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## 2.1 Density Functional Theory

Quantum mechanical study of the solids is a many body problem dealing with the interaction of negatively charged electrons with relatively heavier positively charged nuclei. These problems are governed by so called Schrodinger equation

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

Here  $\Psi$  represents the many body wave function  $\hat{H}$  is Hamiltonian operator with  $E$  as energy eigen values. For solids the exact Hamiltonian in atomic units (i.e.  $\frac{\hbar}{2\pi} = e = m_e = 1$ ) is given by

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\nabla_i^2}{M_i} \left[ -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_j \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|} \right] + \frac{1}{2} \sum_{i,j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (2.2)$$

The equations (2.1) and (2.2) cannot be solved exactly for real systems. Thus, in order to describe the main aspects of the physical problem in hand, we need to make approximations at different levels.

### 2.1.1 Born Oppenheimer approximation [1]

The heavier mass of nucleus as compared to electronic mass makes them much slower than the electrons. The nucleus can therefore be considered at fixed positions in the time scale of electronic motion. As a result, the first term in equation (2.2) corresponding to kinetic energy of nucleus disappears. Hamiltonian can now be expressed as

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{\text{ext}} \quad (2.3)$$

a sum of kinetic energy of electrons, potential energy due to interaction among electrons and potential energy due to interaction of electrons with the potential of nuclei. The potential due to nucleus now becomes external to the electrons.

### 2.1.2 Hohenberg-Kohn Theorems

Although Born Oppenheimer approximation reduces the many body problem to much simpler one, yet it is too much difficult to be solved. One of the most successful approach to reduce further the complexity of the problem, is the density functional

theory (DFT). DFT makes use of two theorems proposed by Hohenberg and Kohn [2] in transforming the many electron wave functions approach to electron density approach. The electron density  $n(\mathbf{r})$  and at a point  $\mathbf{r}$  is defined as the probability of finding an electron in a given infinitesimally small volume element around that point. Mathematically, it can be obtained by integrating the probability density over all the position and spin coordinates. Due to indistinguishable nature of the electrons the total probability of finding an electron of an N-electron system in a small volume element  $dr$  is given by N times the probability for a single electron.

$$n(\mathbf{r}) = N \sum_{s_1} \sum_{\dots} \sum_{s_N} \int \int \dots \int |\Psi|^2 d\mathbf{r} \quad (2.4)$$

such that 
$$\int n(\mathbf{r})d\mathbf{r} = N \quad (2.5)$$

Hence these were the Hohnburg and Kohn theorem which makes it possible to use the electron density as a basic variable instead of wave function theorem According to first theorem, the external potential  $V_{\text{ext}}$  can be expressed uniquely as a functional of ground state electron density of a many electron system. As a consequence, the ground state expectation value of every observable can be expressed as a unique functional of electron density. Hence the expectation value of Hamiltonian operator i.e. total energy of the system can also be expressed in terms of a functional of electron density,  $E[n(\mathbf{r})]$ . The second theorem states that the total energy  $E[n(\mathbf{r})]$ , can be written as a sum of potential energy due to external potential  $E_{\text{ext}}[n(\mathbf{r})]$ , and a term so called universal functional  $F[n]$ . The functional  $F[n]$  is universal in the sense that it has the same mathematical form, irrespective of the choice of the external potential.

$$E[n] = F[n] + E_{\text{ext}}[n] \quad (2.6)$$

where 
$$E_{\text{ext}}[n] = \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad (2.7)$$

and 
$$F[n] = T[n] + E_{\text{ee}}[n] \quad (2.8)$$

In equation (2.8)  $T[n]$  =Kinetic energy of interacting electrons and  $E_{\text{ee}}$ = energy due to  $e^-e^-$  interaction. Further the total energy  $E[n]$  acquires its minimum value for exact ground state density. As a consequence of the second theorem, it is possible now to calculate the ground state energy and hence exact ground state electron density using Rayleigh Reitz variational principle. Once having the exact ground state density, all the information about the system is within reach.

### 2.1.3 Kohn Sham scheme

In 1965, Kohn and Sham [3] introduced an indirect method to approximate the kinetic energy functional and hence the unknown universal functional  $F[n]$ . They proposed to calculate the total energy of interacting system in terms of a fictitious non interacting particle system. The idea is that the assumed system of non interacting particle have the same electron density as the exact ground state density of the real system of interacting particles.

For non interacting particle system the Hamiltonian is given by

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + V_{ks} \quad (2.9)$$

On applying the variational principle to total energy i.e.  $\langle \Psi | \hat{H} | \Psi \rangle$ , a set of equations

$$\left[ -\frac{1}{2}\nabla^2 + V_{ks} \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (2.10)$$

is obtained. Here  $\Psi$  represents the many body wave function of non interacting system and can be expressed as the product of single particle functions  $\phi_i(\mathbf{r})$ . The single particle functions  $\phi_i(\mathbf{r})$  are known as Kohn-Sham orbitals.  $V_{KS}$  in equation (2.9) is the effective potential which is adjusted in such a way that both non interacting and interacting system have the same density. In order to derive  $V_{KS}$ , Kohn and Sham rewrites the universal functional as

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n] \quad (2.11)$$

the first term on the right hand side represents the kinetic energy of non interacting system, the second is the Columbian  $e^-e^-$  interaction energy and the last term  $E_{xc}$ , known as exchange correlation energy corresponds to deviation of non interacting energy from the interacting system energy.

The application of variational principle to total energy functional including the universal functional  $F[n]$  given by equation (2.11) leads to Euler- Lagrangian equation as

$$V_{ks} = V_{ext} + V_H + V_{xc} \quad (2.12)$$

$$V_{xc} = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \quad (2.13)$$

Equation (2.13) represents the exchange correlation potential. Thus in KS-scheme, the exact ground state density of the real interacting system can be obtained in terms of single particle Kohn-Sham orbitals such that

$$n_0(\mathbf{r}) = \sum_i^{\text{occup}} |\varphi_i|^2 \quad (2.14)$$

These orbitals can be computed by solving the single-particle KS equations for which  $V_{\text{KS}}$  is required. However, as per equations (2.12) and (2.13),  $V_{\text{KS}}$  depends upon the electron density which in turn depends upon  $\varphi_i(\mathbf{r})$  which are to be calculated. The solution to such a problem is given by iterative solution scheme [4]. In this scheme, the KS equations are solved with some initial guessed  $V_{\text{KS}}$ , from the solution of KS equations, new density is formed which is used to make a new potential. These iterations continue until the density and potential  $V_{\text{KS}}$  reproduce themselves. Thus we have ground state density and effective potential  $V_{\text{KS}}$  in a self consistent manner.

## 2.2 Exchange-correlation functional

Kohn and Sham mapped the real interacting many electrons system on to a fictitious non interacting uniform electron gas. Both of these systems have the same ground state density. In this scheme, all the many body effects are included in the term, so called exchange correlation (XC) functional. The exact form of exchange correlation functional is not known. It is therefore necessary to make the proper approximation for this part of total energy functional.

In general exchange correlation energy can be decomposed into two parts

$$E_{\text{xc}} = E_{\text{x}} + E_{\text{c}} \quad (2.15)$$

where  $E_{\text{x}}$  (exchange energy) is due to antisymmetric nature of electronic wave function (Pauli's exclusion principle) while  $E_{\text{c}}$  is the correlation energy. The exchange part is due to the fact that an electron present at a given position ( $\mathbf{r}$ ) reduces the probability of existence of other electron with the same spin in its vicinity ( $\mathbf{r}'$ ). Thus, a hole known as exchange hole is created. Further the correlation part  $E_{\text{c}}$  to  $E_{\text{xc}}$  is created due to a columbian interaction between electron with opposite spins. It also gives rise to a hole known as core hole. Therefore, both the above factors reduces the probability for existence of another electron at a position  $\mathbf{r}'$  with an electron at  $\mathbf{r}$ . The resulting hole so created is known as XC hole. The exchange correlation energy can also be considered as due to interaction of an electron with its XC hole [5].

$$E_{xc} [n] = \frac{q^2}{2} \int dr \int dr' \frac{n(\mathbf{r})n_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (2.16)$$

The exchange correlation hole is found to follows the sum rules

$$\int n_x(\mathbf{r},\mathbf{r}')dr' = -1, \quad \int n_c(\mathbf{r},\mathbf{r}')dr' = 0 \quad (2.17)$$

These some rules and some other exact constraints must be satisfied by an approximated XC to behave like an exact XC functional. Therefore, the approximations to XC functionals are designed in such a way that they satisfy as many constraints as possible.

### 2.2.1 Local density approximation

Local density approximation (LDA) defines the simplest form of exchange correlation functional. In this approximation, the whole system is divided into infinitesimal small volume element with uniform density. The exchange correlation energy of each of these volume element is equal to that of an identical volume filled with uniform electron gas (UEG) having same density as in the corresponding element of the given interacting system. Thus total exchange correlation energy can be approximated by integrating the contribution due to volume elements over available space

$$E_{xc}^{LDA} [n] = \int n(\mathbf{r})\epsilon_{xc}^{LDA} [n(\mathbf{r})]dr \quad (2.18)$$

where  $\epsilon_{xc}^{LDA}$  represents the XC energy per particle of UEG. On decomposing into exchange and correlation part the above equation can be written as

$$E_{xc}^{LDA} [n] = \int n(\mathbf{r})\epsilon_x^{LDA} [n(\mathbf{r})]dr + \int n(\mathbf{r})\epsilon_c^{LDA} [n(\mathbf{r})]dr \quad (2.19)$$

Though the exchange part  $\epsilon_x^{LDA}$  can be calculated exactly [6], the correlation part can be approximated by a fit to Quantum Monte Carlo method [7]. The most popular LDA xc functional are Vosko-Wilk-Nusair (VWN) [8], Perdew-Zunger [9] and Perdew-Wang [10], which differ in parameterization for  $\epsilon_x^{LDA}$ .

### 2.2.2 Generalized gradient approximation

In local density approximation the xc energy is calculated by taking into account only local density of electron. However, in real systems, the electron density varies spatially; therefore gradient of the density should also be included in the calculation of exchange correlation energy. The first attempt to make a gradient correction for LDA was made by Kohn and Sham [3]. They expanded the LDAxc

energy in terms of power series of gradient of electron density such that the exchange and correlation part of xc energy are given by

$$E_x^{\text{GEA}}[n] = \int n(\mathbf{r})\epsilon_x^{\text{LDA}}([n(\mathbf{r})], \mathbf{r})[1 + A_x([n(\mathbf{r})], \mathbf{r})s_1^2 + B_x([n(\mathbf{r})], \mathbf{r})s_2^2 + \dots]d\mathbf{r} \quad (2.20)$$

and

$$E_c^{\text{GEA}}[n] = \int n(\mathbf{r})\epsilon_c^{\text{LDA}}([n(\mathbf{r})], \mathbf{r})[1 + A_c([n(\mathbf{r})], \mathbf{r})s_1^2 + B_c([n(\mathbf{r})], \mathbf{r})s_2^2 + \dots]d\mathbf{r} \quad (2.21)$$

$$\text{where } S_m = \frac{|\nabla_n^m|}{(2k_f)^m n} \quad (2.22)$$

In above equations  $s$  represents a dimensionless quantity known as reduced density gradient. It gives a measure of relative change in density in the scale of Fermi wavelength  $\lambda_F = \frac{2\pi}{k_F}$ . Such an approximation is known as gradient expansion approximation (GEA). GEA is an extension to LDA and hence are applicable to systems with slowly varying density. Practically, the lower order terms of equation (2.20) and (2.21) does not improve the results as compared to LDA rather sometime worsen them. On the other hand, the higher order terms are difficult to compute. A solution to this problem is given by introduction of a new approximation so-called generalized gradient approximation according to which the exchange correlation energy functional can be obtained from a general function of  $n(\mathbf{r})$  and  $\nabla n(\mathbf{r})$  as

$$E_{xc}^{\text{GEA}}[n] = \int f(n(\mathbf{r}), \nabla n(\mathbf{r}))d\mathbf{r} \quad (2.23)$$

The different methods for obtaining  $f(n(\mathbf{r}), \nabla n(\mathbf{r}))$  provide different GGAs. One of the most popular GGA is the one proposed by Perdew et.al. [11] and is known as PBE. In PBE-GGA [11] the exchange correlation energy can be written as

$$E_{xc}^{\text{GGA}}[n] = \int n(\mathbf{r})\epsilon_x^{\text{LDA}}([n(\mathbf{r})], \mathbf{r})F_{xc}(\mathbf{r}, s, t)d\mathbf{r} \quad (2.24)$$

where  $F_{xc} = F_x + F_c$  is defined as enhancement factor for exchange correlation energy per particle.  $F_x$  and  $F_c$  are enhancement factors for exchange and correlation part respectively.

In PBE-GGA the correlation enhancement function should have the form  $F_c = \beta t^2$  in the limit of small  $t$  i.e.  $t \rightarrow 0$  where  $\beta = 0.066725$  and

$$t = \left(\frac{\pi}{4}\right)^{1/2} \left(\frac{9\pi}{4}\right)^{1/6} \frac{s}{r_s^{1/2}} \quad (2.25)$$

In equation (2.25),  $t$  represents another reduced density gradient. Further the exchange enhancement

$$F_x(s) = 1 + \mu s^2, \text{ where } \mu=0.21951 \text{ in limit } s \rightarrow 0. \quad (2.26)$$

LDA and PBE are collectively known as standard density-functionals, are most widely used XC functionals for estimating the behaviour of the solids. However, the applications of these functionals by a number of authors for solid state calculation lead to are some general trends in performance of LDA and PBE. Firstly, LDA leads to over binding of constituent particles resulting in an under estimation of lattice parameters of solids. On the other hand, GGA tends to underbined, resulting in the overestimation of lattice parameters. Further, the energy gap calculated with LDA and GGA are too small as compared to experimental results. This under estimation of band gaps by these standard DFT functionals is known as band gap problem. In addition to these, both the functionals suffer from an unphysical problem so called self interaction problem. As a consequence of these facts, it becomes necessary to search for further improvement over standard GGA. Due to flexibility in the mode of including gradient of electron density in the expression for xc functional, a large number of GGAs functionals have been proposed. Some of these new functionals are developed non empirically in way to satisfy some physical constraints while others are derived empirically by fitting parameters to the test set of selected systems [15].

In 2005, a scheme for systematic improvement of exchange correlation functional was proposed called Jacob's ladder [16], consisting of five rungs with each rung indicating the requirements for an improved degree of accuracy and sophistication of XC functional. At the first rung, the LDAxc lie including only the electron density in its expression. All the XC functionals under GGA including gradient of the density as well lie on second rung of Jacob's ladder. On the third rung, the so called meta GGAs which include the kinetic energy density (and hence second order derivative of the density) in addition to the first order gradient and electron density in calculating the xc energy. The fourth rung contains those functionals (hybrid functionals) in which a part of semilocal functional is replaced by Hartre-Fock term. In the highest (the fifth) rung, the functionals of those approximation (e.g. Random Phase Approximation) lie which take into account the high unoccupied orbitals while calculating the many body effects.

We will now give a brief introduction to those newly developed GGA (WC, PBEsol) and meta-GGA(SCAN, TBmBJ) functionals which are considered to be most efficient xc functionals in describing the behaviour of solids in ground and excited states and form the core functionals of this thesis.

In 2006 Wu and Cohen [21] constructed an exchange correlation functional under the generalized gradient approximation. This functional has been constructed in such a manner that the exchange part was modified in order to recover the fourth order parameter in expansion of  $x(s)$  ( $=\mu s^2$ ) given by equation (6) of reference [21], while the correlation energy functional as proposed by Perdew et. al. [11] in PBE, was used. WC functional being a GGA functional has the advantages of high computational efficiency and easy implementation in various computer codes. Further, the WC functional has been found to be suitable for calculations of lattice constant of solids [22].

In order to obtain accurate description of surface energies and lattice constant of solids, Perdew et. al. [23] modified the original PBE functional. This had been done by re parameterizing the coefficient and  $\mu$  and  $\beta$  of PBE functional. The parameter  $\mu$  of the exchange part was adjusted to recover the gradient expansion up to second order while the parameter  $\beta$  of correlation part was set in order to produce good surface energy. The new values of the parameter obtained were  $\mu=10/81$ ,  $\beta=0.046$  [23]. With these parameters, the modified functional so obtained is known as PBEsol. PBEsol have been found to produce the lattice constant of solids much closer to experimental values as compared to original PBE [24].

SCAN (Strongly Constrained and Appropriately Normed) is a meta-GGA type XC functional including the kinetic energy density and hence the second order derivative of electron density also [25]. In general, a meta GGA XC functional can be written in the form as

$$E_{xc} [n] = \int n(\mathbf{r})\epsilon_{xc}([n(\mathbf{r})], \nabla n(\mathbf{r}), \tau) dr \quad (2.27)$$

where

$$\tau = \sum_i^{occup} \frac{1}{2} |\nabla \varphi_i(\mathbf{r})|^2 \quad (2.28)$$

represents the kinetic energy density of the occupied Kohn-Sham orbitals  $\nabla \varphi_i(\mathbf{r})$ . SCAN is a non empirical semi local XC functional which satisfies all the 17 constraints applicable to a meta GGA functional [25]. In addition effect of appropriate norms has also been added in order to get higher accuracy in the calculations of the energies of

rare gas atoms and non bonded interactions. SCAN has been found to predict the exact ground states and formation enthalpy of binary solids in a better way as compared to the standard density functionals [26]. Although the computation cost of scan is more as compared to that of standard GGA, still much lesser than that for hybrid functionals.

In order to resolve the band gap problem produced by the local and semilocal (LDA, GGAs) functionals, Tran and Blaha [26] modified the exchange potential initially proposed by Becke and Johnson [27]. The TBmBJ exchange potential is defined by equation (4) of reference [16]

$$v_x^{TB-mBJ}(\mathbf{r}) = cv_x^{BR}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t(\mathbf{r})}{\rho(\mathbf{r})}} \quad (2.29)$$

Where  $\rho$  being the electron density,  $t$  is the kinetic energy density and  $v_x^{TB-mBJ}$  is the Becke-Russel potential and parameter  $c$  is given by

$$c = A + B\bar{g}^e \quad (2.30)$$

and

$$\bar{g} = \frac{1}{V_{cell}} \int_{cell} \frac{1}{2} \left( \frac{|\nabla\rho\uparrow(\mathbf{r})|}{\rho\downarrow(\mathbf{r})} + \frac{|\nabla\rho\downarrow(\mathbf{r})|}{\rho\uparrow(\mathbf{r})} \right) d^3r \quad (2.31)$$

In equation (2) A, B and e are the parameters whose values are fitted according to the experimental values. The parameters suggested in original and improved form of mBJ approximation are shown in Table 2.1.

**Table 2.1: The values of parameters A, B and e used for calculations of 'c' in [Eq. (2)].**

	A	B	e
$P_{original}$	-0012	1.023	0.5
$P_{semiconductor}$	0.267	0.656	1
$P_{new}$	0.488	0.500	1

In table 2.1,  $P_{original}$ ,  $P_{semiconductor}$  and  $P_{new}$  are the parameterization used for calculation of 'c' in original and improved form of mBJ approximations as suggested by Tran & Blaha [27] and D. Koller respectively [28].

### 2.3 Wien2k

In Kohn-Sham scheme based density functional theory we have to solve the one electron cone some equations of form given by the equations (2.10) the solutions of

such one particle equations needs the calculation of coefficients  $c_{ip}$ , required to expand KS orbitals in a given basis set  $\varphi_p$ .

$$\varphi_i = \sum_{p=1}^P c_{ip} \varphi_p \quad (2.32)$$

In principle, P should be infinite in order to obtain exact wave functions  $\varphi_i$ . However P is limited to finite value by computational limitations. Using a suitable set of basis functions coefficients  $c_{ip}$  of equation (2.32) can be obtained by solving the secular equation

$$\det[H_{pp'} - \epsilon_i S_{pp'}] = 0 \quad (2.33)$$

here  $H_{pp'}$  and  $S_{pp'}$  are hamiltonian and overlap matrices respectively defined by

$$H_{pp'} = \langle \varphi_p | \hat{H}_s | \varphi_{p'} \rangle, S_{pp'} = \langle \varphi_p | \varphi_{p'} \rangle \quad (2.34)$$

With the selected set of basis functions the iteration process for equations (2.10), (2.12) and (2.14) continues until self-consistent solutions are obtained.

Wien2k [29] is one of the most widely used DFT based computational code which can be employed for electronic structure description of the solids. In a DFT based electronic structural method, the accuracy and computational efficiency depends upon, set of basis functions chosen for expanding the one particle KS orbitals, form of initial guess to effective potential to be used in KS equation and number of electrons included in the calculations that is whether all electron or a pseudopotential approach is used. In the former, the core electrons are also included in the calculations in addition to the valence electrons, unlike the pseudopotential approach where only the valence electrons are considered with all the core frozen electrons. Wien2k is an all electron full potential linearized augmented plane wave method based code. The main choices for computation of the properties used in wien2k method are

- **All electron approach** including the core as well as valence electrons for calculations of total energy unlike the pseudopotential method which ignores the core electrons and taking into account only valence electrons for calculating the total energy of the system.
- **Basis set** the whole unit cell is divided into two parts that is non overlapping atomic spheres (atomic polyhedrons as suggested by Wigner) known as Muffin tin sphere and interstitial region. Inside atomic sphere the basis set consist of

atomic like wave function while in interstitial region the plane waves are used for expansion of wave function characterizing the single particle. In addition local orbitals can also be added to expand the basis set for semi core states as used in APW+lo and LAPW+LO approximations. In fact wien2k uses the mixed basis set from APW (+lo) and LAPW (+LO) approximations.

- **Potential** The potential inside the atomic sphere is assumed to be spherically symmetric while in between the spheres is taken to be flat.[30]

## 2.4 TBLMTO

Tight Binding Linear Muffin Tin Orbital (TBLMTO) method is a linear method in which the basis set is constructed from partial wave and the first order derivative with respect to energy. In this method, the crystal is divided into two parts by imagining the hypothetical spheres known as muffin tin wells of radius  $S = (3v_o/4\pi)^{1/3}$  [31] and the interstitial regions. The electronic wave function moving in the periodic potential of the crystal can therefore be expressed in the terms of Bloch sum.

$$\Psi_j(\mathbf{k}, r) = \sum e^{i\mathbf{k}\cdot\mathbf{r}} \sum a_{nlm} \chi_{nlm}(r - R) \quad (2.35)$$

The MT orbital is given by

$$\chi_{nlm} = i^l Y_l^m(r) \phi_l(E, r) + p_l(E)(r/s)^l \quad r < S \quad (2.36)$$

and

$$\chi_{nlm} = i^l Y_l^m(r)(S/r)^{l+1} \quad r > S \quad (2.37)$$

The potential function  $p_l$  is

$$p_l(r) = 2(2l+1) \frac{D_l(E) + l + 1}{D_l(E) - l} \quad (2.38)$$

Where  $D_l(E)$  is the logarithmic derivative function at surface of the sphere. An important feature of this definition is that the function inside the well is regular at origin, while the tail is regular at the infinity. The energy independent MT orbitals will lead to a secular equation which has a non linear energy dependence so that MT orbitals are made energy independent around a fixed energy  $E_v$ . [32,33,34]

These muffin tin orbitals can be obtained as the solution of the radial Schrodinger equation for a given potential  $V_{MT}$ . the energy parameter  $E$  for the MT well is measured relative to potential of the well, and the kinetic energy parameter  $\kappa^2$  may be expressed as  $E - V_0$ [32]. In LMTO method the variational principle for one electron Hamiltonian is used in which trial functions are linear combination of energy independent muffin tin orbitals.

For Bloch sum of muffin tin orbitals to represent the wave function of the crystal, the following condition must be satisfied

$$\sum_{l,m} [p_l(E)\delta_{l',l}\delta_{m,m'} - S_{l'm',lm}^k] = 0 \quad (2.39)$$

These equations have the solutions at those values of  $E$  for which the determinant of the coefficient matrix vanishes i.e.

$$\det[p_l(E)\delta_{l',l}\delta_{m,m'} - S_{l'm',lm}^k] = 0 \quad (2.40)$$

If we neglect the hybridization, the pure nl energy band  $E_{nl}(k)$  is obtained as solution of

$$p_l(E) = S_{li}^k \quad (2.41)$$

To solve these equations a parameterization of the potential function is required which can be done in terms of four potential parameters i.e

$$\omega(D_1), S\phi^2(D), \Phi(D_1) / \Phi(D_2), \left\langle \phi_v^2 \right\rangle \quad (2.42)$$

Once the potential parameters are known a canonical band structure is obtained. From which state density per spin is obtained which in turn provides the number density of electrons. Therefore by representing the Hamiltonian and overlap matrix in terms of the potential parameters, the problem is reduced to find the eigen values from the expression

$$(\underline{H} - E\underline{Q}) = 0 \quad [34]. \quad (2.43)$$

## 2.5 ELK

ELK is an all electron full potential linearised augmented plane wave method based computational code. It can be used for calculating the properties of crystalline solids using first principal based theoretical approaches. Regarding the basis functions used

for expansion of KS orbitals in DFT approximation, the whole space is divided in two regions just as is applied in case of wien2k code, discussed already in the previous sections. In this code, LDA and GGA functionals are incorporated as native exchange correlation functionals,. However, all other xc functionals like meta GGA can also be used through an externally linked libxc functional library (<http://www.tddft.org/programs/octopus/wiki/index.php/Libxc>) . One of the major advantage of this code as compared to wien2k code which attract us for implementing in the present work is availability of the calculations of non linear (NLO) second harmonic generation within random phase approximations. [35]

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