R b^\dagger_{R,\lambda} b_{R,\mu} + \ldots \\
\sum_{RL} \sum_{R',L'} \sum_{\lambda,\mu} (\Delta^B_{RL})^{1/2} S^\theta_{RL,R'L'} \delta \Delta_{R'L'} a^\dagger_R a_{R'} \otimes \tilde{M}^{(R')}_{\lambda,\mu} b^\dagger_{R,\lambda} b_{R',\mu} + \ldots \\
\sum_{RL} \sum_{R',L'} \sum_{\lambda,\mu} \delta \Delta_{RL} S^\theta_{RL,R'L'} (\Delta^B_{RL})^{1/2} a^\dagger_R a_{R'} \otimes \tilde{M}^{(R')}_{\lambda,\mu} b^\dagger_{R,\lambda} b_{R',\mu} + \ldots \\
\sum_{RL} \sum_{R',L'} \sum_{\lambda,\mu} \delta \Delta_{RL} S^\theta_{RL,R'L'} \delta \Delta_{R'L'} a^\dagger_R a_{R'} \otimes \left( \tilde{M}^{(R)}_{\lambda,\mu} \tilde{M}^{(R')}_{\lambda',\mu'} b^\dagger_{R,\lambda} b_{R,\mu} b^\dagger_{R',\lambda'} b_{R',\mu'} \right) \]  \hspace{1cm} (2.44)

A close inspection of eqn.\[2.44\] shows that the augmented space Hamiltonian contains operators of the following types:

(a) \(a^\dagger_R a_{R'}\) with \(R = R'\) and \(R \neq R'\) terms. The operators acting on a vector in the augmented space changes only the real space label, but keeps the configuration part unchanged.

(b) \(a^\dagger_R a_{R'} b^\dagger_{\lambda} b_{\mu}\) with \(R = R'\) and \(R \neq R'\) terms. \(k\) is \(R\) or \(R'\), while, \(\lambda\) and \(\mu\) may take value 0 and 1. These operators acting on an augmented space vector may change the real space label (if \(R \neq R'\)). In addition, they may also change the configuration at the site \(R\) or \(R'\) (if \(\lambda \neq \mu\)). This resembles a single spin flip Ising operator in configuration space.
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(c) $a_R^\dagger a_R$, $b_R^\dagger b_R$, $a_R b_R$, $b_R^\dagger b_R^\dagger$, $b_R b_R^\dagger$ with $\lambda$, $\mu$, $\nu$, $\xi$ taking values 0 and 1. The operators may change the real space label (if $R \neq R'$), as well as the configuration either at $R$ or $R'$ or both. This resembles a double spin flip Ising operator in the configuration space.

In order to facilitate the recursion method in the augmented space, one should have a scheme to represent the basis in the real space and the configuration space. A basis $|m\rangle$ in the Hilbert space $\mathcal{H}$ is represented by a column vector $C_m$ with zeros everywhere except at the $m$-th position. The inner products are defined as

$$\langle m| \langle n \rangle = C_m^T C_n$$

$$a_n^\dagger a_n C_p = \delta_{np} C_m$$

A member of the basis in the configuration space $\Phi = \Pi \phi_R$ has the form

$$|\gamma_{\lambda_1} \otimes \gamma_{\lambda_2} \otimes \ldots \otimes \gamma_{\lambda_m} \rangle$$

where each $\lambda_i$ may be either 0 or 1.

We may represent this basis by a collection of binary words (strings of 0's and 1's). In the usual terminology of ASF the number of 1's define the cardinality of the basis and the sequence of positions at which we have 1's $\{ S_C \}$ called the cardinality sequence labels the basis. Thus a binary sequence $B[ C, \{ S_C \}]$ is a representation of the member of the basis in the configuration space. The dot product between the basis members is then

$$B[C, \{ S_C \}] \otimes B[C', \{ S_{C'} \}] = \delta_{CC'} \delta_{\{ S_C \}=\{ S_{C'} \}}$$

A careful examination of the operations (a) - (c) defined on the configuration space, reveals that these operations when operate on a particular basis in the augmented space changes its cardinality and cardinality sequence. Since a basis in configuration space is stored in bits of words so the operations are defined on these bits of words. One can easily employ the logical functions in a computer, to define these operations.

Once we have defined the Hamiltonian, and its operation in the augmented space, the recursion method on the augmented space gives the configuration averaged Green function $\langle G(z) \rangle_{RL,RL}$. Directly. We first chose the following as the starting state in our recursion scheme:

$$|\Psi_1\rangle = |R, L\rangle \otimes |\gamma_0\rangle$$

The recursion co-efficients $a_n$ and $b_n$ are generated by

$$\hat{H} |\Psi_n\rangle = a_n |\Psi_n\rangle + b_{n+1} |\Psi_{n+1}\rangle + b_n |\Psi_{n-1}\rangle$$

$$a_n = \langle \Psi_n \otimes \hat{H} |\Psi_n\rangle$$

$$b_n = \langle \Psi_{n-1} \otimes \hat{H} |\Psi_n\rangle$$
The continued fraction coefficients are generated to a finite number of steps and finally appended with a suitable terminator. The configuration averaged Green function is related to the density of states by

$$n(E) = \frac{1}{N\pi} \sum_{L} \sum_{R} (G(E + i0))_{RL,RL}$$

(2.45)

## 2.9.1 Multi-Spin Coding

We have already seen that the representation of a basis in the augmented space consists of direct product of the Hilbert space and the configuration space characterized by its cardinality and cardinality sequence. In a computer a basis $| m \rangle$ in the Hilbert space $H$ is represented by a column vector $C_m$ with zeros everywhere except at the $m$-th position. For the configuration space in the binary alloy each site has two degrees of freedom, and it can be either 0 or 1. The storage of information in a computer is usually done in words made up of bits, where each bit is binary and assumes the value 0 or 1. So each state vector for a site may be stored in a bit rather in a single word. So only few words may be utilized to store the entire configuration analogous to the multi-spin coding technique used in the simulations of the Ising model. A state vector in the augmented space may be written as:

$$| m, B[C, S\{C\}] \rangle = \{C_m, W(1), W(2), \ldots, W(n)\}$$

where $C_m$ is a vector which has the information about the site $m$ in the Hilbert space, and $W(1), W(2), \ldots, W(n)$ are the number of words required to store a configuration. In a M-bit machine, each word can represent up to $(M-1)$ terms as a sequence of 0's and 1's and for the configuration of a lattice of size $N$, $N^{M-1} + 1$ words are necessary. In order to facilitate the recursive procedure one has to specify the operation of the Hamiltonian in this basis coupled with the inner products between the basis members as discussed earlier. The various operations of the Hamiltonian may be summarised as follows:

(a) $a_{m}^{\dagger}a_{n}[p, B[C, \{S_c\}]] = \delta_{n,p}| m, B[C, \{S_c\}] \rangle$

This operator does not change the configuration space and operates only on the real space. So the configuration space remains unaltered, but the real space is now represented by a new vector $C_m$ with zeros everywhere except at $m$ provided $p = n$.

(b) $b_{l}^{\dagger}b_{m}[i, B[C, \{S_c\}]] = | i, B[C', \{S_{c'}\}] \rangle$

The above operation in the augmented space involves the following sequence of steps:

1. First one has to determine in which word the $p$-th state vector in the configuration $B[C, \{S_c\}]$ is stored, given by $j = (i/31) + 1$ and the corresponding bit position $k$ in the
word \( j \) given by \( i - (j - 1) \times 31 \). Once these two positions are available one can use the logical operation IBITS available in Fortran language to determine the cardinality at the \( i \)-th site:

\[
\text{IBITS} (W(j), k) = L (0 \text{ or } 1)
\]

(2) Depending on the value of \( \lambda \) and \( \mu \) we have the following possibilities:

(i) if \( \lambda = \mu \) the configuration space remain unchanged and \( C' = C \).

(ii) if \( \lambda \neq \mu \) and \( i \notin \{S_c\} \) then \( C' = C + 1 \) ie. we have to change the \( k \)-th bit of the \( j \)-th word to 1, and in terms of the logical operations \( W'(j) = \text{IBSET}(W(j), k) \). So the cardinality of the configuration space increases by 1.

(iii) if \( \lambda \neq \mu \) and \( i \in \{S_c\} \) then \( C' = C - 1 \) ie. we have to change the \( k \)-th bit of the \( j \)-th word to 0, and in terms of the logical operations \( W'(j) = \text{IBCLR}(W(j), k) \). So the cardinality of the configuration space decreases by 1.

These logical operations which describes the action of the Hamiltonian are computationally very fast and a little manipulation avoids the repetitive use of branching if statements. Such a binary word representation coupled with spin the flip operations has been used extensively for the numerical studies of the Ising model. Such a scheme of calculation results in a large saving of the disk space.

### 2.9.2 The Symmetry And The Recursion Method

The computer implementation of the recursion method can be further optimized, if one exploits the symmetry of the Hamiltonian. The TB-LMTO Hamiltonian contains the information of both, the structure of the underlying lattice and the symmetry of the orbitals. The objective of the symmetry principle is to identify an irreducible subspace of the entire space such that the representation of the Hamiltonian in this space is irreducible, and the recursion is confined within this subspace. In the present thesis we will propose a scheme to identify such an irreducible subspace for a lattice with cubic symmetry in the presence of s-p-d orbitals. We will first illustrate our method for usual scalar recursion and then generalize our methodology to the augmented space recursion.

#### A. Symmetry in real space recursion

It has been shown by Gallagher (1978) that if the starting state of the recursion belongs to an irreducible representation of the Hamiltonian, then the states generated in the process of recursion belong to the same row of the same irreducible representation of the Hamiltonian. Further, the recursion with the starting state corresponding to the different rows of the same irreducible representation are similar. The states belonging to the different irreducible representation or different rows of the same irreducible representation do not mix. So we need to retain only those states belonging to the irreducible representation of the Hamiltonian for the
purpose of recursion and get the same resolution as with all of them. These states belonging to
the irreducible representation of the Hamiltonian are not related to one another by the point
group symmetry of the underlying lattice as well as the symmetry of the orbitals. Once these
state vectors are identified the recursion can be performed in the reduced subspace, with modi-

cified weight factors for each site in the irreducible subspace. These weight factors arise as each
site in the irreducible subspace is a linear combination of the original state vectors. Thus in
computation we need far less storage and time because the dimensionality of the matrix \( H \) is
reduced drastically.

The scheme of calculation then consists of two steps:

1. To identify the non-equivalent sites (NE) sites. These sites are not related to each other
   by the point group symmetry of the underlying lattice and the symmetry of the orbitals.
   These non-equivalent sites can be expressed as a linear combination of the state vectors
   in the original reducible basis.

2. The weight of these sites is equal to the number of distinct sites related to NE by the
   symmetry of the Hamiltonian.

In practice these nonequivalent sites are determined together with their weights. The repre-
sentation of the Hamiltonian in this new basis is irreducible and more sparse. The recursion is
now confined with these non-equivalent sites and the irreducible Hamiltonian. To illustrate our
method let us consider a s-band Hamiltonian defined on a square lattice. As s-orbitals preserve
the symmetry of a square lattice, so the non-equivalent vectors are those which are not related
to one another by the point group symmetry of a square lattice. The number of distinct vectors
obtained from these non-equivalent vectors by the point group symmetry of a square constitutes
their weight. For a square lattice these NE vectors are confined to the \((1/8)^{th}\) portion of the
entire lattice and constitutes the irreducible subspace, where the recursion will be eventually
carried out. It is easy to see for a square lattice the maximum weight of a site is 8 and minimum
is 1. So with these vectors (NE) in the irreducible subspace together with their weights, the
recursion is faster and requires much less storage. Similarly for a Hamiltonian with s -orbital
and with cubic symmetry the irreducible subspace constitutes \((1/48)^{th}\) of the entire space.

However the inclusion of the p-orbitals introduces preffered x,y,z directions and breaks the
symmetry between x,y,z axis. Thus the point group symmetry operations which interchange
between x,y,z co-ordinates are prohibited. Hence the irreducible part of the lattice instead of
being \((1/48)^{th}\) of the entire lattice now becomes \((1/8)^{th}\) . If with each site \( R \) we attach weight
\( W_R \) which is given by the number of basis sets equivalent to \( R \), then the whole process can
be summarised as follows: In the new TB-LMTO reduced basis we have the diagonal matrix
elements of the Hamiltonian as:

\[
\langle RL | H | RL \rangle = C_{RL}^{0}
\]

and the off-diagonal matrix elements are given by:
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\[ (R'L'|H|RL) = (\sqrt{WR'/\sqrt{WR}})(\Delta_{R'L'}^N)^{1/2}S_{R'L'R}^0(\Delta_{R'L'}^N)^{1/2}\beta_R(L, L') \] (2.47)

where \( R \) and \( R' \) both belong to the irreducible part of the lattice. \( \beta_R(L, L') \) is a factor which can be either 0 or 1 depending on whether the position occupied by the site \( R \) is a symmetry position with respect to orbitals \( L \) and \( L' \). This fact can be made more transparent in the following way: the structure matrix element connecting two orbitals occupying two different sites is given by the two centre Slater-Koster integrals. Apart from a factor made of \( \pi \) and \( \sigma \) integrals the Slater-Koster integral contains a factor made up of direction cosines of the vector joining the two basis states between which the matrix element is taken. It reflects the symmetry property of the overlapping orbitals. Now for the different equivalent sites connected to a given site, this direction cosine has different sign. In the effective irreducible basis, which is a linear combination of the old basis, these different signs may give rise to a zero matrix element of a Hamiltonian. We shall call these positions where such zero matrix elements occur, the symmetry positions with respect to orbitals \( L \) and \( L' \). The representation of the Hamiltonian in terms of the irreducible basis set reduces the rank of the Hamiltonian matrix. The workload of the recursion reduces drastically. Such a reduction is absolutely necessary for the purpose of augmented space recursion.

B. Symmetry in augmented space recursion

For a system with uncorrelated disorder there is homogeneity of disorder. So the symmetry considerations due to the homogeneity of disorder may be employed to reduce the rank of the effective Hamiltonian \( \tilde{H} \) in the augmented space.

As discussed earlier the basic step in the symmetry procedure is to identify a set of nonequivalent vectors and their weights. This can be achieved in the following way. Since the augmented space is a direct product of the real space and the configuration space, which are disjoint, symmetry operations on either of them apply independently of each other. For example, if a site is occupied by an A atom, then all the Z configurations in which its (Z-1) neighbours are occupied by A atoms and one by B are equivalent. In practice a site in the augmented space is chosen as \( | R, [ C, \{ S_C \} ] \rangle \). All the equivalent sites are obtained by point group operation \( \Re \) on the site in question.

\[ |R', [C', \{S_{C'}\}] \rangle = \Re |R, [C, \{S_C\}] \rangle = |\Re R, \Re [C, \{S_C\}] \rangle \]

The number of distinct sites obtained in this way is the weight of the site in question. As in the real space recursion only the non equivalent sites (NE) obtained in this way are retained for the purpose of recursion. Incorporating both the symmetry of the lattice and the orbitals, the diagonal matrix element of the Hamiltonian is given by:

\[ \langle RL, [C, \{ S_C \}] | \tilde{H} | RL, [C, \{ S_C \}] \rangle = [\xi_L \tilde{C}_L + (1 - \xi_L) \tilde{C}_L] \] (2.48)
where,

\[ |R L, [C, \{ S_C \}] \rangle \in NE \]

\[ \xi_R = 1 \quad R \in \{ S_C \} \]

\[ \xi_R = 0 \quad R \not\in \{ S_C \} \]

\[ \tilde{c}_{RL} = x_A C^A + (1 - x_A) C^B \]

\[ \tilde{c}_{RL} = (1 - x_A) C^A + x_A C^B \]

The off-diagonal matrix elements of the Hamiltonian are (the angular momentum indices are suppressed for brevity):

\[
\langle R' L', [C', \{ S_{C'} \}] | \hat{H} | R L, [C, \{ S_C \}] \rangle = \sqrt{W_i/W_j} \left( \xi_R \xi_{R'} \Delta S_{RR'} \Delta + \ldots \right)
\]

\[
\xi_R(1 - \xi_{R'}) \Delta S_{RR'} \Delta + (1 - \xi_R) \xi_{R'} \Delta S_{RR'} \Delta + \ldots
\]

\[
(1 - \xi_R)(1 - \xi_{R'}) \Delta S_{RR'} \Delta \beta_{i}(L, L') \delta_{[C, \{ S_C \}], [C'; \{ S_{C'} \}]} + \ldots
\]

\[
\sqrt{W_i/W_j} \left[ \xi_R \Delta S_{RR'} (\delta \Delta) + (1 - \xi_R) \Delta S_{RR'} (\delta \Delta) \right] \beta_{i}(L, L') \delta_{[C, \{ S_C \}], [C'; \{ S_{C'} \}]} + \ldots
\]

\[
\sqrt{W_i/W_j} \left[ \delta \Delta S_{RR'} \delta \Delta \right] \beta_{i}(L, L') \delta_{[C, \{ S_C \}], [C'; \{ S_{C'} \}]} + \ldots
\]

\[
(2.49)
\]

\[
\Delta_{RL} = x_A (\Delta_{RL}^A)^{1/2} + (1 - x_A) (\Delta_{RL}^B)^{1/2}
\]

\[
\Delta_{RL} = (1 - x_A) (\Delta_{RL}^A)^{1/2} + x_A (\Delta_{RL}^B)^{1/2}
\]

\[
\delta \Delta_{RL} = (\Delta_{RL}^A)^{1/2} - (\Delta_{RL}^B)^{1/2}
\]

We denote by I and J the augmented space vectors \(| R L, [ C, \{ S_C \}] \rangle\) and \(| R' L', [ C', \{ S_{C'} \}] \rangle \in NE\) respectively. \(\beta (L, L')\) is 0 or 1 depending on whether the position I is a symmetric position with respect to the orbitals L, L' in augmented space.
2.10 COMPUTATIONAL DETAILS AND METHOD OF SELF-CONSISTENCY:

The augmented space recursion formalism developed in the previous section is applied to calculate the total and local density of states of random binary alloys at various concentrations. We now mention some details concerning the numerical part of the problem. Total energy density-functional calculations are performed for the elements. The Hohenberg-Kohn-Sham equations are solved in the local density approximation (LDA). The LDA is treated within the context of the method of linearized muffin tin orbitals (LMTO) in the atomic sphere approximation. The computations are performed semi-relativistically using the exchange-correlation potential of von Barth and Hedin (1972). The basis set is composed of $l = 0, 1, 2$ orbitals, so that the Hamiltonian element are matrices of order 9. The elemental potential parameters are used to parametrize the alloy Hamiltonian, using the transferability of the LMTO potential parameters from the pure components to the alloy as prescribed by Andersen et. al (1987). This scheme allows one to obtain the potential parameters for an intermetallic compound from those of its constituents, without any self-consistent calculation. For close packed structures where the interstitial space can be packed closely with atomic (or atom centered) spheres, without the introduction of empty spheres (spheres centered about the interstitial sites), the prescription of Andersen et. al (1987) suggests that the estimate of the potential in the compound is simply to use the atomic sphere potentials of the elements. These frozen atomic sphere potentials correspond to neutral spheres, and the lineup of the internal energy zeros is consistent as long as the spheres remain neutral in the compound. Further calculations have indicated indicated that the charge neutrality defined with respect to the atomic spheres of the elements, is maintained within a few tenths of an electron in most cases.

For alloys obeying the Vegard’s law, where the volume per atom in the alloy is simply the concentration-weighted average of the normal pressure atomic volumes of the constituents, the use of normal-pressure values of the constituent’s potential parameters yields a sufficiently accurate potential and charge density. However for alloys showing deviation from Vegard’s law the potentials of the elements should be calculated at such a pressure that the concentration weighted sum of the atomic volumes equals the actual volume per atom in the alloy. Thus for a binary alloy $A_xB_{1-x}$ with volume $V^{\text{alloy}}$ per atom, the atomic volumes of the constituents $V^Q$ ($Q = A, B$) should satisfy the volume constraint:

$$xV^A + (1 - x)V^B = V^{\text{alloy}}$$

(2.50)

The assumption of the pressure volume relation yields:

$$\frac{V^A - V^A_0}{V^A_0} : \frac{V^B - V^B_0}{V^B_0} = \frac{B^B}{B^A}$$

(2.51)

where $V^Q_0$ ($Q = A, B$) are the normal-pressure atomic volumes of the components and $B^Q_0$
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(Q = A,B) are the bulk modulus. The solution of the eqn (2.50) and eqn (2.51) yields the volume of the constituents:

\[ V^A = \frac{B_0^A V_{\text{alloy}}^A + (1 - x)V_0^B(B_0^A - B_0^B)}{xV_0^A B_0^B + (1 - x)V_0^B B_0^A} V_0^A \]

\[ V^B = \frac{B_0^B V_{\text{alloy}}^B + (1 - x)V_0^A(B_0^B - B_0^A)}{xV_0^A B_0^B + (1 - x)V_0^B B_0^A} V_0^B \]

So the potential parameters in the alloy for the component Q (Q=A,B) should be calculated at new radius \( S^Q = (3V^Q/4\pi)^{1/3} \). The values of the potential parameters at the radii appropriate in the alloy phase \( S^Q \) (Q=A,B) can be obtained from the normal pressure radii \( S_0^Q \) and the volume derivatives of the potential parameters. Further, for large differences between \( S^Q \) and \( S_0^Q \) it is important not to interpolate linearly in \( S^Q \), but use the following equations using the logarithmic interpolation:

\[ C_L^Q = C_0^Q + \frac{dC_L^Q}{d\ln S_0^Q} \ln(S^Q/S_0^Q) \]

\[ \gamma_L^Q = \gamma_0^Q + \frac{d\gamma_L^Q}{d\ln S_0^Q} \ln(S^Q/S_0^Q) \]

\[ \Delta_L^Q = \Delta_0^Q \left[ \frac{S_0^Q}{S^Q} \right]^{\frac{d\ln S_0^Q}{d\ln S_0^Q}} \] (2.52)

After extrapolation of the potential parameters to new radii, one must take into account the fact that the alloy Wigner Seitz (WS) radius is different from that of the pure components, where the WS radii are the same as the sphere radii. This affects only two of the parameters, viz \( \Delta \) and \( \gamma \), which should be multiplied by \((S^Q/W)^{2d+1}\), where \( W = (3V_{\text{alloy}}/4\pi)^{1/3} \) is the alloy W-S radius i.e.

\[ (\Lambda_L^Q)_{\text{alloy}} = (S^Q/W)^{2d+1}(\Lambda_L^Q)_{\text{pure-component}} \] (2.53)

where \( \Lambda = \Delta , \gamma \)

The above prescription for obtaining the sphere radii for the components in the alloy leads to only a small charge transfer (within few tenths of an electron) between the spheres, hence the potential parameters so obtained, appropriate for neutral spheres, yield a reasonably accurate electronic structure of the alloy. The charge transfer gives rise to a Madelung term in the one electron potential. The potential in a given sphere undergoes a constant shift depending on the charge transfer for that sphere. The effect of Madelung shift is present in the potential parameters obtained in a self-consistent calculation. However the potential
parameters obtained by using eqn(2.52) and eqn(2.53) are for neutral spheres, and therefore do not show this Madelung shift, resulting in slightly inaccurate positioning of the bands. A small charge transfer, and consequently a small Madelung shift, is most crucial for the success of the above transferability scheme.

The flexibility of the choice of the Wigner-Seitz radius is an advantage in the LMTO method over other muffin-tin methods like KKR. For example in the KKR-CPA one chooses the common radii \( r^{\text{Moy}} \) of the touching muffin-spheres. \( r^{\text{Moy}} = x^r_1 + (1-x) r^2 \) for a random binary alloy \( A_x B_{1-x} \), where \( r^A \) and \( r^B \) are muffin-tin (MT) radii of atoms A and B respectively. The interstitial space between the muffin tin is excluded from self-consistency. The use of common radii, for atoms with different sizes thus introduces charge transfer artificially. The greater atom (A) then becomes overscreened within a smaller muffin-tin with the radius \( r^{\text{alloy}} \) especially for a low concentration of A atoms, when \( r^{\text{alloy}} \approx r^B < r^A \). This overscreening is due to a limited space where the self-consistency is performed, resulting in the impurity potential becoming more attractive. This inconsistency can be relaxed either by a proper treatment of the charge transfer outside the impurity muffin-tin sphere by performing self-consistent calculations for a cluster consisting of a central A atom surrounded by B spheres, or by enlarging the radius of A. Though the results are similar, but the advantage of the latter is that it equally holds good for concentrated alloys.

We have adopted this scheme of self-consistency in our present calculations. It is worth mentioning at this point that the full charge self-consistency in the effective medium can easily be achieved in our formalism in the following way:

From the local density of states one can calculate the energy moments, hence the local charge density through the relation:

\[
n^R(r) = 1/4 \pi \sum \{m^{(0)}_{RL}(r) + 2m^{(1)}_{RL}(r) + m^{(2)}_{RL}(r)\} \tag{2.54}
\]

where

\[
m^{(q)}_{RL} = \int_{-\infty}^{E_F} dE n_{RL}(E)(E - E_{R,L})^q \tag{2.55}
\]

\( n_{RL}(E) \) is the orbital projected partial density of states. From the charge density we calculate the Hartree potential by solving the Poisson’s equation and incorporate the exchange-correlation part by the local density functional formalism. The Schrödinger equation is then solved to obtain the potential parameters for each element in the alloy. The augmented space recursion is then carried out again with these new potential parameters, to obtain the new charge density. The procedure is then iterated till self-consistency is reached.

For the purpose of augmented space recursion, a four shell augmented space map was generated from a cluster of 400 sites, with interactions up to second nearest neighbour for the bcc structure and up to first nearest neighbour for the most closed packed fcc based structures.
We have calculated the component and total density of states through the recursion method with 8 pairs of recursion coefficients and terminated with the Lucini-Nex terminator. In some typical cases (CuZn to be discussed later), the recursion coefficients are calculated up to 10 steps. For the pure elements since the density of state has considerable structure we have employed 15 steps of recursion.

In this thesis we present the result of calculation for total and component densities of states of random substitutional transition metal alloys namely: AgPd, CuZn and TiFe at various concentrations. Our results are summarised in the next section.

2.11 RESULTS AND DISCUSSION.

2.11.1 AgPd

AgPd is one of the typical alloy systems where the disorder is dominated by the diagonal part of the Hamiltonian. Both constituents have roughly the same d-band widths. Since they belong to the same row of the periodic table, they have very little mismatch in atomic sizes. The alloy remains fcc and paramagnetic throughout the concentration regime. Further, since the effect of off-diagonal disorder is weak in this alloy system, the calculations based on CPA are expected to provide good results. AgPd has been studied experimentally using X-ray photoelectron spectra (Hüfner et al., 1973), and theoretically using TB-LMTO CPA (Kudronovsky and Drchal, 1990) and KKR-CPA (Winter and Stocks, 1983). So reliable results are available for comparison.

Before we present and compare our results it is worthwhile to examine the general features of this alloy system. As the d-band of silver and palladium overlap only slightly this alloy falls in the so-called split-band regime. In such a system for small impurity concentrations, e.g., small Pd in Ag, the impurity forms a level halfway between the top of the host d-band and the Fermi-energy. As the impurity concentration increases, the width of the impurity band increases and at the same time host band loses structure. This may be attributed to the fact that due to strong disorder scattering, the \( k \)-vector ceases to be a good quantum number, smearing out all the structures in the density of states. When the concentration of the host and the impurity are equal, two bands appear roughly at the positions of the bands in the pure metal, but their structure is much reduced. Finally, as the impurity concentration exceeds that of the host, the impurity band approaches the shape of the pure metal band and the host atom band narrows down. These features are clearly seen in the valence band photo-electron spectra of AgPd at various concentrations. This is shown in Fig.(2.1).

Further the x-ray photo-electron spectra reveals some interesting trends in the density of states for AgPd alloy system. The centres of the bands are found to be almost independent of the concentration of Ag as well as Pd. This shows that the local potentials at the sites of Ag and Pd are roughly independent of concentration, an assumption which underlies the CPA
Figure 2.1: X-ray photo-electron spectra of the valence-band of AgPd alloys (a) Silver-rich alloys and (b) Palladium-rich alloys
description of the binary alloy systems. So we expect CPA results to be good for this alloy system. The variation of the band-width with concentration is found to be much pronounced for Pd than for Ag.

In Fig.2.2(i) we present the total(solid) and the partial densities of states on Ag(dotted) and Pd(dashed) of AgₙPdₙ₋ₓ at various concentrations obtained by augmented space recursion formalism. In Fig.2.2(ii) we present the corresponding density of states obtained by TBLMTO-CPA calculations (Kudrnovsky and Drchal, 1990).

We find the general considerations presented in the preceding paragraph gets reflected in the density of states obtained by the augmented space recursion. The X-ray photo electron spectra show a distinct Pd based impurity peak around 0.14 Ryd below the Fermi level for low concentrations of Pd (25 % Pd) and a distinct Ag based impurity peak around 0.4 Ryd below the Fermi level for low concentrations of Ag (25 % Ag). In table 2.1 we present the impurity peak position in Ryd, relative to fermi level for various Ag concentrations in AgPd alloys obtained by various methods. We find the peak positions obtained by TBLMTO-ASR calculations agree well with the experimental results.

If we compare our results with the TB-LMTO CPA calculations (fig.2.1(i) with fig2.2(ii)) we note that for all the concentrations quoted there is close agreement both in the dominant peak positions as well as the general shape of the density of states. Comparison with the KKR-CPA results shown in Fig.(2.3) show that though the peak positions match reasonably well with ours, the KKR-CPA impurity peaks are much better resolved from the host density of states compared to the TB-LMTO CPA and TBLMTO ASR calculations. The same trend is seen in the experimental results. This comparison indicates that the poor resolution of the impurity peaks is probably not a consequence of the CPA configuration averaging procedure. It probably arises from the approximations involved in the TB-LMTO. For AgPd, where the Wigner-Seitz radii of the two constituents are almost the same, we expect the KKR to be the more accurate band structure scheme. Table 1 illustrates our point.

2.11.2 CuZn

CuZn is an important alloy system, with both diagonal and off- diagonal disorders. Further since the centre of the Cu d-band and the Zn d-band are well apart, they give rise to bands
Figure 2.2: The total and partial densities of states on Ag and Pd for Ag$_{x}$Pd$_{1-x}$ alloys. The concentrations are from top to bottom: $x=1.0$, 0.75, 0.5, 0.25 and 0.0 for (i) TBLMTO-ASR total(solid), partial Ag(dotted), partial Pd(dashed) (ii) TBLMTO-CPA total(solid), partial Ag(long-dashed) and partial Pd(short-dashed). The vertical line indicate the position of the fermi level.
Figure 2.3: Total density of states obtained by self-consistent KKR-CPA calculations for \( \text{Ag}_x\text{Pd}_{1-x} \) alloys. \( \circ \) silver site; \( \triangle \) palladium site and \( \square \) total. Concentrations from top to bottom are \( x = 0.80, 0.50, 0.20 \). Energies are measured with respect to the Fermi-level.
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which are far apart with a relatively wide gap in between them. For small concentration of Cu or Zn one expects an impurity band splitting into bonding and antibonding peaks, because of the presence of more than one impurity atom. This terminology arises from the fact that in the tight-binding model the corresponding wavefunction combine in the same way as bonding and anti-bonding wavefunction in molecules. Within the 1-CPA, the details of the features of clusters containing more than one impurity atom cannot be accurately resolved resulting in a featureless impurity band broadened by immersion of the atom in an effective medium. So one needs to go beyond the single site CPA to resolve the features of the impurity band, namely the bonding and the anti-bonding peaks.

If we carefully examine the phase diagram of Cu$_x$ Zn$_{1-x}$ alloy, we find that it is dominated by several ordered structures along with both fcc ($\alpha$) and bcc ($\beta$) solid solutions. In our calculation we will assume fcc ($\alpha$) solid solutions for $x > 0.5$ and bcc ($\beta$) solid solutions for $x < 0.5$. For $x = 0.5$ one has the well-known $\beta$-brass, for $x = 0$ hcp Zn and for $x = 1.0$ fcc Cu structure. We have calculated the band energy for Cu$_{50}$Zn$_{50}$ in both the fcc and bcc lattice. Our band energy calculations show $E_{\text{band}}(\text{FCC}) = -1.234\text{Ryd} E_{\text{band}}(\text{BCC}) = -1.363\text{Ryd}$. This clearly indicates the bcc phase to be more stable compared to the fcc phase.

In Fig.(2.4) we show the total density of states for the Cu$_x$Zn$_{1-x}$ alloy for $x > 0.5$ where the lattice structure is taken as fcc and for $x < 0.5$ with the alloy assumed to be in the bcc phase.

We find that the large difference in the d-band centre of the constituents and the difference in their widths gets reflected in the density of states. We notice that the density of states in the bcc phase has similar features as compared to that in the fcc structure.

Figure 2.5(a) shows the Cu$_x$Zn$_{1-x}$ alloy with $x = 0.9$. The dotted figure is obtained by a 4-step recursion and invoking moment argument one can compare this result with the characteristic featureless CPA density of states. (4 step recursion yields 8 moments of the density of states correctly analogous to CPA). The solid one is obtained by a 10 step augmented space recursion. We find that in the latter, the impurity peak due to Zn gets split into bonding and antibonding peaks, because of Zn-Zn clusters in the random background. In figure 2.5(b) we have plotted density of states for Cu$_x$Zn$_{1-x}$ alloy with $x = 0.1$ and we observe the same cluster effects at the Cu-site.

This fine structure in the density of states at the impurity site was first discovered by Dean(1960) in computer simulation experiments. Initially these results were suspected not to be correct, but later careful analysis revealed that these structures arise from resonant scattering from clusters of different sizes and shapes immersed in the infinite matrix. The sizes of the peak are related to the probability of the clusters appearing in a random array, and are therefore strongly influenced by short range order. The CPA being a single site mean-field theory, cannot reproduce such fine structures. Such cluster resonance structures are important and plays a crucial role in the order-disorder transition. Our study of CuZn suggests that the augmented space recursion formalism is capable of taking cluster effects into account.
Figure 2.4: The total density of states for Cu\textsubscript{x}Zn\textsubscript{1-x} alloys (a) bcc with x = 0.1 (b) bcc with x = 0.5 (c) fcc with x = 0.5 (d) fcc with x = 0.75 (e) fcc with x = 0.9. The vertical line indicate the position of the Fermi level.
Figure 2.5: Density of states for CuZn alloys (a) for the Cu impurity band (10 % Cu) (b) for the Zn impurity band (10 % Zn). Dotted lines represent the 4-step recursion result comparable to the CPA while the full line represents 10-step recursion showing effect of impurity clusters.
2.11.3 TiFe.

TiFe alloy exhibits strong diagonal disorder, non-negligible off-diagonal disorder and the constituent atoms have very different sizes. Such difference in constituents radii leads to lattice relaxation effects in this alloy system. The bcc disordered phase exist in Ti-rich alloys with concentration of Ti $\geq 0.77$ and for $x = 0.5$ the ordered CsCl phase is known to exist and is found to be very stable. We have calculated the density of states of disordered TiFe by augmented space recursion (ASR) in the bcc phase at various concentrations. Theoretical band structure calculations fo TiFe are available in both TB-LMTO CPA(Kudrnovský and Drchal, 1990) as well as KKR CPA (DaSilva et. al., 1987), so that we can compare our results.

In order to understand the effect of disorder on the density of states of TiFe we have shown in Fig.(2.6a) the density of states of ordered 50-50 TiFe in the CsCl structure obtained by the LMTO method. We find the d-band complex due to Fe and Ti breaks into two gaps, separated by a deep minima where the Fermi energy $E_F$ falls. The lower states are predominantly Fe d states while the states above minima are mostly Ti d states. Further the states lying below the minimum may be interpreted as Fe-Ti bonding states while those above the minimum are the anti-bonding states. Since the bonding states are filled, therefore the ordered system is energetically favoured. In Fig. (2.6b) we show the corresponding density of states of disordered Ti-Fe in the bcc phase obtained by KKR-CPA calculations. We find that there is marked broadening of all the structures which is a clear indication of strong disorder scattering. The most interesting effect is the supression of the gap at $E = E_F$. This suggests that many filled (unfilled) levels have been raised (lowered) in energy, so the energy of the disordered phase is higher.

In Fig2.7(i) we have presented our ASR calculations for $\text{TixFe}_{1-x}$ at various concentrations (from top to bottom $x=0.0 \ 0.5 \ 0.8 \ 1.0$). We find the gap in the density of states dissapears due to disorder scattering analogous to the KKR-CPA result. Similar feature is observed in TBLMTO-CPA calculations shown in Fig2.7(ii).

Our calculations excluding lattice relaxation and proper treatment of charge transfer effect shows that the results compare satisfactorily with earlier calculations, proving the applicability of the methodology to different alloy systems.

2.12 CONCLUSIONS

In this chapter we have developed a calculation scheme which allows to treat electronic properties of disordered alloys on the first principles level. This scheme:

(1) describes electronic states within first-principles TB-LMTO.

(2) includes electron correlations within local spin density functional approximation.
Figure 2.6: Density of States for 50-50 TiFe alloy (a) ordered obtained from LMTO (b) Disordered obtained from KKR-CPA
Figure 2.7: Total and partial density of states for FeTi alloys (i) TB-LMTO-ASR total(solid), partial Fe(dashed) and partial Ti(dotted) (ii) TB-LMTO-CPA total(solid), partial Fe(long-dashed) and partial Ti(short-dashed)
(3) employs augmented space recursion to describe disorder. Both diagonal and off-diagonal disorder can be treated on an equal footing.

(4) calculation is done in real space as a result lattice periodicity is not required and allows to treat surfaces, substitutional and topologically disordered bulk alloys within an unified framework.

The TB-LMTO Hamiltonian used in our calculation is free from fitted parameters. The potential parameters entering into the Hamiltonian are derived self-consistently. However, it carries with it the approximations involved in the linearization which leads to the LMTO. The recursion method requires the use of a sparse Hamiltonian. So we have to base our method on a less accurate Hamiltonian (which is a truncation of the infinite series [eqn(2.13)]) than the Hamiltonian in the so-called γ representation used in the CPA calculations (Kudrnovský and Drchal, 1990). However, Nowak et al. (1991) have shown that the calculations for the density of states converge rapidly as we take more terms in the series in eqn(2.13).

The configuration averaging scheme based on the Augmented Space Theorem, is formally exact. The use of the recursion technique with suitable terminators on the augmented space, so constructed, makes sure of the fact that the TBLMTO-ASR Green functions retain the essential Herglotz analytic properties. In addition, the method can take into account cluster effects, off-diagonal effects arising due to disorder in the structure matrix and correlated disorder.

The recursion method carries errors which are dependent on the finite cluster size and the nature of terminators used, both of which cause the electrons to experience a medium that deviates from the intended structures away from the central sites. The choice of proper terminators partially solves the problem and one should choose larger clusters with greater number of recursion steps for more accuracy. The recursion method is a well established procedure that has proven to produce a very accurate density of states for d-bands for 8 to 15 recursion steps (that is it yields 16 to 30 moments of the density of states exactly).

In summary, we have demonstrated that TB-LMTO ASR as a simple, accurate and computationally efficient method for the first-principles calculation of electronic structure of disordered alloys.