CHAPTER 2

ENERGY BAND CALCULATION AND ITS VARIOUS METHODS

2.1   INTRODUCTION

Electronic structure calculations are becoming tools used by both theorists and experimentalists, in order to understand characteristic properties of matter. The basic concepts of quantum mechanics and quantum mechanical techniques are used to understand the wide variety of electronic properties of solids and their applications. The computational methods based on Density Functional Theory (DFT) have been successfully used to calculate the energy bands of matter. The greatest achievements arising from the band theory are in the field of semiconductors and solid state electronic devices (Dan WEI 2008).

A good knowledge of the energy levels of electrons is of fundamental importance in computing the physical properties of solids such as metals, alloys, compounds, semiconductors, narrow band semiconductors, semimetals. It is often possible to calculate band structures, cohesive energy, lattice constants, bulk modulus and elastic constants and hence the Debye temperature and melting point, electronic specific heat from first principles, transport properties, optical phenomena, Fermi surface studies, lattice dynamics, alloying, magnetism, superconductivity, nuclear magnetic resonance, mossbaeur spectra, positron annihilation, etc., are directly dependent on the electronic structure. Hence the electronic structure

calculation serves as a powerful technique for the solid state physicists and materials researchers for the analysis of properties of solids.

2.2 OUTLINE OF THE BAND THEORY OF SOLIDS

The band theory assumes that the potential experienced by an electron in a crystal is periodic with period equal to the lattice constant. This periodic potential forms the basis of the band theory of solids. The behaviour of an electron in this potential is described by constructing the electron wave functions using one-electron approximation. The motion of an electron in a periodic potential yields the following results: (a) Exist allowed energy bands separated by forbidden regions or band gaps. (b) The electronic energy functions E (k) are periodic in the wave vector k. The existence of band gaps is the most important new property which emerges when the free electron theory is extended to include the effect of periodic potential of the ion cores. The results of the band gaps are due to the interaction of the conduction electron waves with ion cores of the crystal. This result will be illustrated using the Kronig-Penney One-Dimensional model. The distribution of electrons in the allowed energy levels follows the Pauli's exclusion principle. The total number of possible states in any energy band is equal to the number of primitive unit cells N. Since each band can be occupied by a maximum of two electrons, each band can accommodate a maximum of $2N$ electrons. This result is quite important for explaining the distinction between metals, insulators and semiconductors (Puri 1997).

The origin of the electronic band structure, i.e., the existence of allowed and forbidden energy regions for a crystal electron, was attributed to the presence of Bragg reflections, which cause certain regions of the continuous spectrum of free-electron states to become forbidden. The alternative, but equally important, approach starts from the discrete energy levels of the free atom and explains the evolution of bands as a quasi-

continuous splitting of the atomic levels due to the interaction with the other atoms of the crystal lattice. The entire information about the one-electron states in the periodic potential is of course contained in a representation of the complete E (k) surfaces in wave-vector space. In order to simply portray the often complicated surfaces, one considers cross sections through the energy surfaces along directions of high symmetry in the first Brillouin zone (Ibach-Luth 1991). These energy gaps are of decisive significance in determining whether a solid is an insulator or a conductor (Kittel 2008). The quantum mechanical approach to electrical conductivity of different solids leads to the band theory of solids.

The application of Schrodinger equation to the electron made possible to obtain the expressions for the density of states, Fermi energy E_F and the number of density of states at this energy N (E_F). All solid state properties can be understood in terms of electrons, phonons, magnons etc. For instance, phonons can be used to understand the heat capacity. In insulators heat is transmitted by phonons and the magnitude of the thermal conductivity is determined by the phonon mean free paths. The electron-phonon interaction is important in giving an attractive interaction between pairs of electrons in some solids that leads to superconductivity. The electronic charge density decides the bonding behaviour and other mechanical properties of a solid. Fermi surface measurements can be evaluated theoretically which could be compared with the experimental Fermi surface measurements. The most accurate technique of measuring the energy gap in the semiconductors is by optical absorption method. Understanding of these properties of materials from band structure methods, the detailed knowledge of the behaviour of electrons in solids and various theories have been developed for such studies.

Most of the thermal, 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 neighbouring cells, and thus fulfil 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 Tin 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

$$\psi(r) = \sum a_j \chi_j(r) \tag{2.1}$$

a_j's are the expansion coefficients and χ_j's are the basis functions and ψ (r) the solution of the Schrodinger equation given by

$$H\psi \text{ (r)} = [-\nabla^2 + V \text{ (r)}] \bullet \psi(r) \; =\mathcal{E}\psi(r) \qquad (2.2)$$

Where V(r) is the electrostatic potential experienced by all the electrons due to all the ions and electrons in the solid, and $\mathcal{E}$ is the resulting one electron eigenvalue. Substituting (2.1) in (2.2) and multiplying the left hand side by χ_j's and integrating, we get a set of equations

$$\sum_j(H_{ij} - \mathcal{E}O_{ij})a_j = 0 \qquad (2.3)$$

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

$$Det |\hat{H} - \varepsilon\hat{O}| = 0 \qquad . \qquad (2.4)$$

Having obtained $\mathcal{E}$ values we solve (2.3) 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 ψ 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.

2.3   THE BAND STRUCTURE METHODS

Various approaches have been used in the calculation of the electron states in solids and, hence, of the actual form of the band structure. Those in common use includes the Korringa, Kohn and Rostoker (KKR) method, the augmented plane waves (APW) method, the orthogonalised plane wave (OPW) method, and the linear combination of atomic orbitals (LCAO)

method (Ziman1972, Lovett 1977, Kachhava1990, Neil Ashcroft 2005, Kittel 2008). The main features of the band structure are determined by the crystal structure, and the nature of the actual atoms becomes a perturbation to the calculation. The tight-binding approximation which starts from wave functions for the free atoms is particularly good for the core electrons. The wave functions are added linearly (hence the so-called LCAO method- linear combination of atomic orbitals method) and is particularly useful in quantum chemistry for obtaining molecular wave functions. However, the method is not very successful for obtaining Bloch functions in solids, although the problem has been overcome to a certain extent, particularly for the alkali metals, by the use of cellular methods. The nearly-free electron model is a good starting point for the conduction electrons. The N.F.M model is very useful as a means of illustrating the behaviour of the function ε (k) in k-space. Here the method satisfactorily shows the presence of energy gaps as a consequence of the periodicity of the lattice which leads to discontinuities at the Brillouin zone boundaries. The problem is one of introducing the potential arising from the ion cores. Until pseudo-potentials were introduced, the strong fields around the ion cores necessitated the introduction of short-wavelength Fourier components and hence of a large number of terms.

2.3.1   Wigner-Seitz Cellular Method

The aim of the Wigner-Seitz cellular method is to make the maximum use of the spherical symmetry of the atom and the translational symmetry of the crystal in the integration of the wave function within each atomic polyhedron (Wigner-Seitz) in a crystal. The cellular method looks simple and direct. The unit cell is a well defined geometrical concept, and the Bloch condition can easily be set down. 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 function as a linear combination of atomic functions. 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. The result of the Wigner-Seitz method depends upon the atomic volume and not upon the crystal structure.

2.3.2   Orthogonal Plane Wave (OPW) Method

Herring (1940) introduced the concept of orthogonalised plane wave. This is the simple method of expanding the valence and conduction states as plane waves; here, in addition, the wave functions for the outer states are expanded as sets of plane waves which are orthogonalised to the wave functions of the energies. Hence the method is called the orthogonalised plane wave (OPW) method and overcomes the difficulty   of describing the rapid variation of the wave-function near an atomic nucleus. The normalised OPW function can be combined in a similar way to plane waves at points of high symmetry in the Brillouin zone to form the basis functions for the irreducible representation of the crystal space group.

2.3.3   Augmented Plane Wave (APW) Method

The Augmented Plane Wave (APW) method is the most advanced form of the cellular method. This method was originated by (Slater 1937) in which augmentation of atomic like character is done on the plane waves. This uses the so-called muffin-tin potentials consists of spherically symmetric potential regions centred at the ion sites with a constant potential in the interstitial regions. The wave function is made to exhibit atomic like oscillatory behaviour near the core and plane wave like behaviour in the

constant potential region. The Schrodinger equation for the motion of an electron in the spherically symmetric potential can be solved in spherical polar coordinates. The augmented plane wave after which the method is named is equal to the plane wave outside the regions of spherical potential symmetry, and to a general linear combination of spherical harmonics multiplied by radial functions within the spherically symmetric potential. 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

$$\psi_k(r) = \sum_l \sum_m A_{lm} R_l(E,r) Y_{lm}(\theta,\phi) \ \textit{for} \ r < r_{MT} \quad (2.5)$$

$$= e^{ikr} \ \textit{for} \ r > r_{MT} \quad (2.6)$$

Equation (2.5) is a linear combination of atomic orbitals and A_{lm}'s is 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

$$\psi_k(r) = e^{(ik.r)} \ r > r_{MT} \quad (2.7)$$

$$= 4\pi e^{(ik.r)} \sum_l \sum_m i^l j_l(kS_v) Y_{lm}^*(\hat{k}) Y_{lm}^*(\hat{\rho}) \left(\frac{R_l(\rho)}{R_l(S_v)} \right) r < r_{MT} \quad (2.8)$$

The position vectors r and ρ and the radius of the MT sphere S$_v$, and j_l's are the spherical Bessel functions.

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

$$\psi = \sum_k c_k \psi_k(r) \tag{2.9}$$

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. The number of APW functions required depends on the crystal structure and the type of band involved. It is usual that s and p bands give more rapid convergence than d bands. 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.

2.3.4   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 Schrodinger 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. GW is nothing else but a 'screened' version of Hartee-Fock. Hamada and co-

workers 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 co-workers (Usuda et al 2002) in the GW-LAPW study in wurtzite ZnO.

2.3.5 Korringa-Kohn-Rostoker (KKR) Method

This method was proposed independently by (Korringa 1947, Kohn & Rostoker 1954), incorporating a muffin-tin potential. The KKR method (also sometimes called the Green function 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 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.

2.3.6 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 Schrodinger equation.

2.3.7   The k. p Method

This is a method using quantum perturbation theory in conjunction with requirements from crystal symmetry to investigate the wave functions and form of the energy bands at particular points in k-space and particularly at k = 0. The band structure at a particular point can be determined by obtaining experimentally a limited number of parameters such as bandgaps and electron and hole effective masses. The limitation on the method for obtaining the band structure throughout k-space is the detail and accuracy with which the k. p matrix can be determined, and, because the matrix depends on a great many parameters, it is not easy to determine it experimentally in full. The method has been extensively developed by (Kane 1957, 1966) and its application

leads to the so-called Kane band form which is of considerable importance for narrow-gap materials (Lovett 1977).

2.3.8 Linear Muffin Tin Orbital (LMTO) Method

To understand the dynamics of electrons in solid, several band structure methods were proposed to understand the behaviour of the electrons in solids. Depending upon the basic orbital employed in the linear band structure methods, they may be classified as fixed basis methods and partial wave methods. In the fixed basis method, the wave function expansion is made by the fixed basis 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 Korringa-Kohn-Rostocker (KKR) and the Augmented Plane Wave (APW) methods. The KKR and APW methods based on the scattering theory have proven to be highly accurate but they are numerically cumbersome. The Linear Combination of Atomic Orbital (LCAO) method, when used as a first principle method, is cumbersome and when parameterized, it has either too many parameters, or the wave functions are ill-defined. The Linear Combination of Gaussian Orbitals (LCGO) methods have some computational advantages but it needs at least twice as many basis functions as, say, the KKR method has. The first principle pseudopotential method meets the requirements, but it is limited to treating mostly the sp-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 (Andersen

1971). The LMTO method was devised by Andersen, 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 Helmoltz 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 functionsfrom 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

$$V_{MT}(r) = \begin{cases} V(r) - V_{MTZ} & r \le S_{MT} \\ 0 & r \ge S_{MT} \end{cases}$$

(2.10)

The solution of the Schrodinger equation

$$\left(-\nabla^2 + V_{MT}(r) - k^2 \right) \psi_{l,m}(E,r) = 0$$

(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_{MTZ}. 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

$$\left(-\frac{d^2}{dr^2} + \frac{l(1+1)}{r^2} + V_{MT}(r) - k^2 \right) r\psi_1(E,r) = 0$$

(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 $V_{MT}(r) = 0$.

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - k^2 \right) \psi_l(E,r) = 0$$

(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

$$\psi_{l,m}(E,k,r) = i^l Y_l^m(\hat{r})\psi_l(E,r) \ r \le S_{MT}$$

$$= i^l Y_l^m(\hat{r})k[\eta_l(kr) - \cot(\eta_l)j_l(kr)] \ r \ge S_{MT} \qquad (2.14)$$

The constant of integration $\cot(\eta_l)$ is chosen in such a way, that the partial wave is everywhere continuous and differentiable. This will lead to the form

$$\cot(\eta_l) = \left[\left(\frac{\eta_l(kr)}{j_l(kr)}\right)\left(\frac{D_l(E) - kr\eta_l'(kr)/\eta_l(kr)}{D_l(E) - krj_l'(kr)/j_l(kr)}\right)\right]_{r=S_{MT}} \qquad (2.15)$$

where the logarithmic derivative is defined as

$$D_l(E) = \frac{S}{\psi_l(E.S)}\left(\frac{\partial\psi_l(E,r)}{\partial r}\right)\Bigg|_{r=S} \qquad (2.16)$$

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

$$P_l(E) = 2(2l+1)\left(\frac{D_l(E)+l+1}{D_l(E)-l}\right) \qquad (2.17)$$

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 MTOs 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.

2.3.8.1 Muffin-tin orbitals

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

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

$$= i^l Y_l^m(\hat{r})k\eta_l(kr) \, r \ge S_{MT} \tag{2.18}$$

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 muffin-tin wells, the energy dependent muffin-tin orbitals 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

$$\hat{M}(E).b = 0 \tag{2.19}$$

That will provide the exact solutions for muffin-tin 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

$$\left(\hat{H} - E\hat{O}\right).a = 0 \qquad (2.20)$$

2.3.8.2 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

$$\eta_L\left(k, r - R\right) = 4\pi \sum_{L'} \sum_{L''} C_{LL'L''} j_{L'}\left(k, r - R'\right)\eta_{L''}^{*}\left(k, R - R'\right) \qquad (2.21)$$

where

$$C_{LL'L''} = \int Y_l^m\left(\hat{k}\right) Y_{l'}^{m'}\left(\hat{k}\right)^{*} Y_{l''}^{m''}\left(\hat{k}\right) d\hat{k} \qquad (2.22)$$

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

2.3.8.3   Energy-independent muffin-tin orbitals

If the muffin-tin orbital is made energy independent, it can be used in the eigenvalue Equation (2.20). In order to achieve this, the muffin-tin orbitals will be augmented, and the augmented muffin-tin orbitals will be made energy independent around fixed energy E_v, for a particular choice of the augmented spherical Bessel and Neumann functions. The augmented muffin-tin orbitals may written as

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

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

For a particular choice of the augmented spherical Bessel $J_1(kr)$ and Neumann $N_l(kr)$ functions, the muffin-tin orbital may be made energy independent around fixed energy E_v to first order in $(E-E_v)$. At the same time, the muffin-tin orbital 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)

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

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

$$J_l(kr) = -\psi_l(E_v,r)/k \cot(\eta_l(E_v)) \ r \le S_{MT}$$

$$= j_l(kr) \ r \ge S_{MT} \tag{2.25}$$

This will make the muffin-tin orbital energy independent to first order in $(E - E_v)$; since the muffin-tin orbital (2.18) is continuous and differentiable, one can obtain

$$= \eta_l(kr) = \psi_l(E,r) + k \cot(\eta_l(E))j_l(kr) \tag{2.26}$$

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

$$0 = \psi_l(E_v,r) + k \cot(\eta_l(E_v))j_l(kr) \tag{2.27}$$

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

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

$$\text{for } |r - R'| < S_{MT} \ \nabla R' \ne R$$

$$= \eta_L(k,r-R') \text{ otherwise} \tag{2.28}$$

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

$$X_L(k,r) = i^l Y_l^m(\hat{r}) \frac{k\eta_l(kS)}{\phi_l(D(\eta_l),S)}\phi_l(D(\eta_l),r) \ r \le S_{MT}$$

$$= i^l Y_l^m(\hat{r}) k N_l(kr) \ r \ \geq \ S_{MT} \tag{2.29}$$

and the augmented Bessel function as

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

$$= j_l(kr) \ r \geq S_{MT} \tag{2.30}$$

The augmented muffin-tin orbital (2.29) are everywhere continuous and differentiable, and orthogonal to the core states of all the muffin tins. Hence, these orbitals are suited to the variation principle.

2.3.8.4 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

$$\Delta V(r) = \left(V_{MTZ} - E - k^2\right)\left(\theta_{WS}(r) - \theta_{MT}(r)\right) \tag{2.31}$$

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

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.