

CHAPTER 3

TIGHT BINDING LINEAR MUFFIN TIN ORBITAL (TB-LMTO) METHOD AND CALCULATIONS OF THERMAL AND SUPERCONDUCTING PROPERTIES

3.1 INTRODUCTION

The Linear Muffin- Tin Orbitals (LMTO) method has the advantage of using both the methods, i.e., the fixed basis methods and the partial wave methods. It is computationally efficient as well as accurate. The basic advantage of the conventional solid-state Muffin-Tin Orbitals (MTOs) are all in the infinite range, and their limited applications to structure constants have to be summed up by the Ewald sphere. This is the main disadvantage of the LMTO method. Hence, it is necessary to transform the base of the Muffin Tin orbitals into a Tight Binding (TB) or screened basis, to speed up the computation of one electron eigen values and eigen states.

Andersen & Jepsen (1984) succeeded in transforming the minimal but long ranged base of Muffin Tin Orbitals used in the LMTO method into the TB basis. Since, the transformation is exact; all the results obtained with the LMTO method would be reproduced by the TB-LMTO method. The TB-MTOs have almost a universal decay with the ASA, and this method can be cast into two center forms. The main advantage of this method is that it is computationally efficient due to screening. A minimal set of orbitals possesses only one radial function per site, \bar{R} and angular momentum, lm . Each orbital must, therefore, approximately satisfy the Schrödinger



differential equation in the region between the atoms. The formalism of this method (Andersen & Jepsen 1984, Andersen et al 1986) described briefly, is as follows. Further, the details about the calculation of Cohesive energy and Heat of formation, Debye temperature, Electronic specific heat coefficient, electron-phonon coupling constants as well as the superconducting transition temperature from the band structure results, Bulk modulus, Density of states, Energy band gap, Fermi energy, Total energy, Pressure derivation from the total energy studies using equation of state (EOS) analysis are also discussed.

3.2 CANONICAL STRUCTURE MATRIX

A conventional MTO X_{lm}^0 is proportional to the 2^l -pole field $r^{-l-1}Y_{lm}(\hat{r})$ in the interstitial region.

$$J_l^0(r) = \left(\frac{1}{2(2l+1)} \right) \left(\frac{r}{\omega} \right)^l \quad (3.1)$$

The MTO need not be a solution of Laplace's equation inside the neighbouring atoms, where it will be modified through augmentation. Therefore, the MTOs are localized by screening with multiples added on the neighbouring sites. Let us define the regular and irregular radial Laplace solutions as

and
$$K_l(r) = \left(\frac{r}{\omega} \right)^{-l-1} \quad (3.2)$$

the modified function as

$$J_l^\alpha(r) = J_l'(r) - \alpha_l K_l(r) \quad (3.3)$$



to which the amount $-\alpha$ of irregular solution has been added. Here, ω is some length scale introduced to make the functions and screening constants α dimensionless. Let us denote $|J_{Rlm}^0\rangle$, $|K_{Rlm}\rangle$ and $|J_{Rlm}^\alpha\rangle$ as the radial functions multiplied by Y_{lm} and centered at site R. These functions are defined to vanish outside some Wigner-Seitz cell or sphere centered at R. The bare 2^{lj} -pole field at R_j , extending in all space is denoted by $|K_j^0\rangle$ where j is the short hand notation for $R_j|j|_m_j$. This bare field equals $|K_j\rangle$ inside its own cell and inside any other cell, say the one at R_i ; it may be expanded in an $l_i m_i$ series of the regular Laplace solutions $|J_i^0\rangle$; i.e.,

$$|K_j^0\rangle = \sum_i \left(|K_i\rangle \delta_{ij} - |J_i^0\rangle S_{ij}^0 \right) \quad (3.4)$$

The expansion coefficients S^0 form a Hermitian matrix, which is dimensionless and independent of the scale of the structure. This is the so-called Canonical Structure matrix. It vanishes for $R_i=R_j$ and as a function of the inter-atomic distance $d = |R_i - R_j|$, it decays like $(w/d)^n$ with $n = l_i + l_j + 1$. In analogy to (2.35), the screened field is defined by

$$|K^\alpha\rangle = |K\rangle - |J^\alpha\rangle S^\alpha \quad (3.5)$$

where the subscripts are dropped. The screened field is given by the superposition of the bare fields

$$|K^\alpha\rangle = |K^0\rangle (1 + \alpha S^\alpha) = |K^0\rangle (1 - \alpha S^0)^{-1} \quad (3.6)$$



The relation between the bare and screened structure matrices is given by

$$S^\alpha = S^0 (1 - \alpha S^0)^{-1} \quad (3.7)$$

where α is now regarded as a diagonal matrix with elements $\alpha_{R,l}$. From (2.37) αS^α is identified as the Screening Charge, i.e., $\alpha_i S_{ij}^\alpha$ is the relative strength of the 2^i pole at R_i screening the 2^j pole at R_j . The decay of S^α is a function of $(-\lambda d/w)$ λ -constant and the spectrum of S^0 , which is the so called canonical band which is upwards bound. For an assumed lattice and α , the behavior of S^α is found to be the following:

- The range of S^α may be limited to essentially the second-nearest neighbours.
- The corresponding α is independent of the structure, provided that w is taken as the average Wigner-Seitz radius, and measures the density of multipoles.
- The screened structure matrix S^α depends almost on (d/w) and hardly on the structure, i.e., the screened structure matrix is almost universal.

For a given α , let us form a set of MTOs by augmenting the corresponding set of multipoles (2.37) inside each atom. In the one-center expansions (2.36) let us substitute each radial function J_l^α by some regular function $J_{R,l}^\alpha$ and each radial function K_l by a linear combination of $J_{R,l}^\alpha$ and the regular solution $\phi_{r,l}(E)$ at energy E of the radial Schrodinger for the potential spherically averaged around site R . The functions match



continuously, and are differentiable at a MT sphere surrounding the atom so that

$$|K\rangle = |\phi(E)\rangle N^\alpha(E) + |J^\alpha\rangle P^\alpha(E) \quad (3.8)$$

at and near the sphere surface and the elements of the diagonal matrices P and N are given by

$$P^\alpha(E) = \frac{P^0(E)}{1 - \alpha P^0(E)} \quad (3.9)$$

$$N^\alpha(E) = (\omega/2)^{1/2} P^\alpha(E)^{1/2} \text{ is the normalization factor} \quad (3.10)$$

where $P^0(E)$ is the conventional (bare) potential function which is essentially the cotangent of the phase shift. The set of energy dependent MTOs $|X^\alpha\rangle$, thus equals $|K^\alpha\rangle$ in the interstitial region, and

$$|\phi(E)\rangle N^\alpha(E) + |\overline{J^\alpha}\rangle [P^\alpha(E) - S^\alpha] \quad (3.11)$$

in the spheres. The linear combination $|X^\alpha(E)\rangle u^\alpha$, specified by a column vector u^α , is seen to be a solution of Schrodinger at energy E for the MT potential, if it equals the one-center expansions $|\phi(E)\rangle N^\alpha(E) u^\alpha$ in the spheres; i.e., if the set of linear homogeneous equations $[P^\alpha(E) - S^\alpha] u^\alpha = 0$ has a proper solution. This is the generalization of the so called tail cancellation or Korringa-Kohn-Rostoker (KKR) condition.



3.3 TIGHT BINDING HAMILTONIAN

The secular matrix $P^\alpha(E) - S^\alpha$ depends on the potential only through the potential functions along the diagonal, and for the most localized set; it has the TB two center forms. The potential functions may be parameterized like

$$\alpha + P^\alpha(E)^{-1} \equiv P^O(E)^{-1} \approx \gamma + \frac{\Delta}{(E - C)} \quad (3.12)$$

where C , Δ and γ are the conventional potential parameters, describing the position, width and shape of the R/band respectively. The KKR equations have the form of an eigen value problem, if P^α is a linear function of E . This is true if α is equal to the potential parameter γ , in which case the effective two center Hamiltonian is seen to be

$$H_{ij}^\gamma = C_i \delta_{ij} + (\sqrt{\Delta_i}) S_{ij}^\gamma (\sqrt{\Delta_j}) \quad (3.13)$$

This will turn out to be the MT in a base $|X^\gamma\rangle$ of energy independent, nearly orthogonal MTOs. S^γ depend on the potential through γ and its exponential decay exhibits potential and structure dependence.

In order to solve the eigen value problem when $\alpha \neq \gamma$, energy independent orbitals are needed. Now, $|X^\alpha(E)\rangle$ is independent of E in the interstitial region and in the spheres, its first energy derivative at E_γ will vanish if $\overline{J^\alpha}$ is proportional to the energy derivative function



$$\begin{aligned}
|\phi^\alpha\rangle &= [\partial|\phi(E)\rangle N^\alpha(E)/\partial(E)]/N^\alpha \\
&= |\phi^\gamma\rangle + |\phi\rangle N^\alpha/N^\alpha = |\phi^\gamma\rangle + |\phi\rangle o^\alpha
\end{aligned} \tag{3.14}$$

and $|\phi^\gamma\rangle$ corresponds to α value for which N^α vanishes, and according to (3.10) and (3.12), this is γ . The overlap $\langle\phi|\phi^\alpha\rangle = o^\alpha$ is a potential parameter. The set $|X^\alpha\rangle$ is thus complete, to the first order in $E - E_\gamma$, and can yield variation energy estimates correct to the third order. If we normalize $|X^\alpha\rangle$ to equal $|K^\alpha\rangle N^\alpha$ in the interstitial region is seen to be

$$|\chi^\alpha\rangle = |\phi\rangle + |\phi^\alpha\rangle h^\alpha \tag{3.15}$$

$$h^\alpha = -\left(P^\alpha / \dot{P}^\alpha\right) + \left(\dot{P}^\alpha\right)^{-1/2} S^\alpha \left(\dot{P}^\alpha\right)^{-1/2} \tag{3.16}$$

in the spheres, and h is the effective two center Hamiltonian in terms of S and the potential parameters. In this base, the MT parts of the overlap and Hamiltonian matrices are

$$\langle\chi|\chi\rangle = (1+ho)(1+oh) + hph \tag{3.17}$$

$$\langle\chi|H - E_\gamma|\chi\rangle = h(1+oh) \tag{3.18}$$

Because $(H - E)|\phi(E)\rangle = 0$ and $p = \langle(\phi^\gamma)^2\rangle$. $h + E_\gamma$ is the effective two-center TB Hamiltonian, and has the same form as the Hamiltonian (3.13), and it reduces to it when $\alpha \neq \gamma$. Since all the MTO sets are obtained by the substitution of each radical (K, J^0) Hilbert space by the (ϕ, ϕ^γ) space, all the



MTO sets span the same Hilbert space, and transform to each other, according to (3.6) and (3.10). An equivalent of expressing this linear transformation follows by inserting (3.14) in (3.15). The γ set, characterized by having $o^\gamma = 0$ is

$$|\chi^\gamma\rangle = |\chi\rangle(1+oh)^{-1} = |\chi\rangle(1-oh^\gamma) \quad (3.19)$$

in terms of any other set. According to (3.17), the γ representation is orthogonal to the first order in h^γ , and its Hamiltonian matrix is simply

$$\begin{aligned} \langle \chi^\gamma | H - E_v | \chi^\gamma \rangle &= h^\gamma = h(1+oh)^{-1} \\ &= h - hoh + \dots \end{aligned} \quad (3.20)$$

and
$$\langle \chi^\gamma | \chi^\gamma \rangle^{-1/2} = 1 - h^\gamma ph^\gamma / 2 + \dots \quad (3.21)$$

from the right and left hand sides it may be transformed into a fully orthogonal base, where the Hamiltonian is seen to be expressible as a power series in the effective two-center TB Hamiltonian h . This power series, together with the fact that the eigenvectors of h transform the orbital base (3.15) into one-center expansions for the wave functions (tail cancellation), make self-consistent calculations with recursion or moment techniques feasible.

3.4 TOTAL ENERGY

Using the site decomposed total energy analysis; one can have an insight into the factors favouring the ‘good’ sites or ‘bad’ sites for 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 ASA expression for the total energy per cell of the valence electrons and the ions

$$E_{tot} = T_{kin} + \sum_R U_R + \sum_R \sum_{R'} Z_R Z_{R'} \sum_T |R-R'-T|^{-1} \quad (3.22)$$

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. Therefore, in the ASA

$$T_{kin} = \int_0^{E_F} EN(E)dE - \sum_R \int_0^{S_R} v_R(r)n_R(r)4\pi r^2 dr \quad (3.23)$$

where $N(E) = \sum_{Rl} N_{Rl}(E)$ 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 (3.22) 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

$$U_R = \int_0^{S_R} n_R(r) \left(E_{xc}[n_R(r)] - 2Z_R r^{-1} + \int_0^{S_R} n_R(r') |r-r'|^{-1} 4\pi r'^2 dr' \right) dr \quad (3.24)$$

The third term in (3.22) 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. Equation (3.22) has proved useful for self-consistent calculations of the total site decomposed energies in the cell, and one can use it to investigate the local picture of the structural energies (Dew-Hughes 1974).



3.5 EQUATION OF STATE STUDIES

The total energy of the compounds under consideration has been calculated for different reduced and extended volumes, and is fitted with the sixth order polynomial. From the first derivative of the polynomial, the P-V data in their stable structures are generated. From the total energy curves, the pressure corresponding to the different volumes are obtained from the following relation

$$P(V) = -\left(\frac{dU}{dV}\right)_{T=0} \quad (3.26)$$

Although different classes of solids exhibit different bonding natures, (Vinet et al 1986) have argued that under compression, the pressure volume relation is dominated by the overlap interaction for all the classes of solids. On account of this, the empirical evidence of the applicability of the universal equation of state (UEOS) for different classes of solids has been demonstrated. As the chemical bonding in our inter-metallic systems is of a mixed nature, the universal equation of state is appropriate for our EOS analysis. It has been defined as a universal binding energy-distance relationship of the form, where the universal is function of the scaled length and is the total energy at equilibrium. This universal energy relation leading to the universal equation of state is put forth by Vinet et al as follows

$$P(V) = 3B_0 \left[\frac{1-X}{X^2} \right] e^{\eta(1-X)} \quad (3.27)$$

The above expression accurately represents the P-V relation for all the classes of solids under compression, where $X = \left(\frac{v}{v_0}\right)^{1/3}$, B_0 is the



isothermal bulk modulus and V_0 is the equilibrium volume, $\eta = 3 \left[B_0' - 1 \right] / 2$ and $B_0' = (dB/dp)_{P=0}$.

According to the theory of Vinet et al, if one defines $H(x)$ as $X^2 P(x) / 3(1-x)$, then the $\ln[H(x)]$ versus $1-x$ curve should be nearly linear and is given by

$$\ln[H(x)] \approx \ln B_0 + \eta(1-x) \quad (3.28)$$

where the slope of the curve (η) is related to the pressure derivative of the bulk modulus (B_0') by

$$\eta = \frac{3}{2} [B_0' - 1] \quad (3.29)$$

Using the above Equations (3.28, 3.29), the bulk modulus and its pressure derivative of the compounds are estimated. In the present studies, the curve was obtained by fitting the $E_T - V$ data to Murnaghan's equation of state (Murnaghan 1944).

$$E(V) = V \frac{B_0}{B_0'} \left[\frac{\left(\frac{V_0}{V} \right)^{B_0'}}{B_0' - 1} + 1 \right] + \text{const} \quad (3.30)$$

where B_0 is the bulk modulus and B_0' is the pressure derivative of B_0 . The equilibrium lattice parameters were obtained by minimizing the total energy, by varying the cell volumes of the compounds.



3.6 DENSITY - FUNCTIONAL THEORY

Since its introduction in the 1960s, the Density functional theory has evolved as a powerful tool that is widely used in condensed matter theory and materials, for the calculation of the electronic, magnetic and structural properties of solids (Hohenberg & Kohn 1964, Kohn & Sham 1965, Sham & Kohn 1966, Kohn 1999). The method has been remarkably successful in predicting, reproducing, and explaining a wide variety of materials' phenomena. Density functional formalism is based on two theorems, by Hohenberg & Kohn (1964). According to that, the Hamiltonian

$$H = T + U + V \quad (3.31)$$

$$= \sum_i^M (-\nabla_i^2) + \frac{1}{2} \sum_{i \neq j}^M \frac{2}{r_{ij}} + \sum_i^M V_{ext}(\vec{r}_i) \quad (3.32)$$

is a system of M interacting electrons moving in some fixed external potential V_{ext} . Here T is the kinetic energy, U is the electron-electron coulomb repulsion, and V is the interaction with the external potential, which includes the electrostatic interaction with the fixed nuclei.

First, they assumed that the external potential is a unique functional of the electron density $n(\vec{r})$, the ground-state Φ and the energy functionals,

$$\langle \Phi | H | \Phi \rangle = F[n] + \int V_{ext}(\vec{r}) n(\vec{r}) d\vec{r} \quad (3.33)$$

$$F[n] = \langle \Phi | T + U | \Phi \rangle \quad (3.34)$$

are unique functionals of $n(\vec{r})$. Here, they separated the classical Hartree contribution by defining yet another functional $G[n]$, which represents the kinetic energy plus the difference between the interaction energy.



$$F[n] = \frac{1}{2} \iint \frac{2n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + G[n] \quad (3.35)$$

Next, Hohenberg & Kohn (1964) showed that the energy functional assumes its minimum value, the ground-state energy, for the correct ground-state density. If the functional $F[n]$ and $G[n]$ which are universal were known, then the variational principle can be used to determine the ground state energy. Unfortunately the functional is not known. This theory is exact in two limiting cases (Kohn & Sham 1965),

- (i) for slowly varying $n(\vec{r})$ and
- (ii) for a density which is an average of a fluctuations.

In this situation, Sham et al (1966) devised a set of equations that could be used to calculate the energy of a system. The starting point of such a calculation involves creating a fictitious system of “non-interacting” electrons whose ground state electron density is identical to that of a real system where the electrons interact. The energy functional of such a system is written in the form,

$$G[n] = T_s[n] + E_{xc}[n] \quad (3.36)$$

Here, $T_s[n]$ is the kinetic energy of the non-interacting electrons of density $n(\vec{r})$,

$$\langle \Phi_s | T | \Phi_s \rangle = \sum_{jk}^{occ.} \int \psi_j^*(\vec{k}, \vec{r}) (-\nabla^2) \psi_j(\vec{k}, \vec{r}) d\vec{r} \quad (3.37)$$

and $E_{xc}[n]$ is the so-called exchange-correlation energy functional. $E_{xc}[n]$ describes the difference between the true kinetic energy and that of the non-interacting system, plus the difference between the true interaction



energy and that included by the hartree contribution. The exchange-correlation energy functional, $E_{xc}[n]$ can be written within the local-density approximation (LDA) (Hedin & Lundqvist 1971, von Barth and Hedin 1972, Gunnarsson & Lundqvist 1976),

$$E_{xc}[n] = \int n(\vec{r}) \varepsilon_{xc}(n(\vec{r})) d\vec{r} \quad (3.38)$$

which is exact in the limit of slowly varying and high density limits. The exchange-correlation energy density $\varepsilon_{xc}(n)$ is obtained from a homogeneous electron gas of density $n(\vec{r})$. Following Kohn and Sham, the total energy functional can now be written in the form

$$\langle \Phi | H | \Phi \rangle = \langle \Phi_s | T | \Phi_s \rangle + \int \left\{ \frac{1}{2} \int \frac{2n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{ext}(\vec{r}) + \varepsilon_{xc}(n(\vec{r})) \right\} n(\vec{r}) d\vec{r} \quad (3.39)$$

and minimization with respect to the density $n(\vec{r})$, leads to the effective one-electron Schrödinger equation

$$\left\{ -\nabla^2 + \int \frac{2n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{ext}(\vec{r}) + V_{xc}(n(\vec{r})) \right\} \psi_j(\vec{k}, \vec{r}) = E_j(\vec{k}) \psi_j(\vec{k}, \vec{r}) \quad (3.40)$$

The exchange-correlation potential $V_{xc}(\vec{r})$ is given by

$$V_{xc}(\vec{r}) = \frac{d[n\varepsilon_{xc}(n)]}{dn} \equiv \mu_{xc}[n(\vec{r})] \quad (3.41)$$

Here μ_{xc} is the exchange-correlation part of the chemical potential in a homogeneous electron gas of density $n(\vec{r})$. In general, the exchange part of the potential is proportional to $n(\vec{r})$. There are different schemes for calculating $\mu_{xc}[n(\vec{r})]$.



3.6.1 Spin-Density -Functional Theory

The Density functional formalism may be extended to a spin-density formalism, in which the spin-up and spin-down densities $n_{\uparrow}(\vec{r})$ and $n_{\downarrow}(\vec{r})$ are the independent variables. In terms of these variables, the electron and magnetization densities can be written in the form

$$n(\vec{r}) = n_{\uparrow}(\vec{r}) + n_{\downarrow}(\vec{r}); m(\vec{r}) = n_{\uparrow}(\vec{r}) - n_{\downarrow}(\vec{r}) \quad (3.42)$$

respectively. Allowing the spin polarization, minimize the energy functional

$$\langle \Phi | H | \Phi \rangle = T_s[n_{\uparrow}] + T_s[n_{\downarrow}] + \int \left\{ \frac{1}{2} \int \frac{2n(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{ext}(\vec{r}) + \varepsilon_{xc}[n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r})] \right\} n(\vec{r}) d\vec{r} \quad (3.43)$$

and obtain an effective one-electron Schrödinger equation for each spin direction. For the spin-up case,

$$\left\{ -\nabla^2 + \int \frac{2n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{exc}^{\uparrow}(\vec{r}) + V_{xc}^{\uparrow}[n_{\uparrow}(\vec{r})] \right\} \psi_j^{\uparrow}(\vec{k}, \vec{r}) = E_j^{\uparrow}(\vec{k}) \psi_j^{\uparrow}(\vec{k}, \vec{r}) \quad (3.44)$$

Here the exchange-correlation potential is given by,

$$V_{xc}^{\uparrow}(n_{\uparrow}, n_{\downarrow}) = \frac{d[n\varepsilon_{xc}(n_{\uparrow}, n_{\downarrow})]}{dn_{\downarrow}} \quad (3.45)$$

In the present calculation, von Barth & Hedin (1972) scheme has been used. Equation (3.39) can be used to calculate the ground state properties of the interacting systems.



3.6.2 Local Density Approximation (LDA)

In the band calculations, usually certain approximations for the exchange-correlation potential $V_{xc}(\vec{r})$ are used. The simplest and most frequently used is the local density approximation (LDA), where $n_{xc}(\vec{r}, \vec{r}' - \vec{r})$ has a form similar to that of a homogeneous electron gas. However, with density at every point of the space replaced by the local value of the charge density $n(\vec{r})$, the LDA is,

$$E_{xc}[n] = \int n(\vec{r}) \varepsilon_{xc}(n) d\vec{r} \quad (3.46)$$

Here, ε_{xc} is the contribution of the exchange and correlation to the total energy of a homogeneous interacting electron gas with the density $n(\vec{r})$. The expression $\varepsilon_{xc}(n)$ was given by Hedin & Lundqvist (1971). In this approximation, the effective potential is based on the chemical potential of a homogeneous interacting electron gas with the local density. For a spin-polarized system,

$$E_{xc}[n^+, n^-] = \int n(\vec{r}) \varepsilon_{xc}(n^+(\vec{r}), n^-(\vec{r})) d\vec{r} \quad (3.47)$$

Here $\varepsilon_{xc}(n^+, n^-)$ is the exchange-correlation energy per electron of a homogeneous system with densities $n^+(\vec{r})$ and $n^-(\vec{r})$ for the spin up and spin down, respectively.

3.6.3 Advantages of TB-LMTO Method

Andersen & co-workers (1984) 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 co-workers, of the TB-LMTO method and its generalization. The Schrodinger 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 co-workers 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 (Andersen1984). 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 charge 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 of disordered solids, be it configurational (in case of substitutional alloys) or topological (in case of amorphous materials, metglass or quasi-crystals).

3.7 CALCULATIONS OF THERMAL AND SUPERCONDUCTING PROPERTIES

3.7.1 Cohesive Energy and the Heat of Formation

The cohesive energy of a crystal is the measure of how strongly its constituent atoms are bound. The cohesive energy (E_{coh}) in a given phase is defined as the difference in the total energy of the constituent atoms at infinite separation and the total energy of the particular phase. Cohesive energy and the heat of formation are calculated using the formula

$$E_{\text{coh}}^{\text{AB}} = \left[E_{\text{atom}}^{\text{A}} + E_{\text{atom}}^{\text{B}} - E_{\text{total}}^{\text{AB}} \right] \quad (3.48)$$

$$E_{\text{form}}^{\text{AB}} = \left[E_{\text{total}}^{\text{AB}} - \left(E_{\text{solid}}^{\text{A}} + E_{\text{solid}}^{\text{B}} \right) \right] \quad (3.49)$$

Where $E_{\text{atom}}^{\text{AB}}$ refers to the total energy of the compound and $E_{\text{atom}}^{\text{A}}$ and $E_{\text{atom}}^{\text{B}}$ refer to the atomic energies of the pure constituents.



3.7.2 Debye Temperature and Gruneisen Constant

The Debye temperature (Θ_D) and Gruneisen constant (γ_G) are important parameters that are closely related to the thermal properties of materials. To calculate the thermal properties of a vibrating Debye lattice, we have used the Debye-Gruneisen model (Debye 1912). In the present work, the Debye temperature is calculated using the equation (3.50, 3.51) (Moruzzi et al 1988).

$$\Theta_D = 67.48 \sqrt{\frac{r_0 B_0}{M}} \quad (3.50)$$

and

$$\Theta_D = 41.63 \sqrt{\frac{r_0 B_0}{M}} \quad (3.51)$$

Where r_0 is the Wigner-Seitz radius in a.u., at equilibrium, B_0 is the bulk modulus in kbar and M is the average atomic weight. The Gruneisen constant (γ_G) is related to the Debye temperature (Θ_D) and the volume of the unit cell (V) by the relation (Shashikala et al 1987)

$$\gamma_G = \frac{\partial \ln \Theta_D}{\partial \ln V} \quad (3.52)$$

3.7.3 Electronic Specific Heat Coefficient

The electronic specific heat coefficient (γ) is related to the density of states $N(E_F)$ and the electron phonon mass enhancement factor (λ) using the expression

$$\gamma = (1 + \lambda) \frac{1}{3} \pi^2 k_B^2 N(E_F) \quad (3.53)$$



Where k_B is the Boltzmann constant.

3.7.4 Electron-Phonon Coupling Constant and Superconducting Transition Temperature

The electron-phonon coupling constant λ can be estimated using the electronic band structure results, by using the relation

$$\lambda = \frac{N(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle} \quad (3.54)$$

where I^2 is the electron-phonon interaction matrix element averaged over the Fermi surface (Skriver and Mertig 1985), M is the molecular mass, and $\langle \omega^2 \rangle$ is the mean square phonon frequency given by (AshwaniKumar&Ojha 2011),

$$\langle \omega^2 \rangle = \frac{1}{2} \Theta_D^2 \quad (3.55)$$

with Θ_D in energy units. The quantity $\langle I^2 \rangle$ is determined by the relation

$$\langle I^2 \rangle = 2 \sum_l \frac{(l+1)}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)} \quad (3.56)$$

where $M_{l,l+1}$ is the electron-phonon matrix element which can be expressed in terms of the logarithmic derivate (Dl)

$$M_{l,l+1} = -\phi_l \phi_{l+1} \left[(D(E_F) - l)(D_{l+1}(E_F) + l + 2) + (E_F - V(S))S^2 \right] \quad (3.57)$$



Where $V(S)$ is the one-electron potential at the atomic sphere boundary, and ϕ_l is the amplitude of the l -th partial wave function evaluated at E_F . Here, $N_l(E_F)$ in Equation (3.7) is the partial density of states for the angular momentum quantum number l . The superconducting state parameters have computed the McMillan's formation for strong coupled materials (McMillan 1965) and the Allen-Dyne's formation for weak coupled materials (Allen & Dynes 1975). The superconducting transition temperature can be calculated using McMillan's formula,

$$T_C = \frac{\langle \Theta_D \rangle}{1.45} \exp \left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] \quad (3.58)$$

The superconducting transition temperature is calculated using Allen-Dyne's formula

$$T_C = \frac{\langle \omega \rangle}{1.2} \exp \left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] \quad (3.59)$$

where λ is the electron-phonon coupling constant which can be estimated as detailed above, and μ^* is the electron-electron interaction constant. The μ^* can be obtained from the empirical relation given by Bennemann & Garland (1971).

$$\mu^* = \frac{0.26 N(E_F)}{1 + N(E_F)} \quad (3.60)$$

The above properties have been calculated using the results of bandstructure computations and presented in the forthcoming chapters for the Pyrite structure CuS_2 , metallic compound, A15-structure Ti_3M ($\text{M}=\text{Au}$, Pt and Ir) A_3B inter metallic compounds, and V-VI layered $\text{Sb}_2\text{Te}_x\text{Se}_{3-x}$ ($x=3, 2, 1, 0$) semi-metallic compounds (Sb_2Te_3 , $\text{Sb}_2\text{Te}_2\text{Se}$, $\text{Sb}_2\text{Te}_2\text{Se}$, Sb_2Se_3) considered in the present work.

