CHAPTER I

BAND STRUCTURE METHODS

1.1 INTRODUCTION

Solid state physics is making its records in the major achievements of mankind much faster than ever before since the development of sophisticated computers. From the realm of bulk elemental solids and model materials, we have now come to multi-component metallic and semi-conducting alloys with tunable physical properties, artificially structured multilayers and superlattices, nanostructured materials in reduced dimension, etc. Most of the cohesive, electronic, optical, magnetic and superconducting properties exhibited by solids are dictated by the behaviour of electrons in the field of the nuclei. This is essentially a many body problem which is difficult to solve even in the fastest computer without introducing some simplifying but reasonable approximations.

Different classes of solid state properties can be explained on the basis of the different levels of sophistication with which one can treat the electron-electron interactions in solids. (a) free electron approximation (ie. neglecting ions altogether), (b) independent electron approximation (ie. neglecting electron-electron interaction), (c) self-consistent field (SCF) approximation (ie) electrons moving in the mean field of the other electrons and ions (d) Landau's Fermi 'liquid' description of the interacting electrons via the so-called quasi-particles, and so on.

The band theory of solids has emerged from the self-consistent field approximation (Slater, 1974) and has proved to be immensely successful, especially in the physics of metals and semiconductors. It provides us with the
most handy first-principles tool to verify as well as predict the properties of materials with meaningful quantitative accuracy. Today it is possible to calculate total energies of solids with meV accuracy, that is desirable to investigate the intricate behaviour of solids.

In this chapter the band structure method used for the present thesis work is briefly discussed starting with the density functional approach in which the energy band description of solids is based.

1.2 DENSITY FUNCTIONAL APPROACH

The density functional approach maps the ground state of an interacting electron gas onto the ground state of non-interacting electrons that experience an effective potential. The most crucial term inside this effective potential is the exchange-correlation potential which appears due to the quantum mechanical interactions between the electrons. One electron band structure methods, where this exchange-correlation term is treated in a mean-field sense, is surprisingly successful in yielding the correct ground state properties of a large variety of solids that are of interest in materials science.

The simplest problem in quantum mechanics is that of hydrogen atom with simple electron-nucleus system, for example, the hydrogen atom whose Schrödinger equation in atomic units.

\[
[-\nabla^2 + V(r)] \psi_j(r) = E_j \psi_j(r)
\]  

(1.1)

can be exactly solved as the potential energy \(V(r)\) of the electron in the electrostatic field of the proton is known to be \(-2/r\) where \(r\) is the electron-nucleus distance. The wave function \(\psi_j(r)\) and the energy levels \(E_j\) are
obtainable analytically. However, as one moves towards higher Z elements and their compounds, the electrostatic repulsion amongst multiple electrons in presence of attractive centers (i.e. the nuclei) make the exact solution of the problem intractable. The only plausible way is to somehow replace the many-electron problem to an effective one-electron problem, but this has to be at the cost of introducing certain approximations. The first approximation was the Born-Oppenheimer approximation which decouples the ionic motion and the second one is the one-electron approximation according to which the electrons are assumed to move in the mean field of other electrons and ions. The first self-consistent field approximation (Slater, 1974) was the Hatree-Fock theory which treats parallel spin electron exchange interactions only by introducing the determinantal wave function but completely neglecting the anti-parallel spin electrons, (electrostatic contribution due to coulomb correlation). The first successful theory which treated both exchange and correlation on the same footing, approximately, was the density functional theory (DFT) of Hohenberg-Kohn-Sham (Hohenberg and Kohn, 1964; Kohn and Sham, 1965).

The basic idea of DFT originated from the query "can we arrive at a potential \( V(\vec{r}) \) uniquely, given the charge density \( \rho(\vec{r}) \) of the system?" However, it has to be noted that the conventional Schrödinger and Poisson equations suggest the opposite to be true (i.e.) given \( V(\vec{r}) \), one can easily obtain \( \rho(\vec{r}) \). It is this unique search prescription that gave birth to DFT. According to Hohenberg and Kohn, the Hamiltonian of a system of \( N \) interacting fermions moving in some fixed external potential \( V_{ext} \) is

\[
H = T + U + V
\]

\[
= \sum_{i=1}^{N} (-\nabla^2_i) + \frac{1}{2} \sum_{i,j}^{N} \frac{2}{|\vec{r}_{ij}|} + \sum_{i=1}^{N} V_{ext}(\vec{r}_i) \]

(1.3)
N is the total number of electrons in the system, T is the kinetic energy and U is the electron-electron Coulombic repulsion. The external potential $V_{\text{ext}}(\vec{r})$ of an interacting homogeneous non-degenerate electron system is a unique functional of the electron density $n(\vec{r})$ and so the ground state $\Phi$ and the energy functionals,

$$
\langle \Phi | H | \Phi \rangle = F[n] + \int V_{\text{ext}}(\vec{r}) n(\vec{r}) \, d\vec{r} \tag{1.4}
$$

$$
F[n] = \langle \Phi | T + U | \Phi \rangle \tag{1.5}
$$

are unique functionals of $n(\vec{r})$. Further they separated $F[n]$ as

$$
F[n] = \frac{1}{2} \int \frac{2n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}' + G[n] \tag{1.6}
$$

The first term on the RHS of the equation (1.6) is the classical Coulomb interaction (U). The second term $G[n]$, an universal functional of $n(\vec{r})$ is further simplified by Kohn and Sham (1965) as

$$
G[n] = T_s[n] + E_{\text{xc}}[n] \tag{1.7}
$$

where

$$
T_s[n] = \langle \Phi_s | T | \Phi_s \rangle
= \sum_{jk} \int \Psi_j^*(\vec{k}, \vec{r}) (-\nabla^2) \Psi_j(\vec{k}, \vec{r}) \, d\vec{r} \tag{1.8}
$$

is the kinetic energy of a system of non-interacting electrons of density $n(\vec{r})$. $\Psi_j$ in the above expression represents the eigen state of the non-interacting...
electrons in an effective potential $V_{g}(r)$ such that the ground state density $n(r)$ is the same as that of the interacting system i.e.

$$n (r) = \sum_{j,k} |\Psi_j (\vec{k}, r)|^2$$

(1.9)

$E_{xc}[n]$ is the exchange-correlation energy functional which describes the energy difference between the true kinetic energy and that of non-interacting system plus the difference between the true interacting energy and that included by the classical Hartree contribution. Estimation of this $E_{xc}[n]$ as such is very difficult. Therefore, an approximation, known as the local density approximation (LDA) was introduced by which

$$E_{xc}[n] = \int n (r) \epsilon_{xc} (n(r)) \, dr$$

(1.10)

LDA means that the external potential at a point is a function of the density only at that point. It is to be noted that usage of the LDA leads to errors in band structure calculations (Hamann, 1979). Specifically, LDA based calculations underestimate the zero pressure band gap of conventional insulators (Hamann, 1979) as the position of the conduction bands relative to the valence bands is not calculated accurately. However, works by Levine and Louie (1982), Sham and Schluter (1983), Wang and Pickett (1983), van Camp et al (1986) have shown that the error due to LDA decreases near insulator-metal-transition (IMT) or when systems become more metallic. This error can be corrected to a certain extent by considering non-local effects (Langreth and Mehl, 1983; Anisimov et al 1993; Bylander and Kleinman, 1994) or self interaction corrections (SIC) (Perdew and Zunger, 1981; Perdew and Levy, 1983; Svane and Gunnarsson 1990; Svane, 1992; Miyazaki et al 1993). In the LDA, each electron has a unphysical interaction with itself. In the SIC-LDA this interaction is subtracted, leading to the energy expression...
\[
\begin{align*}
E_{xc}[n] &= E_{xc}^{\text{LDA}}[n] - \sum_i \int d^3 r \frac{n_i(r) n_i(r)}{|r - r'|} \\
&\quad + \int d^3 r n_i(r) \varepsilon_{xc}(n_i(r), 0) \\
&= \sum_i \int d^3 r \frac{n_i(r) n_i(r)}{|r - r'|} + \int d^3 r n_i(r) \varepsilon_{xc}(n_i(r), 0) \\
&= \sum_i \int d^3 r \frac{n_i(r) n_i(r)}{|r - r'|} + \int d^3 r n_i(r) \varepsilon_{xc}(n_i(r), 0)
\end{align*}
\]

(1.11)

where \(n_i(r)\) is the charge density corresponding to the solution \(i\) of the SIC-LDA equation. The second term subtracts the non-physical Coulomb interaction of an electron with itself as well as the corresponding LDA exchange-correlation energy. The corresponding exchange-correlation potential is state dependent which allows the wave functions to localise (Zunger et al. 1980; Perdew and Zunger 1981; Svane and Gunnarsson 1988; Heaton et al. 1982, 1983; Norman and Perdew 1983; Erwin and Lin 1988).

The energy functional \(<\Phi | H | \Phi>\) can then be written as

\[
<\Phi | H | \Phi> = <\Phi_\Phi | T | \Phi_\Phi> + \int \frac{2n(r)}{|r - r'|} dr + V_{\text{ext}}(r) + \varepsilon_{\text{xc}}[n(r)] n(r) dr
\]

(1.12)

A minimisation with respect to \(n(r)\) now leads to the effective single particle Schrodinger equation,

\[
-\nabla^2 + \frac{2n(r)}{|r - r'|} dr + V_{\text{ext}}(r) + V_x(r) \rightarrow \Psi_j(k, r)
\]
The equation that one obtains when the non-interacting electrons are subjected to an effective potential $V_s$ is given by

\[
V_s = \frac{1}{2} \left[ \int \frac{2n(r)dr}{|r - r'|} - \frac{2Z}{r} + \epsilon_{xc}[n(r)] \right]
\]  (1.14)

where the exchange correlation potential

\[
\nu_{xc}(r) = \frac{d}{dn} [n \epsilon_{xc}(n)] = \mu_{xc}[n(r)]
\]

$\mu_{xc}$ being the exchange - correlation part of the chemical potential in a homogeneous electron gas of density ‘n’ whose exchange part is proportional to $n(r)^{1/3}$ (Hedin and Lundqvist 1971). However, we have made use of the von Barth and Hedin (1972) exchange scheme in our calculation throughout according to which

\[
V_{xc}^+(r_s,x) = A(r_s)(2x)^{1/6} + B(r_s)
\]  (1.15)

where, + means electrons with up sign and $x = (n'/n) = \frac{1}{2}$ for the paramagnetic case, $A(r_s) = \mu_s(r_s) + V_c(r_s)$ and $B(r_s) = \mu_c(r_s) - V_c(r_s)$. Here, the subscripts x and c corresponds to exchange and correlation respectively.
In the actual calculations, the kinetic energy term has been evaluated within the ASA as

\[ < \Phi_i | T | \Phi_S >_{ASA} = \sum_j \frac{\partial^2}{\partial \vec{r}_j} \cdot \int_S V_s(\vec{r}) n(\vec{r}) \, d\vec{r} \]  

(1.16)

and the Hartree term as

\[ V_H(r) = \int_S \left( \frac{2n(\vec{r})}{|\vec{r} - \vec{r}'|} \right) \, d\vec{r}' \]  

(1.17)

where \( S \) is the atomic sphere radius equal to the muffin-tin radius and the external potential has been taken as the electron-nuclear interaction plus the nuclear-nuclear repulsion i.e.,

\[ V_{ext}(\vec{r}) = -\frac{2Z}{|\vec{r} - \vec{R}|} + \frac{1}{2} \sum_i \sum_j \frac{Z_i Z_j}{|\vec{R} - \vec{R}'|} \]  

(1.18)

1.3 ENERGY BAND METHODS

1.3.1 Basic Philosophy

The wave function of the electron when it is very close to a nucleus should be atomic like which is rapidly oscillating and the wave function of electrons when it is in between the two nuclei, where the potential smoothly varies or remains almost constant should be plane wave like. Hence, in all methods the basis function should be so chosen that it rapidly oscillates when it is close to the nucleus and a smoothly varying function in the constant potential region. The final wave function will be a linear combination of such a basis set. Several band structure methods have been developed to
understand the dynamics of electrons in a solid. Depending on the choice of the basis set for the wave functions of an electron in the solid, the band structure methods may be classified as fixed basis methods and partial wave methods.

1.3.2 Fixed Basis Methods

In the Fixed basis method, the wave functions are expressed as a linear combination of some fixed basis functions, say plane waves or atomic orbitals. A typical example is the linear combination of atomic orbitals (LCAO) method (Mott and Jones, 1936), in which the wave function is expressed as a linear combination of the eigen functions of the bound states of a free atom, \( \chi_{n{l}{l}{m}}(r) \). Then the wave function in the solid is the Bloch sum of the linear combination of \( \chi_{n{l}{l}{m}} \) s.

\[
\Psi(k, r) = \sum_{n{l}{l}{m}} e^{i{k}{r}{R}} \chi_{n{l}{l}{m}}(r - R)
\]  

where \( l \) and \( m \) are the quantum numbers of the angular momentum and its projection along the Z-axis of an electron in a band with band index \( n \) whose atomic analog is the principal quantum number.

By standard variational techniques, one may obtain a set of equations in terms of the Hamiltonian \( H \) and overlap matrices \( O \) as

\[
(H - EO) \psi = 0
\]  

which may be solved to get the eigen values \( E \) and the expansion coefficients.
Difficulties in this method lie in the choice of a sufficiently small and accurate basis set and the calculation of a large number of integrals involving potentials and orbitals centred at two and three different sites.

1.3.3 Partial Wave Methods

In the partial wave approach, the spherical symmetry of the potential is extended all the way to the boundaries of an atomic polyhedron. The cellular method (Wigner and Seitz 1934), the augmented plane wave (APW) method (Slater 1937), the Korringa-Kohn-Rostoker (KKR) method (Korringa 1947; Kohn and Rostoker 1954) and the Orthogonal Plane Wave (OPW) method (Herring 1940) are examples of partial wave methods.

In the cellular method, the wave functions in the solid are described as a Bloch sum of partial waves as

\[
\Psi_{\ell m}(k, r) = \sum_{l, m} \Phi_{l, m}(r - R) \theta(r - R) \Psi_l(E, r - R) \frac{Y_{\ell m}^*}{\sqrt{4\pi}} (r - R)
\]

(1.21)

where \( b \) is the expansion coefficient, \( \Psi \) the radial solution, \( Y_{\ell m} \) the spherical harmonics and \( \theta \) is the step function which is unity inside the atomic polyhedron and zero outside. This method is not very much used because of the difficulties in applying the boundary condition across the atomic polyhedron. This difficulty has been mitigated in the APW method by inscribing a muffin-tin (MT) sphere in each atomic polyhedron. Inside the sphere (where the potential is spherically symmetric) the wave function is expanded in terms of partial waves and outside (where the potential is assumed to be constant) a plane wave expansion is used for the wave function.
The KKR method employs partial waves inside and phase-shifted spherical waves outside the MT sphere as the basis set. The APW and KKR methods are the most widely used computational techniques in band theory.

The wave functions in the OPW method are expressed in terms of plane waves which are orthogonal to the core states. The algebraic formulation of the matching condition differs for the various partial wave methods, but in general, the result is a set of linear homogenous equations of the form,

\[ \mathbf{M}(E) \cdot \mathbf{b} = 0 \] (1.22)

where the secular matrix \( \mathbf{M} \) has a complicated non-linear energy dependence and the \( E_j \)'s must be found individually by tracing the roots of the determinant of \( \mathbf{M} \) as a function of \( E \).

The above facts indicate the requirement of a hybrid scheme which has the advantages of both fixed basis methods as well as partial wave methods. The linear muffin-tin orbital (LMTO) method (Andersen 1975) is one such method which is computationally efficient as well as accurate. The basic disadvantage of the conventional solid state MTO's is their infinite range. This has limited its application to those cases where the structure constants can be summed up by the Ewald procedure, that is, where the sites form a periodic lattice. Hence, it is necessary to transform the basis of muffin-tin orbitals into a tight-binding (TB) basis to speed up the computation of the one-electron eigen values and eigen states. Andersen and Jepsen succeeded in transforming the minimal but long-ranged basis of muffin-tin orbitals into a TB basis (Andersen and Jepsen 1984).
1.4 THE LMTO METHOD

The Linear Muffin Tin Orbital method devised by O.K. Andersen is the linearized version of the KKR multiple scattering method leading to the smallest Hamiltonian and overlap matrices and hence fastest from computational point of view. It uses a simple basis set in the form of muffin-tin orbitals. It employs the concept of canonical bands, and it is that which raises the LMTO method above the level of just being a new method of calculating the band structure. With the use of the canonical bands, the energy band problem may be separated into two parts, one which depends on the crystal structure and the other which depends on the crystal potential. A detailed description of this method can be found in the book "LMTO" Method : by Skriver (1984). The potential is assumed to be spherically symmetric within a sphere of radius $S_{\text{MT}}$ and constant outside the sphere.

$$V(r) = V_{\text{MT}}(r) \text{ for } r \leq S_{\text{MT}}$$

$$= V_{\text{MTZ}}(r) \text{ for } r \geq S_{\text{MT}} \quad (1.23)$$

With this choice of potential, one can obtain partial waves as the solution for the one electron Schrödinger equation.

$$(-\nabla^2 + V(r)) \Psi_j(k, r) = E_j(k) \Psi_j(k, r) \quad (1.24)$$

as

$$\Psi_L(E, \kappa, r) = i^l \mathbf{Y}^m_l(r) \begin{cases} \Psi_1(E, r) & r \leq S_{\text{MT}} \\ \kappa \eta_l(\kappa r) - \kappa \cot \eta_l(\kappa r) & r \geq S_{\text{MT}} \end{cases} \quad (1.25)$$

But partial waves can be normalised, for negative $\kappa^2$, only at the eigenvalues of the single well and besides, they are energy dependent. This is not advisable for linearising the problem. As a partial remedy, MTO's as defined
below, can be normalised for all values of $\kappa^2$ and are approximately energy independent and reasonably localised.

\[
\chi_i (E, \kappa, r) = i^l Y_i^m (r) \begin{cases} 
\Psi_i (E, r) + \kappa \cot \eta_l (\kappa r) & \text{for } r < SMT \\
\kappa \eta_l (\kappa r) & \text{for } r \geq SMT
\end{cases}
\] (1.26)

Here, $Y_i^m (r)$ are the well known spherical harmonics, $\kappa^2 = E - V_{MT}$ is the kinetic energy in the interstitial region, $n_l (\kappa r)$ and $j_l (\kappa r)$ are the spherical Neumann and Bessel functions, both of which are regular at infinity, while $n_l (\kappa r)$ is singular at the origin and $\Psi_i (E, r)$ is the solution of the radial Schrödinger equation,

\[
\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} + \frac{V_{MT} (r) - \kappa^2 r}{r^2} \Psi_i (E, r) = 0
\] (1.27)

where,

\[
\cot \eta_l (E, r) = \frac{n_l (\kappa r)}{j_l (\kappa r)} \frac{D_l (E) - \kappa j_l (\kappa r) n_l (\kappa r)}{D_l (E) - \kappa n_l (\kappa r) j_l (\kappa r)}
\] (1.28)

Here $\eta_l$ is the usual phase shift, the primes denote partial differentiation with respect to $r$. The logarithmic derivative,

\[
D_l (E) = \frac{S}{\Psi_i (E, s)} \frac{\partial \Psi_i (E, r)}{\partial r} \bigg|_{r = SMT}
\] (1.29)

Now the electronic wave functions can be obtained as the linear combination of the MTOs

\[
\Psi (E, r) = \sum L \alpha_L^k \chi_L^k (E, \kappa, r)
\] (1.30)
where $\alpha^2_L$ is the expansion coefficient and $\chi^x_L(E, \kappa, \vec{r})$ is the Bloch sum of the MTOs i.e.,

$$\chi^x_L(E, \kappa, \vec{r}) = \sum_{\vec{R}} \exp \left( i \vec{k} \cdot \vec{R} \right) \chi^x_L(E, \kappa, \vec{r} - \vec{R})$$

(1.31)

The above mentioned MTOs are still a function of $E$. In order to linearise the problem, the energy dependence of the MTO has to be suppressed with a suitable choice of augmentation. For this $E$ and $\kappa$ are treated independently by fixing $\kappa$ at a characteristic value. Augmentation not only makes the basis to become energy independent around a fixed energy $E_v$ to first order in $(E - E_v)$ but also to become orthogonal to the core states. This ensures that the LMTO method does not converge to core eigenvalues. These augmented MTOs are,

$$\chi_L(E, \kappa, \vec{r}) = i \vec{Y}_1^m(\vec{r}) \begin{cases} \Psi_1(E, \vec{r}) + \kappa \cot \eta \eta_1(\kappa \vec{r}) & r \leq S_{MT} \\ \kappa N_1(\kappa \vec{r}) & r \geq S_{MT} \end{cases}$$

(1.32)

where $J$ and $N$ are particular choice of augmented spherical Bessel and Neumann functions. The definition of the augmented spherical Bessel $J_i$ and Neumann $N_i$ functions may be obtained from the condition that the energy derivative of the MTO.

$$\chi_L(E, \kappa, \vec{r}) = \Psi_1(E, \vec{r}) + \kappa \cot \eta \eta_1(\kappa \vec{r})$$

(1.33)

is zero at $E - E_v$. The augmented MTO is everywhere continuous and differentiable and is orthogonal to the core states of all the muffin-tins. Hence these orbitals are well suited for use in connection with the variational principle.
Using the Rayleigh-Ritz variational principle the LCMTO secular matrix may be obtained. According to the Rayleigh-Ritz variational principle one varies $\Psi$ to make the energy functional stationary i.e.,

$$\delta < \Psi | H - E | \Psi > = 0$$

(1.34)

where $E$ is the Lagrange multiplier needed to ensure normalisation of $\Psi$

Equation (1.34) has solution whenever

$$\det \left\{ < \chi_L^\kappa - | H - E | \chi_L^\kappa > \right\} = 0$$

(1.35)

The wave function for the muffin-tin potential $V_{MT}(|r-R|)$ centred at site $R$ of a three dimensional periodic lattice may be written as

$$\Psi(E, r) = \sum_{L} \alpha_L^\kappa \chi_L^\kappa (E, \kappa, r)$$

(1.36)

where

$$\chi_L^\kappa (E, \kappa, r) = \sum_R e^{i\kappa R} \chi_L (E, r - R)$$

(1.37)

(which is a Bloch sum of MTO's)

The above multicentre expansion may be rewritten as

$$\chi_L^\kappa (E, \kappa, r) = \chi_L (E, \kappa, r) + \sum_{R \neq 0} e^{i\kappa R} \chi_L (E, \kappa, r - R)$$

(1.38)

Recalling that the last term in equation (1.38) is the sum of the tails coming from all the muffin tin orbitals centred at all sites except at $R=0$, the sum may be replaced by
\[ \sum_{R=0} e^{i\mathbf{k} \cdot \mathbf{R}} \chi_L (E, \kappa, \mathbf{r} - \mathbf{R}) = \sum_{R=0} e^{i\mathbf{k} \cdot \mathbf{R}} \kappa N_L (\kappa, \mathbf{r} - \mathbf{R}) \]

\[ = \sum L' J_L (\kappa, \mathbf{r}) B_{L' L}^\kappa (\kappa) \]

(1.39)

where \( B_{L' L}^\kappa (\kappa) \) are the KKR structure constants and are given as

\[ B_{L' L}^\kappa = 4\pi \Sigma_{C_{L' L}} \sum_{R=0} e^{i\mathbf{k} \cdot \mathbf{R}} \mathbf{n}_{L'}^\kappa \mathbf{n}_{L}^\kappa (\kappa, \mathbf{R}) \]

(1.40)

and \( C_{L' L} \) are the Gaunt coefficients.

Since the muffin tin orbital is everywhere continuous and differentiable, the integral over all space in equation (1.38) may be evaluated as a sum of integrals over all atomic polyhedra. After repeated use of the Bloch condition the well known result

\[ N^{-1} \langle \chi_L^\kappa \mid H - E \mid \chi_L^\kappa \rangle = \langle \chi_L^\kappa \mid H - E \mid \chi_L^\kappa \rangle_0 \]

(1.41)

may be obtained, where the integral extends only over the polyhedron at the origin.

The LCMTO secular matrix is obtained by inserting the one centre expansion into the matrix (1.41) as

\[ \sum_{L'} \left[ \langle \chi_{L'} \mid H - E \mid J_{L'} \rangle_0 B_{L' L}^\kappa + \langle J_{L'} \mid H - E \mid \chi_L \rangle_0 B_{L' L}^\kappa \right] \]
The cellular potential used here is spherically symmetric and therefore the cellular integrals in equation (1.42) become diagonal in $L$ and thus

$$<\chi_L | H - E | \chi_L>_0 = <\chi_i | H - E | \chi_i>_0$$  

(1.43)

The secular matrix then reduces to

$$<\chi_{L'} | H - E | \chi_{L'}>_0 = <\chi_i | H - E | \chi_i>_0 \delta_{LL'} +$$

$$\{ <\chi_{L'} | H - E | J_{L'}>_0 + <J_i | H - E | \chi_i>_0 \} B_{L'LL}^L +$$

(1.44)

Thus the LCMTO secular matrix which is closely related to the LCAO method forms the basis of the LMTO band structure technique. The LCMTO method is converted into an efficient calculational technique by introducing the atomic sphere approximation and parametrising the energy dependence of the one, two and three centre integrals.

Hence, the generalised eigenvalue problem,

$$\Sigma (H_{LL'}^{\vec{r}} - E^{\vec{r}} \Omega_{LL'}^{\vec{r}}) \alpha_{L}^{\vec{k}} = 0$$

(1.45)

is obtained which may be solved to get the eigen values $E^{\vec{k}}$ and eigen vectors $\alpha^{\vec{k}}$. 
1.5 TIGHT BINDING LMTO METHOD

All the advantages of the LMTO method discussed in the last section, such as the basis set being fixed, minimal, localised, normalisable for all values of \( k^2 \) and energy independent and the method being linear and accurate within an energy scale of 1 Ry around the Fermi energy (\( E_F \)) follow in the TB-LMTO method (Andersen and Jepsen 1984, Andersen et al. 1975, 1986). This is because the conventional long ranged MTO's used in the first principle band structure calculations have been exactly transformed into the TB or screened basis. In other words, the screened MTO's are another representation of the conventional MTOs. The TB-LMTO's have almost universal decay and with the ASA, this method, further, can be cast in two-centre form and therefore this method is much more computationally efficient. The idea behind this transformation is simple. A conventional MTO in the interstitial region, the tail, which is the solution of Laplace's equation, is proportional to the 2\(^1\)-pole field \( r^{-1}Y_1^m (\hat{r}) \). An MTO however, need not be a solution of Laplace's equation inside the other neighbouring atoms where it will be modified through augmentation. Hence, the MTO's are localised by screening with the multipoles added on the neighbouring sites. The formalism (Andersen and Jepsen 1984) briefly, is as follows;

The regular \( (j^0) \) and irregular \( (n) \) solutions of Laplace's equation and a modified function \( (j^n) \) within the ASA are defined as,

\[
\begin{align*}
 j_0^0 (r) &= \frac{[2(2l+1)]^{-1} (r/w)^l}{l!} \\
 n_l(r) &= (r/w)^{l+1} \\
 j_l^n (r) &= j_l^0 (r) - \alpha_n(r)
\end{align*}
\]

where a length scale 'w' has been introduced to make the functions and the screening constant '\( \alpha \)' dimensionless. These radial functions are defined to...
vanish outside some Wigner-Seitz cell or sphere centered at $\mathbf{R}$. Now, the bare tail (without screening) $n_{i}^{0}$ is equal to $n_{i}$ inside its own cell, and inside any other cell, say the one at $\mathbf{R}_{j}$, it may be expanded in terms of $j_{i}^{0}$ as,

$$N_{i}^{0} (r) = \sum \left( N_{i} (r) \delta_{ij} - J_{i}^{0} (r) S_{ij}^{0} \right)$$

(1.49)

where $i'$ is a shorthand notation for $R$, $l$, $m$, and $N_{i}'$s and $J_{i}'$s are that of $n_{i}'$s and $j_{i}'$s multiplied by $Y_{i} (r)$ and $S_{ij}^{0}$, the canonical (bare) structure constant matrix. This expansion coefficient $S_{ij}^{0}$ is Hermitian, dimensionless and independent of the scale of the structure. $S_{ij}^{0}$ vanishes for $R_{i} = R_{j}$ and it decays as a function of the interatomic distance ($d$) like $(w/d)^{2m+j+1}$. The screened field is also defined in the same way as in equation (1.49) as,

$$N^{s}(r) = N(r) - J^{s}(r)S^{s}$$

(1.50)

which is to be seen as a vector equation. From equations (1.49) and (1.50), it follows that the screened field can be expanded in terms of the bare fields as,

$$N^{s}(r) = N^{0} (r) (1 + \alpha S^{s}) = N^{0} (r) (1 - \alpha S^{0})^{-1}$$

(1.51)

and

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

(1.52)

Now $\alpha S^{s}$ can be identified as the 'screening charge' which is physically the relative strength of the $2_{l}^{i}$ pole at $\mathbf{R}_{i}$ screening the $2_{j}^{i}$ pole at $\mathbf{R}_{j}$. For small but positive $\alpha$ values, the decay of $S^{s}$ as a function of $d/w$ is exponential. Determination of $S^{s}$ is as follows: for an assumed $\alpha$ such that $\alpha = 0$ for $1 > 2$ (only with $s$, $p$ and $d$ MTO's) and lattice, invert the Hermitian Matrix $(\alpha^{-1} - S^{0} (\mathbf{k}))$ as a function of $\mathbf{k}$ and whose subsequent
Fourier transformation then yields $S^a$ (in real space). $S^a$ has been found to have the following properties:

1. the range of $S^a$ is limited to essentially second-nearest neighbours.

2. the corresponding $\alpha$ is independent of the structure with $w$ as the average Wigner-Seitz radius, and

3. it is almost universal.

Also, since $S^a$ specifies the screened field through the one-centre expansion equation (1.50) and since this field is appropriately normalised, will be the envelope of the tail of the TB base, the latter has a nearly universal decay. A set of screened MTO's can be formed for a given $\alpha$, by augmenting the corresponding set of $N^a(r)$'s in equation (1.50) inside each atom, i.e., by substitution $J^a(r)$ in one centre expansions equation (1.50) by some regular function $J^a_m(r)$ and each $N^a(r)$ by a linear combination of $J^a_m(r)$ and $\Psi_m(E)$, at an energy $E$ of the radial Schrodinger equation. Continuity and differentiability conditions at the MT sphere leads to

$$N(r) = \Psi^a_m(E) M^a(E) + J^a(r) P^a(E)$$ \hspace{1cm} (1.53)

With

$$P^a(E) = P^0(E) (1 - \alpha P^0(E))^{-1}$$ \hspace{1cm} (1.54)

$$M^a(E) = (w/2)^{\frac{3}{2}} (P^a(E))^{\frac{1}{2}}$$ \hspace{1cm} (1.55)
where $\dot{P} = \partial P/\partial E$ and $\Psi_1$ is normalised to unity in its sphere such that $\langle \Psi(E) \dot{\Psi}(E) \rangle = 0$ and $\Psi(E) \dot{\Psi}(E) - \Psi(E) \dot{\Psi}(E) = -1 P_{\text{mt}}(E)$ is the conventional potential function which is essentially the cot $(\eta)$. 

Thus the set of energy dependent TB-MTO's $(X_{\alpha}(E))$ within the ASA are,

$$\chi_{\alpha}(E, k, r) = iY_{\alpha}^{m}(r) \begin{cases} \Psi(E, r) M_{\alpha}^{\alpha}(E) + j_{\alpha}^{\alpha}(r) [P_{\eta}(E) - S_{\alpha}] & r \leq S_{\text{MT}} \\ \eta_{\alpha}^{\text{str}} & r \geq S_{\text{MT}} \end{cases}$$

The linear combination $\chi_{\alpha}(E, r) u_{\alpha}(r)$ is seen to be a solution of the Schrödinger equation at energy $E$ for the MT potential if it equals the one centre expansions $\Psi_{\alpha}(E, r) M_{\alpha}^{\alpha}(E) u_{\alpha}(r)$ in the spheres. In other words, the set of linear homogeneous equations given below has a proper solution.

$$(P_{\alpha}(E) - S_{\alpha}) u_{\alpha}(r) = 0 \quad (1.57)$$

where $u_{\alpha}$ is a column vector. This is the generalisation of the so called tail cancellation or KKR condition (Andersen 1975, 1984; Skriver 1984). Thus each set $X_{\alpha}(E, r)$ is complete for the MT potential.

The secular matrix $(P_{\alpha}(E) - S_{\alpha})$ depends on the potential only through the potential functions along the diagonal and it has the TB two-centre form with $S_{\alpha}$ playing the role of the transfer integral for the most localised set. The potential functions may be parameterised as,

$$\alpha + (P_{\alpha}(E))^{-1} = (P_{0}(E))^{-1} = (r + \Delta / (E - C)) \quad (1.58)$$

where, $C_{\text{mt}}$, $\Delta_{\text{mt}}$, and $\gamma_{\text{mt}}$ are the conventional potential parameters representing the position, width, and the shape of the $R_1$ band, respectively. The KKR equations have the form of an eigen value problem if $P_{\alpha}$ is a
linear function of $E$. This is true if we choose 'α' equal to the potential parameter $\gamma$ in which case the effective two-centre Hamiltonian is seen to be

$$H_{ij} = C_i \delta_{ij} + (\sqrt{\Delta_j}) S^i_j (\sqrt{\Delta_j})$$

(1.59)

This is the MT or ASA Hamiltonian in a nearly orthogonal MTO's and energy independent TB base ($\chi'(E_r)$). $S'$ whose exponential decay exhibits potential and structure dependent damped oscillations, depends on the potential only through $\gamma$.

For the $\alpha \neq \gamma$ case energy dependent orbitals are needed. Now, $\chi'(E_r)$ is independent of $E$ in the interstitial region and its first derivative at $E_0$ (some fixed energy), $\Psi^\alpha (E,r)$ will vanish inside the spheres if we choose $J_i^\alpha (r) \alpha \Psi^\alpha (E,r)$. In other words usual augmentation as in the case of the conventional LMTO method is adopted to linearise the problem. Here,

$$\Psi^\alpha (E,r) = \left[ \frac{\partial (\Psi_\gamma (E) M_i (E))}{\partial E} \right] / M_i^\alpha (E)$$

$$= \Psi'_\gamma (E) + \Psi'_\gamma (E)\left( \frac{M_i^\alpha}{M_i^\alpha} \right) \mid E = E_0$$

$$= \Psi'_\gamma + \Psi'_\gamma O_\alpha \mid E = E_0$$

(1.60)

where $O_\alpha = < \Psi_1^\alpha \Psi_1^\alpha >$ is the overlap matrix. Thus the set $\chi^\alpha$ is complete to first order in $(E-E_0)$ and therefore can yield variational estimates correct to third order inside the spheres as,

$$\chi^\alpha (E,r) = \Psi (E, \gamma) + \Psi^\alpha (E,r) h^\alpha$$

(1.61)
\[ h^a = \frac{P^a(E)}{\hat{P}^a(E)} + (P^a(E))^{1/2} S^a (P^a(E))^{1/2} \quad (1.62) \]

Now, the MT or AS parts of the overlap and Hamiltonian Matrices are,

\[ < \chi | \chi > = (1 + hO)(1 + Oh) + hPh \quad (1.63) \]
\[ < \chi | H - Ev | \chi > = h(1 + Oh) \quad (1.64) \]

with \((H-E) | \Psi(E) > = 0\) and \(P = < \Psi^a >\)

All the quantities in equations (1.61) to (1.64) are expressed in terms of only one non diagonal matrix \(S\) or equivalently, the two centre Hamiltonian, \(h\), defined in terms of \(S\) and potential parameters in equation (1.62). For a fixed \(\alpha\), \(h + Ev\) is the effective two-centre Hamiltonian which has a shorter range than that in equation (1.63).

Since, by the substitution of each radial \((N, J^\sigma)\) Hilbert space by \((\Psi, \Psi^\sigma)\) space all energy independent MTO sets are obtained, all MTO sets span the same Hilbert space and transform into each other according to equations (1.51) and (1.55).

### 1.6 CALCULATION OF TOTAL ENERGY

From the site decomposed total energy analysis, one can have an insight into the factors favouring the 'good' sites or the 'bad' sites for the structural stability with a potential of the atomic sphere type and the electronic density \(n(r)\) which is also approximated by the spherically averaged value, one can obtain the following simple expression for the total energy per cell of the valence electrons and the ions,

\[ E_{tot} = T_{kin} + \sum_{R} U_R + \sum_{R, R'} Z_{RR} \sum \frac{1}{R - R' - T} \quad (1.65) \]
where the first term is the kinetic energy of the valence electrons which should be expressed as the difference between the total energy and the potential energy of the non-interacting electrons. In the ASA, therefore,

\[
T_{\text{kin}} = \int_0^F E N(E) dE - \sum_{\text{R}} \int_0^R v_R(r)n_R 4\pi r^2 dr \tag{1.66}
\]

where \( N(E) = \Sigma_R N_R(E) \) is the sum of the projected DOS, \( v_R(r) \) is the one electron potential in the sphere at \( R \) and \( n_R(r) \) is the spherically averaged charge density. The second term in equation (1.65) is the sum of the intra-sphere interaction energy between the electrons themselves and between the electrons and the nucleus in that sphere and it can be expressed as

\[
U_R = \int_0^R n_R(r) (E_{xc}[n_R(r)] - 2Z_R r^{-1}) + \int_0^R n_R(r') |r-r'|^{1/2} 4\pi r'^2 dr' \tag{1.67}
\]

The third term in equation (1.65) is the inter sphere Coulomb (or Madelung) energy. Here, \( Z_R \) is the difference between the nuclear charge and the electronic charge in the sphere at \( R \).

The present study on pnictides reported in the following chapters is based on the theories outlined in this chapter.