CHAPTER 2

AN OVERVIEW OF BAND STRUCTURE METHODS

2.1 INTRODUCTION

The calculation of the electronic structure of materials needs an understanding of the behavior of solids. The properties of matter under normal conditions are governed by the behavior of electrons that move around the heavier nuclei. The stationary states of a system of electrons moving in the mean electrostatic fields of the electrons themselves and the nuclei can be revealed by the electronic structure calculations.

All solid state properties can be understood in terms of electrons, phonons, magnons etc. For instance, electrical resistivity as well as superconductivity is due to the electron-phonon interaction, and the electronic charge density decides the bonding behavior and other mechanical properties of a solid. Understanding of these properties of materials requires a detailed knowledge of the behavior of electrons in solids, and various theories have been developed for such studies.

Most of the electrical, magnetic and optical properties of solids are described based on the crystalline potential of the freely moving electrons in the valence and conduction bands and the results of the Band structure calculations such as the values of the Fermi energy ($E_F$), the Density of States (DOS) at $E_F$ and wave function of the electron. Band structure calculations can be broadly classified as non-linear and linear. The non-linear method
obeys the Bloch condition explicitly. The disadvantage of the non-linear method is that the wave functions are fixed, and lead to great difficulties in obtaining a sufficiently converged basic set. In the linear method, the wave functions are varied by introducing energy dependent wave functions. Here, the Bloch conditions are not automatically satisfied, but the solutions in one unit cell are so chosen, that they fit smoothly onto those of the neighboring cells, and thus fulfill the Bloch condition indirectly.

Let us consider the overview of the linear methods of Band structure, which are widely used as tools to investigate materials. In real solids, the wave function should have the features of both the atomic and plane wave-like characteristics. When the electron is very close to the nucleus, it experiences a large potential energy and to counteract it, the kinetic energy (momentum) of the electron is very large. Since, the momentum operator is $-i\hbar \partial / \partial x$, the slope of the radial function should also be large. Hence, the wave function should exhibit rapid oscillations in that region similar to the atomic wave functions. On the contrary, in the interstitial region between two nuclei, where the potential energy varies smoothly or remains a constant, the wave function can be written in terms of plane waves. The crystalline wave functions are written in terms of the Augmented Plane Wave (APW) or Muffin Tim Orbitals (MTO) in band structure calculations, and we try to solve the one electron Schrodinger equation by expanding the crystalline wave function in terms of certain basic functions as

$$\psi(r) = \sum a_j X_j(r)$$  \hspace{1cm} (2.1)

where $a_j$'s are the expansion coefficients and $X_j$'s are the basis functions, and $\psi(r)$ is the solution of the Schrodinger equation given by

$$H \psi(r) = \left[-\nabla^2 + V(r)\right] \psi(r) = E \psi(r)$$  \hspace{1cm} (2.2)
where $V(r)$ is the electrostatic potential experienced by all the electrons due to all the ions and electrons in the solid, and $\epsilon$ is the resulting one electron eigenvalue. Substituting (2.1) in (2.2) and multiplying the left hand side by $\gamma_j$s and integrating, we get a set of equations

$$
\sum_j \left( H_{ij} - \epsilon O_{ij} \right) a_{ij} = 0 \tag{2.3}
$$

where $H_{ij} = \int \chi_i^* H \chi_j dr$ and $O_{ij} = \int \chi_i^* \chi_j dr$ are the energy and overlap matrices respectively. Equation (2.3) constitutes a set of homogeneous equations with the unknown $a_{ij}$s. They have a nontrivial solution only if

$$
\text{Det}\left[ \hat{H} - \epsilon \hat{O} \right] = 0 \tag{2.4}
$$

Having obtained $\epsilon$ values we solve (2.4) for the expansion coefficients and at the next step we get $\psi(r)$. The dispersion relation connecting $E$ and $k$ is very complicated, but the expansion of $\psi$ in terms of trial functions is a common feature for all band structure methods. The different Band structure methods are described briefly in the following sections.

2.2 BAND STRUCTURE METHODS

2.2.1 Wigner-Seitz Cellular Method

This is the first Band structure method proposed by Wigner & Seitz (1934). They chose the Wigner-Seitz cell (which will be a truncated polyhedron) as the unit cell, and wrote the crystalline wave function as a linear combination of atomic functions. They assumed the potential inside the polyhedron as spherically symmetric. The potential employed is that due to a single ion, which does not take in to account the interactions arising from its
neighbours. It has a discontinuous derivative across the boundary between the cells. But in reality, it is continuous and flat in the region across the cell boundary. The other difficulty is the arbitrary selection of points in the cell boundary and the enormous amount of labour involved in matching the boundary conditions.

2.2.2 Augmented Plane Wave (APW) Method

The Augmented Plane Wave Method (APW) was proposed by Slater (1937), and is physically much more transparent. He divided the unit cell into what are called as Muffin-Tin (MT) spheres which are constructed around the nuclei and an interstitial region. Obviously, the potential will be sharp around the nucleus, and it will slowly vary between the two nuclei. The crystalline wave functions in the two regions were written as

\[ \psi_k(r) = \sum_{lm} A_{lm} R_l(E, r) Y_{lm} (\theta, \phi) \quad \text{for} \quad r < r_{MT} \]  
\[ = e^{ikr} \quad \text{for} \quad r > r_{MT} \]  
\[ \psi_k(r) = e^{i(k.r)} r > r_{MT} \]

Equation (2.5) is a linear combination of atomic orbitals and the expansion coefficients, and \( r_{MT} \) is the Muffin-Tin radius. The expansion coefficients are evaluated by matching the RHS of (2.5) and (2.6) at the muffin sphere boundary. The APW has the following form

\[ \psi_k(r) = 4\pi e^{i(k.r)} \sum_{lm} \sum_i l j_l(kS_v) Y_{lm}^* (k) Y_{lm}^* (\rho) \left( \frac{R_l(\rho)}{R_l(S_v)} \right) r < r_{MT} \]

(2.8)
where \( r \) and \( \rho \) are position vectors, \( S_V \) is the radius of the MT sphere and \( j \) \( l \)\s are the spherical Bessel functions.

The wave function of the electron in the solid is given by

\[
\psi = \sum c_k \psi_k (r) \tag{2.9}
\]

where \( \psi_k (r) \) is an APW, and the expansion coefficients are to be obtained by the variation principle. It has been found that the above plane waves will be sufficient enough to represent the linear wave function. The matrix element in the APW method or the relation connecting \( E \) and \( k \) will be more complex containing non-spherical functions. The secular determinant obtained in this method is such that the energy is contained in the half diagonal elements, which requires a search for the zero \( s \) of the secular determinant to obtain the Eigen values. For solids with higher atomic numbers, the relativistic effects are important. Taking spin into consideration and solving the Dirac equation, the order of the determinant gets doubled, and it is called as the Relativistic APW (RAPW) method.

2.2.3 The Linearized Augmented Plane Wave (LAPW) Method

The LAPW method is one of the most popular methods for the electronic structure study. The basis consists of local functions, obtained from the Schrödinger equation for atomic-like potential in a muffin-tin sphere on some radial mesh, and plane waves, which describe the interstitial region. The local functions are matched on the sphere to plane waves. Such combination of two different kinds of basis functions makes the LAPW method extremely accurate for systems with localized or delocalised electrons. Also the plane waves are better suited for high energy states, which are usually badly represented by a conventional tight-binding method. All this makes the
LAPW method attractive for the GW implementation. Hamada and coworkers developed a GW method with the LAPW (Hamada et al 1990) and applied it to Si. 45 basis functions per Si atom were needed which corresponds to a reduction by factor of five compared to plane wave calculations. But the computational afford is comparable with the pseudo-potential calculations because the evaluation of matrix elements is more expensive. Although a GW-LAPW realization was successfully used also for Ni (Aryasetiawan 1992), the method did not become very popular because of the computational costs. With further development of computer technology this method may become very promising, as it was shown recently by Usuda and coworkers (Usuda et al 2002) in the GW-LAPW study in wurtzite ZnO.

2.2.4 Korringa-Kohn-Rostoker (KKR) Method

This method was proposed independently by Korringa (1947), Kohn & Rostoker (1954), incorporating a muffin-tin potential. This method is similar to the APW method in two aspects; namely, both make use of the muffin tin potential and search for the zeros of the determinant for determining the eigen values. The Schrodinger equation in this method is written in the integral representation as

\[ \psi(r) = \int_{\Omega} G(r,r') V(r') \psi(r') \, dr' \]  

(2.10)

where \( \Omega \) is the volume in the unit cell and \( G(r,r') \) is the Green’s function, which depends on the chosen \( k \) and \( E \). The crystal wave function within the muffin tin potential is written in the same way as in the APW method, but outside it is written in terms of the Bessel and Neumann functions. The calculation of the matrix elements here is more complicated, and involves scattering phase shifts. This method is a time consuming one, and also it is not linearized.
2.2.5 Pseudopotential Method

It is the most popular method for calculations of the electronic structure and various physical properties of crystals. This method makes use of a potential which imitates the potential employed by the methods described so far. As the properties of the solids depend on the electrons in the valence-conduction bands, these electrons which move in the solid are found outside the atomic core. Thus, we should be concerned with the description of the wave functions of the electron outside the atomic core. Hence, pseudopotential is one which gives rise to essentially the same wave function outside the atomic core, as the original atomic potential. The pseudopotential concept is to replace the atomic potential by a weak one, which gives rise to the same scattering amplitude for the conduction electrons. This method has been used to obtain the Band structure of many metals and semiconductors.

Now, the band theory has several pseudopotential-generation schemes (Hamman et al 1979, Kerker 1980, Louie et al 1982, Vanderbilt 1990, Rappe et al 1990, Troullier & Martins 1991), most of them focused on reducing the number of plane waves needed in expanding the electron wave function. The majority of the pseudopotentials currently used in electronic structure calculations are generated from all-electron atomic calculations. Within the density-functional theory this is done by assuming a spherical screening approximation, and self-consistently solving the radial Schrödinger equation.

2.2.6 Linear Muffin Tin Orbital (LMTO) Method

Many Band structure methods were proposed to understand the behavior of the electrons in solids. Depending upon the basis orbitals employed in the linear Band structure methods, they may be classified as fixed wave methods and partial wave methods. In the fixed wave methods,
the wave function expansion is made by the basic functions like atomic orbitals, Gaussians, or plane waves. In the partial wave methods, the wave functions are expanded in terms of a set of energy and potential dependent partial waves, as is done in the KKR and APW methods, and are based on the scattering theory proven to be highly accurate, they are not easily manageable numerically. The Linear Combination of Atomic Orbitals (LCAO) method, when used as a first principle method, is cumbersome and has too many parameters, or the wave functions are ill-defined. The first principle pseudopotential method meets the requirements, but it is limited to treating mostly like valence and conduction electrons only. However, computationally this can be remedied by the addition of the localized orbitals to the plane wave basis set. The above facts have led us to find a hybrid scheme which has the advantages of both the fixed and partial wave methods.

The history and development of the linear methods is given in literatures (Skriver 1984). The first postulation of linear methods including muffin-tin orbitals, and the tail cancellation theorem were given by Anderson (1971). The LMTO method was devised by Anderson, and it introduces the concept of canonical bands, with the help of which, the energy band problem can be separated into two parts: one which depends on the one-electron potential and atomic volume, and the other on the crystal symmetry. To solve a one-electron problem in the solid, one has to construct a crystal potential. In 1972, the concept of potential parameters and the atomic sphere approximation (ASA) was reported. Later the expression of the LMTO secular matrix, the energy-independent structure constants, and canonical bands, and the linear combination of the muffin-tin-orbital (LCMTO) technique were proposed (Andersen & Kasowski 1971, Kasowski & Andersen 1972, Andersen 1973). It has also the tight-binding LMTO (Andersen & Jepsen 1984, Andersen et al 1986) and full-potential LMTO forms (Sprinborg & Andersen 1987, Weyrich 1988, Methfessel 1988,
Savrasov & Yu 1992). The Augmented Spherical Wave (ASW) method (Williams et al 1979) is a modification of the LMTO method. The basis function of this method is expanded into a series, in terms of the energy independent augmented spherical waves. The ASW function in the muffin-tin region is the solution of the Helmholtz equation. This improves the convergence. The Linear KKR (LKKR) method (Hubbard 1967, Pettifor 1972, Fleck et al 1980) has been realized on the basis of the KKR method. In this method, the energy dependence of the matrix element is ensured by the transformation of the KKR method. It may be called the linearization method with mixed basis sets.

In the LMTO method, the basis orbitals are the so called Muffin Tin Orbitals which are constructed from the partial wave and their first derivatives evaluated at the atomic sphere boundary.

Let us consider the partial waves inside a single Muffin Tin well, and a sphere of radius of $S_{MT}$ centered at the atom. Within the sphere, the potential $V(r)$ is assumed to be spherically symmetric, and is assumed to have a value $V_{MTZ}$ outside the sphere. This kind of potential is called Muffin Tin potential, and it is designed to facilitate the matching of the wave functions from cell to cell, through the assumption that the electrons propagate freely between the spheres with a constant wave number $k = \sqrt{E - V_{MTZ}}$. The justification behind this is that, the wave length $2\pi/k$ is large, when compared to the thickness of the interstitial region. Thus the Muffin Tin potential is defined as

$$V_{MT}(r) = \begin{cases} V(r) - V_{MTZ} & r \leq S_{MT} \\ 0 & r \geq S_{MT} \end{cases}$$
The solution of the Schrödinger equation

\[ (-\nabla^2 + V_{MT}(r) - k^2) \psi_{l,m}(E,r) = 0 \]  \hspace{1cm} (2.11)

for all values of \( k^2 \) for an electron moving in the potential from an isolated Muffin Tin well embedded in a flat potential is \( V_{MT} \). Inside the MT sphere, the radial part \( \psi_l(E, r) \) has to be regular at the origin in order to be normalisable. It is obtained by the numerical integration of the radial Schrodinger equation

\[ \left( -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{MT}(r) - k^2 \right) r^{l/2}(E,r) = 0 \]  \hspace{1cm} (2.12)

In the region of the constant potential, the solution of (2.11) are spherical waves with the wavenumber \( k \), and their radial parts satisfy (2.12) with \( V_{MT}(r) = 0 \).

\[ \left( -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - k^2 \right) \psi_l(E,r) = 0 \]  \hspace{1cm} (2.13)

This is the well-known Helmholtz wave equation, which has two linearly independent solutions, namely, the spherical Bessel function \( j_l(kr) \) and the Neumann function \( \eta_l(kr) \). Hence, the solution of (2.11) will have the form

\[ \psi_{l,m}(E,k,r) = i^l Y^m_l(\hat{r}) \psi_l(E,r) \quad r \leq S_{MT} \]

\[ = i^l Y^m_l(\hat{r}) k[\eta_l(kr) - \cot(\eta_l) j_l(kr)] \quad r \geq S_{MT} \]  \hspace{1cm} (2.14)
The constant of integration \( \cot(n_l) \) is chosen in such a way, that the partial wave is everywhere continuous and differentiable. This will lead to the form

\[
cot(n_l) = \left[ \frac{n_l(kr)}{j_l(kr)} \left( \frac{D_l(E) - krn'_l(kr) / n_l(kr)}{D_l(E) - krj'_l(kr) / j_l(kr)} \right) \right]_{r=S}^{r=MT} \tag{2.15}
\]

where the logarithmic derivative is defined as

\[
D_l(E) = \frac{S}{\psi_l(E, S)} \left( \frac{\partial \psi_l(E, r)}{\partial r} \right) \bigg|_{r=S} \tag{2.16}
\]

This is the monotonically decreasing function of energy except at its singularities. The potential function is defined as

\[
P_l(E) = 2(2l + 1) \frac{D_l(E) + l + 1}{D_l(E) - l} \tag{2.17}
\]

and it is an increasing function of energy. It may be shown that the energy derivations D and P are related to the amplitudes of the MTO s at the sphere boundary. It can be seen that the solution (2.14) is unbounded, and is a delta function normalisable when \( k^2 \) is positive. When \( k^2 \) is negative, it can be normalized only at the Eigen values of the single Muffin Tin, where the constant of integration is zero. For these reasons, these partial waves are not well suited for basic functions. The LMTO method combines all the desirable features of the traditional methods using the fixed basis functions with those of the partial waves. Even though the LMTO method lags behind the LAPW method in terms of accuracy, it is highly efficient, conceptually transparent, and especially well-suited for self-consistent calculations.
2.2.6.1 Muffin tin orbitals (MTO)

In order to obtain suitable basis functions, Anderson introduced the Muffin Tin Orbital (MTO), that is reasonably localized, normalisable for all values of $k^2$ and thus constitutes an efficient basis set for the first principle electronic structure calculations. The MTO is written as

$$
\chi_l(E,k,r) = i^l Y^m_l(\hat{r})\left[\psi_l(E,r) + k \cot(l\eta_l) j_l(kr)\right] \quad r \leq S_{MT}
$$

$$
= i^l Y^m_l(\hat{r}) k \eta_l(kr) \quad r \geq S_{MT} \quad (2.18)
$$

The important feature of the orbital (2.18) is that the functions inside the well are regular at the origin, while the tail of $k \eta_l(kr)$ is regular at infinity. If we approximate the crystal potential by an array of non-overlapping MT wells, the energy dependent MTO's may be used in conjunction with the tail cancellation theorem (according to which, inside the Muffin Tin sphere at R, the tails coming from all other spheres must interfere destructively) to obtain a secular equation of the form

$$
\mathcal{M}(E)b = 0 \quad (2.19)
$$

That will provide the exact solutions for MT geometry. Computationally, however, they are rather inefficient, and it is therefore desirable to develop a method based on the variation principle, which will lead to the computationally efficient Eigen value problem in the form

$$
\left(\hat{H} - E\hat{O}\right)a = 0 \quad (2.20)
$$
2.2.6.2 Energy dependent MTO – expansion theorem for MTO tails

One reason for choosing the tails of the MTO as a solution of the translationally invariant Helmholtz wave equation, is the extremely simple expansion theorem

\[ n_L(k, r - R) = 4\pi \sum_{\ell} \sum_{m} C_{\ell \ell' \ell''} j_{\ell}(k, r - R') n_{\ell''}(k, R - R') \]  

(2.21)

where

\[ C_{\ell \ell' \ell''} = \int Y_{l}^{m}(\hat{k}) Y_{l'}^{m'}(\hat{k}) Y_{\ell''}^{m''}(\hat{k}) d\hat{k} \]  

(2.22)

are the Gaunt coefficients, \( L \) denotes the quantum numbers \( l \) and \( m \). This expansion is valid inside the sphere centered at \( R' \) and passing through \( R \); that is, for \( |r - R'| < |R - R| \). The expansion theorem means that the tail of the MTO positioned at \( R \) is a spherical Neumann function, including the angular part \( Y_{l}^{m}(\hat{r}) \) which may be expanded in terms of the spherical Bessel functions centered at \( R' \). The reason for the expansion is that the Neumann functions centered at \( R \) is regular at the origin, and therefore, expandable in the form of regular solutions of the wave equation. Consequently, inside any MT spheres the tails from the other spheres will have the same functional form as the term proportional to \( \cot(\eta_{l}) \).

2.2.6.3 Energy independent MTO

If the MTO is made energy independent, it can be used in (2.20). In order to achieve this, the MTO will be augmented, and the augmented MTO will be made energy independent around fixed energy \( E_{V} \), for a
particular choice of the augmented spherical Bessel and Neumann functions. The augmented MTO may written as

$$ XL(E, k, r) = i^l Y_l^m(\hat{r})[\psi_l(E, r) + k \cot(\eta_l) J_l(kr)] \quad r \leq S_{MT} $$

$$ = i^l Y_l^m(\hat{r})kN_l(kr) \quad r \geq S_{MT} \quad (2.23) $$

For a particular choice of the augmented spherical Bessel $J_l(kr)$ and Neumann $N_l(kr)$ functions, the MTO may be made energy independent around fixed energy $E$, to first order in $(E - E_V)$. At the same time, the MTO method becomes orthogonal to the core states, ensuring that the LMTO method does not converge to the core Eigen values. In connection with the augmentation, one should realize that once $k$ has been fixed, the Bessel and Neumann functions lose their special significance as exact solutions of the Schrodinger equation in the region of the flat potential. Hence, these functions are replaced by more appropriate functions, which are attached to them at the sphere in a continuous and differential fashion. The augmented Bessel function is obtained by the condition that the energy derivative of (2.23)

$$ X_l(E, k, r) = \psi_l(E, r) + k \cot(\eta_l(E)) j_l(kr) \quad r \leq S_{MT} \quad (2.24) $$

be zero at $E = E_V$. Thus, the augmented Bessel function becomes

$$ J_l(kr) = -\psi_l(E_V, r)/k \cot(\eta_l(E_V)) \quad r \leq S_{MT} $$

$$ = j_l(kr) \quad r \geq S_{MT} \quad (2.25) $$

This will make the MTOs energy independent to first order in $(E - E_V)$; since the MTO (2.18) is continuous and differentiable, one can obtain
\[ \eta_l(kr) = \psi_l(E,r) + k \cot(\eta_l(E)) j_l(kr) \]  

(2.26)

near the sphere boundary. Taking the energy derivative of (2.26) gives

\[ 0 = \psi_l(E_V,r) + k \cot(\eta_l(E_V)) j_l(kr) \]  

(2.27)

which implies that (2.23) is continuous and differentiable at \( r = S_{MT} \). It also implies that \( \psi_l(E_V) \) and \( j_l(kr) \) will have the same logarithmic derivative at \( S_{MT} \). In the same manner as in (2.21), the tail \( N_l(kr) \) can be defined as

\[ N_L(k, r - R) = 4\pi \sum_{L,L'} C_{L,L'} J_L(k, r - R') \eta_{L'}^*(k, R - R') \]

\[ \text{for} \quad |r - R'| < S_{MT} \quad \nabla \quad R' \neq R \]

\[ = \eta_L(k, r - R') \quad \text{otherwise} \]  

(2.28)

Here also \( N_l(k, r - R) \) is continuous and differentiable and further more orthogonal to the core states of all MT wells except the one centered at \( R \). Finally, the energy independent MTO may be written as

\[ X_L(k,r) = i^l Y^m(\hat{r}) \frac{k \eta_l(kS)}{\phi_l(D(\eta_l), S)} \phi_{l'}(D(\eta_l), r) \quad r \leq S_{MT} \]

\[ = i^l Y^m(\hat{r}) k N_l(kr) \quad r \geq S_{MT} \]  

(2.29)

and the augmented Bessel function as

\[ J_l(k,r) = \left( \frac{j_l(kS)}{\phi(D(j_l), S)} \right) \phi(D(j_l), r) \quad r \leq S_{MT} \]

\[ = j_l(kr) \quad r \geq S_{MT} \]  

(2.30)
The augmented MTOs (2.29) are everywhere continuous and
differentiable, and orthogonal to the core states of all the MTs. Hence, these
orbitals are suited to the variation principle.

2.2.6.4 The Combined Correction Term

The Atomic Sphere Approximation (ASA) introduces errors in the
calculated energy bands. When energy bands of high accuracy are needed,
one should include the perturbation (2.31) and the correction term amounts to
the first order for the differences between the atomic or muffin-tin sphere and
the atomic polyhedron, and re-establishes the correct kinetic energy in the
region between the sphere and polyhedron, and corrections for the neglect of
higher partial waves. The extra terms added to the LMTO matrices which
accomplish these corrections, are called combined correction terms. The
perturbation to the potential is given by

\[ \Delta V(r) = \left[ V_{MTZ} - E - k^2 \right] \left( \varphi_{WS}(r) - \varphi_{MT}(r) \right) \]  

(2.31)

With the combined correction terms included in an LMTO
calculation, one can reduce the errors of the ASA to the first order in
\( E - V_{MTZ} - k^2 \).

2.3 VIENNA AB INITIO SIMULATION PACKAGE

The Vienna Ab initio Simulation Package (VASP) is a computer
program for atomic scale materials modelling, e.g. electronic structure
calculations and quantum-mechanical molecular dynamics, from first
principles. The approach implemented in VASP is based on a finite-
temperature local-density approximation (with the free energy as variational
quantity) and an exact evaluation of the instantaneous electronic ground state
at each MD-step using efficient matrix diagonalization schemes and an efficient Pulay mixing. These techniques avoid all problems occurring in the original Car-Parrinello method which is based on the simultaneous integration of electronic and ionic equations of motion. The interaction between ions and electrons is described using ultrasoft Vanderbilt pseudopotentials (US-PP) or the projector augmented wave method (PAW). Both techniques allow a considerable reduction of the necessary number of plane-waves per atom for transition metals and first row elements. Forces and stress can be easily calculated with VASP and used to relax atoms into their instantaneous ground state.

2.4 WIEN2k

The program package WIEN2k allows performing electronic structure calculations of solids using density functional theory (DFT). It is based on the full-potential (linearized) augmented plane-wave ((L) APW) + local orbitals (lo) method, one among the most accurate schemes for band structure calculations. In DFT the local (spin) density approximation (LDA) or the improved version of the generalized gradient approximation (GGA) can be used. The WIEN2k method is an all-electron scheme including relativistic effects. Recently, Salehi (2011) calculated the electronic structure, density of states and electronic density of SrTiO3 in the paraelectric phase by the FP-LAPW method with the DFT in GGA using WIEN2k package.

2.5 ADVANTAGES OF TB-LMTO METHOD

In 1984, O.K. Anderson and coworkers introduced a localized LMTO basis set. This new approach, called Tight-Binding LMTO (TB-LMTO), has paved the way to an order-\(N\) scheme, giving new impetus to the study of numerous physical properties of systems with large number of atoms. It starts with a review, by Andersen and coworkers, of the TB-LMTO
method and its generalization. The Schrödinger equation of $N$ th order in the energy expansion for an overlapping muffin-tin potential is solved using a minimal basis set. The aim of this third generation LMTO method is to take a further step beyond the limitations of the popular atomic-sphere approximation. The present approach uses wave functions which are accurate not only in the muffin-tin spheres but also in the interstitial region. Another spectacular use of the TB-LMTO method is given by Kudrnovsky and coworkers on the Interlayer Exchange Coupling (IEC) (Kudrnovsky et al 1997). Ab initio formulations of the IEC between non-collinearly aligned magnetic slabs lead to results in good agreement with experiment.

1. The advantage of the TB-LMTO method over the standard LMTO method is its simplicity and the possibility of performing the calculation in real space. The Hamiltonian matrix is the only one to be treated. If the potential parameters are known, the construction of the Hamiltonian matrix is straightforward.

2. One advantage of the TB-LMTO is its use to describe disordered systems such as alloys with the precision of ab initio methods.

3. TB-LMTO method based on the local density functional theory is one of the most efficient states of art computational tools which yield the ground state properties of solids with satisfactory accuracies.

4. The original infinite ranged LMTO basis set can be transformed exactly into short-ranged or localized basis sets, with varying degree of localization in real space (Andersen 1984). This has extended the applicability of this so called TB-LMTO method to large super cells and to non-periodic
solids. Furthermore, TB-LMTO also yields the full non-spherical change density (Andersen et al 1986), needed for accurate total energy and force calculations.

5. Couplings of TB-LMTO method with coherent potential approximation (CPA) (Kudrnorsky & Drchal 1990) cluster CPA (Razee & Prasad 1993) Recursion method (Nowak et al 1991) And Augmented space Formalism, have opened the flood-gates of applications to all kinds if disordered solids, be it configurational (in case of substitutional alloys) or topological (in case of amorphous materials, metglass or quasi-crystals).

The present work is carried out by employing the TB-LMTO method. A more detailed description of the TB-LMTO is presented in the next Chapter 3.