Chapter 2

A Review of Theoretical Methodology

In this chapter, we discuss in brief the theoretical methodology that had been developed to study the electronic, optical, transport and structural properties of solids. Since the objectives of this thesis have been to study the electronic, optical, transport and structural properties of bimetallic atomic chains, we focus more on the methods that had been used to investigate the properties of atomic chains.

2.1 Background

An ab-initio calculation or equivalently called "from first principles" is generally referred to a "bottom-up" material modelling" using mathematical model. These theoretical modelling techniques relies mostly on simple input parameters like atomic number Z and does not require any empirical or experimental parameters to predict and describe the system consisting of atoms, molecules and solids.

The corner stone of modern material modelling techniques is Quantum Mechanics. Simple rules and formulation of Quantum mechanics is in fact a spectacular "engineering tool" for understanding and predicting many properties of materials. The use of Quantum Mechanics in the study of materials goes through the solution of Schrödinger equation. A numerical solution of the wave equation of a system reveals most of its properties. However, the real system consisting of number of particles, nucleus and number of electrons, is a many-body problem. The exact solution of a many bodies problem remains difficult task as they are solvable in time scaling exponentially with system size. Many approximations are introduced to solve the many body equation numerically without losing much of the accuracy and predictive power.

Most of the complexity of the problem arise from the treatment of electron-electron interactions. The physical and chemical properties of a system depend principally on the interaction of the electrons with each other and with the atomic cores. These interactions cannot easily be separated out or treated without approximation. Another complexity arises from the many body nature of the problem concerning solids. There is no analytical solution to interacting many body problem. Since early nineteen seventies different numerical methods have been employed to solve the Schrödinger equation for atoms and molecules. These methods are referred to as 'wave-function based methods'. In spite of the rapid growth of computer power and the available computational resources, it is still not feasible to calculate directly systems involving more than 10 electrons.[72] To treat the complexity of many body problem and the electron-electron interaction several techniques were developed. Among different computational and theoretical techniques, one of the prestigious methods widely used for predicting ground state properties of materials with large number of electrons is density functional theory (DFT). DFT converts the complex electron-electron interaction into a simpler effective one-electron potential. This effective one-electron potential is functional of the electron density only. That is the reduction in the 3N degrees of freedom to 3 by incorporating overall electron density instead of number density for constructing the wave-function.

Utilizing DFT, one can solve time-independent Schrödinger like Kohn-Sham equation for studying the properties of bulk, nano materials as well as complex systems of bio molecules with nano materials. This theory is the developed version of Thomas and Fermi model proposed in early twentieth century, and further treated by Hartree, Fock, Dirac and Slater.

The foundation of DFT was formulated by the two famous theories, one proposed by Hohenberg and Kohn[73] and later by Kohn and Sham[74] which provides an inexpensive tool for calculating the ground state properties of many electron systems. In the following sections, we briefly discuss the mathematical basis of theoretical techniques.

2.2 The Many Particle Solids

Any solution of the time-independent Schrödinger equation starts with constructing the Hamiltonian of a system of N_e interacting electrons and N_n nuclei:

$$H = T_e + T_n + V_{nn} + V_{ee} + V_{ne} \qquad (2.1)$$

$$H = -\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \bar{r}_i^{\,2}} - \frac{\hbar^2}{2M}\sum_l \frac{\partial^2}{\partial \bar{R}_l^{\,2}} + \frac{1}{2}\sum_{\substack{l,l' \\ l\neq l'}} \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l Z_{l'}}{|\bar{R}_l - \bar{R}_{l'}|}$$

$$+\frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\bar{r}_i - \bar{r}_j|} - \sum_i \sum_l \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l}{|\bar{r}_i - \bar{R}_l|} \qquad (2.2)$$

Here, T_e and T_n are the kinetic energy of electrons and ions, while V_{nn}, V_{ee}, and V_{ne} are potential energy of two nuclei, two electrons and nuclei-electron system respectively. The indices *i* and *l* runs for electron and nuclei, m_e and M stands for the mass of electron and nuclei, Z_l and Z_l' defines the charges on different nuclei, $\bar{\boldsymbol{r}}_i - \bar{\boldsymbol{r}}_j, \bar{\boldsymbol{R}}_l - \bar{\boldsymbol{R}}_l'$ and $\bar{\boldsymbol{r}}_i - \bar{\boldsymbol{R}}_l$ represents distances between electron-electron, nuclei-nuclei and electron-nuclei respectively. The constants ħ and e are the reduced Plank constant and the electron charge, respectively.

We seek the solution of the eigenvalue equation:

$$H\psi = E\psi \qquad (2.3)$$

Here, H is the Hamiltonian of the system, ψ is the wave function and E is the energy eigenvalue of the system known as total energy of the system.

Solving equation 2.3 yields the energy eigenvalue known as total energy of the system. Ground state properties of materials at equilibrium condition can be calculated from total energy of the system. The only parameter required for solution of equation 2.3 are atomic mass, charge of electron, atomic number and mass of nuclei. It does not require any adjustable parameter and hence it is known to be first principles calculation.

2.3 Wave Function Based Methods to Solve a Many Particle Problem

An exact solution of eqn.(2.3) is not possible. There had been several approximations to solve a many particle eigenvalue equation. Some of these are as follows:

2.3.1 Born-Oppenheimer Approximation

The mass of electrons and ions are hugely different ($m_e/M_I \approx 10^{-3}$ - 10^{-6}). This large difference of mass makes it possible to decouple the electron and ionic parts of the Hamiltonian.Such decoupling does a major simplification of the many-body Hamiltonian and is known as Born-Oppenheimer approximation.[75] Here, electrons are regarded as responding instantaneously to changes in the nuclear positions, which in turn are kept fixed. Following the Born-Oppenheimer approximation, the many body wave function can be expressed as:

$$\psi = \chi_i(\bar{R})\, \Psi_E(\bar{r},\, \bar{R}) \tag{2.4}$$

Here $\chi_i(\bar{R})$ represents ionic, while $\Psi_E(\bar{r},\, \bar{R})$ stands for electronic wave function. Separated ionic and electronic part of wave function leads to following equations:

$$\left[-\frac{\hbar^2}{2M}\sum_l \frac{\partial^2}{\partial \bar{R}_l{}^2} + V_{nn}(\bar{R}) + E_e(\bar{R})\right]\chi_l(\vec{R}) = E\chi_l(\bar{R}) \tag{2.5}$$

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \overline{\bar{r}_l}^2} + V_{ne}(\bar{r},\, \bar{R}) + V_{ee}(\bar{r})\right]\Psi_e(\bar{r},\, \bar{R}) = E_e\Psi_e(\bar{r},\, \bar{R}) \tag{2.6}$$

As ions are considered stationary, the kinetic energy term for ions vanishes and ion-ion potential becomes constant in equation 2.5, whereas electron-ion interaction depends on position of electrons only.

2.3.2 Hartree Approximation

Taking further the Born-Oppenheimer approximation to reduce the complexity of many-body interaction Hartree treated electrons independently and their interaction was treated via the average charge. This is equivalent to representing the total wave function as a product of individual one-electron wave equation.[76] Therefore, electronic wave function is written as:

$$\Psi_H = \Psi(\overline{r_1}, \sigma_1)\Psi(\overline{r_2}, \sigma_2) \dots \Psi(\overline{r_N}, \sigma_N) \qquad (2.7)$$

where, $\Psi(\overline{r_\iota}, \sigma_i)$ determines the wave function of i$^{\text{th}}$ electron, $\overline{r_\iota}$ is the postion coordinate of ith electron with spin σ_i. Thus, as per Hartree approximation one uses the Hamiltonian of equation 2.6 and wave function from equation 2.7 for constructing the complete Schrödinger equation for electronic part which is written as:

$$-\frac{\hbar^2}{2m_e}\nabla_i{}^2\Psi_i - \frac{1}{4\pi\varepsilon_0}\sum_l \frac{Ze^2}{|\bar{r}_i - \bar{R}_l|}\Psi_i + \frac{1}{4\pi\varepsilon_0}\sum_{j\neq i}\int \frac{e^2|\Psi_j|^2}{|\bar{r}_i - \bar{r}_j|}d^3r_j = \epsilon_i\,\Psi_i \qquad (2.8)$$

The first term in left hand side of the equation is the kinetic energy, second term represents the ion-electron interaction (V_{IE}) which depends only on the position of electron and the last term represents the Hartree potential, V_H. The solution of Hartree equation is given by variational principle which provides exact ground state energy through-minimization of expectation value of energy E.

$$E = \frac{\langle \Psi_H | H | \Psi_H \rangle}{\langle \Psi_H | \Psi_H \rangle} \qquad (2.9)$$

The independent electron approximation given by Hartree did not consider the asymmetry of wave function of electrons and this was modified in Hartree-Fock approximation. Also, the independency of electron neglects correlation between electrons.

2.3.3 Hartree-Fock Approximation

Considering the asymmetric nature of a wave function and the effect of correlation the Hartree-Fock approximation takes as a trial function that is a set of N-particle Slater determinant.

$$\Psi_{HF}(\overline{r_1}, \sigma_1, \dots, \overline{r_N}, \sigma_N) = \begin{vmatrix} \Psi_1(\overline{r_1}, \sigma_1) & \Psi_1(\overline{r_2}, \sigma_2) \dots & \Psi_1(\overline{r_N}, \sigma_N) \\ \Psi_2(\overline{r_2}, \sigma_2) & \Psi_2(\overline{r_2}, \sigma_2) \dots & \Psi_2(\overline{r_N}, \sigma_N) \\ \dots & \dots & \dots \\ \Psi_N(\overline{r_N}, \sigma_N) & \Psi_N(\overline{r_N}, \sigma_N) \dots & \Psi_N(\overline{r_N}, \sigma_N) \end{vmatrix} \qquad (2.10)$$

The determinant of the wave function can be written as:

$$\Psi_{HF} = \frac{1}{N!}\sum_P (-1)^p P\, \Psi_1(x_1)\, \Psi_2(x_2) \dots \Psi_N(x_N) \tag{2.11}$$

Where, $x = (\bar{r}, \sigma)$, P is the permutation number and p is number of interchanges making up this permutation. Substituting the determinant form of equation in variational principle (equation 2.9) gives expectation value of Hamiltonian:

$$E = \sum_i \int \Psi^*(\vec{r}) \left[-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + V_l(\vec{r}) \right] \Psi(\vec{r}) d^3r$$
$$+ \frac{1}{2} \sum_i \sum_{i \neq j} \iint \frac{e^2}{4\pi\varepsilon_0} \frac{|\Psi_i(x_i)||\Psi_j(x_j)|^2}{|\vec{r} - \vec{r}'|} d^3r d^3r'$$
$$- \frac{1}{2} \sum_{i,j} \sum_{j \neq i} \iint \frac{e^2}{4\pi\varepsilon_0} \frac{\Psi_i^*(\vec{r}) \Psi_j^*(\vec{r}')\, \Psi_i(\vec{r}')\, \Psi_j(\vec{r})}{|\vec{r} - \vec{r}'|} d^3r d^3r' \tag{2.12}$$

The first term of above equation consist of kinetic energy and interaction of external potential, the second term represents Hartree potential and the last term appeared due to the Pauli's exclusion principle also known as exchange energy. Minimization of equation 2.12 leads to canonical form of Hartree-Fock equation:

$$\left[-\frac{\hbar^2}{2m_e} \sum_i \nabla^2 - V_l(\vec{r}) + V_H(\vec{r}) \right] \Psi_i(\vec{r})$$
$$- \frac{1}{2} \sum_{i,j} \sum_{j \neq i} \iint \frac{e^2}{4\pi\varepsilon_0} \frac{\Psi_j^*(\vec{r}')\, \Psi_i(\vec{r}')\, \Psi_j(\vec{r})}{|\vec{r} - \vec{r}'|} d^3r d^3r' = \in_i \Psi_i(\vec{r}) \tag{2.13}$$

The Slater determinant approximation does not take into account the Coulomb correlations of electrons, the total electronic energy is different from the exact solution of non-relativistic Schrödinger equation within Born-Oppenheimer approximation. Therefore Hartree-Fock Energy is always above the exact energy. This difference is called the correlation energy. Apart from the coulomb correlation, one major short coming of Hartree-Fock approximation is the lengthy minimization over sum of N particle Slater's determinant which makes it computationally very costly.

2.4 Density Functional Theory

The Density based methods provide a convenient way to solve the electronic problem within the mean field-like approximation to overcome the limitation of high computational cost of solving equations containing 3N variables. In Density based methods the interaction energy and potential depend only on density of electrons. Density based methods for calculating ground state energy was first proposed by Thomas and Fermi(TF).[77,78] The TF theory states that the total energy of the system can be written as a functional of electron density. Here the basic variable is electron density instead of single particle wave function or orbitals. TF theory understandably had several shortcomings. The oversimplified description of the electron-electron interaction which was treated classically. Nevertheless, TF theory contains all necessary ingredients which paved the way to the modern DFT.

2.4.1 Hohenberg and Kohn Theorems

DFT is based on the famous theorems by Hohenberg and Kohn. These theorems demonstrate that the total energy of a many-electron system in an external potential is a unique functional of the electron density and that this functional has its minimum at the ground state density. Further development of these two theorems were done by Kohn and Sham. Kohn and Sham expressed the electron density as a sum over one-electron densities and used one-electron wave functions as the variation parameters. Here the exchange correlation potential had been expressed as the functional derivatives of the exchange correlation energy. However, the exact form of exchange-correlation functional is unknown, the Hohenberg-Kohn theorems and Kohn-Sham equation constitutes the core elements of DFT.

The first Hohenberg-Kohn theorem states that, *the external potential V(r) is a unique functional of electron density n(r). As result, the total ground state energy E of any many electrons system is also unique functional of n(r),* $\mathrm{E} = \mathrm{E}[\mathrm{n}]$.

The second Hohenberg-Kohn theorem states that *the functional* $E[n]$ *for the total energy has a minimum equal to the ground state energy at the ground state density*.

The unique external potential determined using density is used to determine the electronic wave function and all other observables. The total energy then can be written as:

$$E[n] = T[n] + E_{int}[n] + \int V_{ext}(r)n(r) + E_{II} \tag{2.14}$$

$$E[n] \equiv F[n] + \int V_{ext}(r)n(r) + E_{II} \tag{2.15}$$

Here, the encapsulated F[n] is the interaction potential of electrons and kinetic energy of electrons for all systems. The ground state energy determined by unique ground state density is.

$$E^{(1)} = E\left[n^{(1)}\right] = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle \tag{2.16}$$

Here, total energy can be written as functional of n(r). F[n] in equation 2.15 can be written as a functional of density n(r)

$$F[n] = T_s[n] + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')\,n(\vec{r})}{|\vec{r}-\vec{r}'|}d^3r d^3r' + E_{XC}[n] \tag{2.17}$$

By knowing F[n], we can vary density until minimization of total energy for the system. Thus, the knowledge of total energy is sufficient to determine the ground state energy and density.

2.4.2 Kohn-Sham Equation

Hohenberg and Kohn theorems are basically the reformulation of many body interacting systems in terms of electron density. Unfortunately, the form of the functional $E_{XC}[n]$ in equation 2.17 is not known. The form of the functional and inclusion of exchange and correlation was addressed by Kohn and Sham. They assumed that for a given interacting ground state density *n(r)* there exists a potential such that the ground state density of the non-interacting Hamiltonian $\mathrm{H} = \mathrm{T_s} + \mathrm{V_{ext}}$ is equal to the Hamiltonian of the interacting ground state density *n(r)* such that we get the energy density functional:

$$E[n(\bar{r})] = \int V(\bar{r})n(\bar{r})d^3r \ + T_s[n] + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')\,n(\vec{r})}{|\vec{r}-\vec{r}'|}d^3r d^3r' + E_{XC}[n] \tag{2.18}$$

In other words, KS replaced the potential of interacting system by an auxiliary non-interacting system with assumption of same ground state density and then same ground state properties. For this ground breaking work, Walter Kohn was awarded Nobel prize in chemistry in 1998.[74] Now, $T_s[n]$ is independent kinetic energy and $V_{ext}(\vec{r})$ is replaced by $V(\vec{r})$, which is the potential between electrons and nuclei. The many body quantum mechanical effect is accounted by the last term $E_{XC}[n]$ which is the exchange and correlation energy.

Minimization of the energy is done by taking the functional derivative of equation 2.18 which gives:

$$\frac{\delta E[n]}{\delta n(\bar{r})} - \mu = 0 \qquad (2.19)$$

$$\frac{\delta T_S[n]}{\delta n(\bar{r})} + V(\bar{r}) + V_H(\bar{r}) + V_{XC}(\bar{r}) - \mu = 0 \qquad (2.20)$$

Here, $V_H(\bar{r})$ is the Hartree potential in terms of electron density and $V_{XC}(\bar{r}) = \frac{\delta E_{xc}[n]}{\delta n(\bar{r})}$ solution of equation will give the electron density and further it leads to total energy of system.

Two unknowns $T_s[n]$ and exchange correlation potential $V_{XC}(\bar{r})$ arising from Pauli and Coulomb interaction are a limitation of equation 2.20. To overcome the problem Hartree considered density as square of orbitals of the system.

$$n(\bar{r}) = \sum_{i=1}^{N} | \Psi_i(\bar{r})|^2 \qquad (2.21)$$

Where, KS orbitals are determined by $\Psi_i(\bar{r})$. KS Kinetic energy can be written as a single particle by following expression.

$$T_s[n] = -\frac{\hbar^2}{2m_e}\sum_i^N \langle \Psi_i(\bar{r})|\nabla^2| \Psi_i(\bar{r})\rangle = -\frac{\hbar^2}{2m_e}\nabla^2 \qquad (2.22)$$

Here, $T_s[n]$ is responsible for density oscillation of shell structure and it has large part of the total kinetic energy of system. Here, $E_{xc}[n]$ is the sum of electron exchange and correlation energy i.e., $E_{xc}[n] = E_x[n] + E_c[n]$, where Slater's determinant $E_x[n]$ is generally given by Slater's determinant (equation 2.11). By solving equation 2.18 we get

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\bar{r})\right] \Psi_i(\bar{r}) = \epsilon_i \Psi_i(\vec{r}) \qquad (2.23)$$

Here, $V_{eff}(\bar{r})$ is known as effective potential and determined by sum of external potential, $V_{ext}(\bar{r})$, Hartee potential, $V_H(\bar{r})$ and exchange-correlation potential, $V_{XC}(\bar{r})$.

Equation 2.23 is Kohn-Sham equation, and it is exactly same as the many body Schrödinger equation. For the exact form of exchange-correlation functional different approximations such as local density approximation (LDA) and generalized gradient approximation (GGA) are taken into account. We discuss these approximations briefly in the subsequent section.

Solution of KS equation yields exact ground state energy, and it describes behaviour of one electron moving in multiple electron system by effective potential. Since the solution of KS equation depends only on density of electrons and it has only 3 variables, the computational cost reduces to a great extent. This makes KS theory a powerful tool in determination of ground state properties of materials.

2.5 Exchange and Correlation Functional

In principle the Kohn-Sham scheme is exact, however the expression for the exchange and correlation functional $E_{xc}[n]$ unknown. As the exchange correlation functional includes many body effects the form of $E_{xc}[n]$ needs to be re-constructed so as to make the underlying physics clear. The exchange interaction term which is the repulsion between electrons defined as:

$$E_x[n] = \langle \Psi[n] | V_{EE} | \Psi[n] \rangle - U[n] \tag{2.24}$$

The correlation term can be determined by the following expression:

$$E_c[n] = F[n] - T_S[n] - U[n] - E_X[n] \tag{2.25}$$

Till date, exact formalism of exchange correlation is still not available.

2.5.1 Local Density Approximation

Local Density Approximation (LDA) is one the most popular and one of the earliest developed approximation to find the form of exchange and correlation functional. The main idea behind LDA is to consider general inhomogeneous electronic system as locally homogenous system. Since the form of homogenous electron gas is very well known, it can be used to evaluate the exchange energy exactly and it is possible to determine the correlation energy using numerical techniques. In contrast to the exchange energy, for the correlation energy of the electron gas, there does not exist simple analytic expression. Nonetheless, it has been possible to calculate the correlation energy for this simple model by solving directly the many-particle Schrödinger equation using stochastic numerical methods (Ceperley and Alder, 1980).[79] The correlation energy of the electron gas can be extracted from the data of Ceperley and Alder by removing the known kinetic, Hartree and exchange contributions from the calculated total energies. The data calculated by Ceperley and Alder were subsequently parameterized by Perdew and Zunger (1981).[80] Using above approximations the exchange-correlation energy and potentials are obtained as

$$E_{xc}^{LDA}[n(r)] = \int dr\ n(r)\ \epsilon_{xc}^{LDA}[n(r)] \tag{2.26}$$

$$V_{xc}[n(r)] = \left(E_{xc}[n] + n\frac{\delta E_{xc}[n]}{\delta n}\right)_{n=n(r)} \tag{2.27}$$

where, $E_{xc}[n]$ is the exchange-correlation energy per electron in a homogeneous electron with density, n.

While the electron density in materials may not resemble at all the homogeneous electron gas, this simple model can be used in order to describe the exchange and correlation energy in those regions where the density is slowly varying. However, there are some limitations of LDA. The main limitation is its applicability for strongly correlated systems and its failure for describing properties of transition metals. In the field of quantum chemistry, LDA overestimates intermolecular bonds and molecular binding energy. To overcome this problem several efforts have been put to find better functional. For a system that contains an odd number of electrons, pure LDA performs badly, since it makes no difference between polarized and unpolarized densities.

2.5.2 Generalized Gradient Approximation

In complex systems, electron density may vary with the volume element, so LDA can fail to determine ground state properties. To overcome this problem Generalized Gradient Approximation (GGA) was developed. The idea of GGA is to use gradient of electron density in addition to the electron density for evaluating the exchange and correlation term which yields:

$$E_{xc}^{GGA}[n(r)] = \int dr\, n(r)\, \epsilon_{xc}^{GGA}(n(r), \nabla n(r), \dots) \tag{2.28}$$

Exchange and correlation are now semi-empirical functional, and degree of non-locality have a dependency of electron density. GGA favours density inhomogeneity more than LDA by the non-locality of the exchange with most common densities. This approximation assumes a gradient in the charge density. It can be written as:

$$E_{xc}[n] = \int \varepsilon_{xc}(n)\,|_{n=n(r)} n(r) F_{xc}[n(r), \nabla n(r)] dr \tag{2.29}$$

For more simplification in calculation, E_{xc} and F_{xc} must be parameterized by analytic functions. Perdew, Burke, and Ernzerhof[108] have parameterized E_{xc} and F_{xc} from first principles calculation. In predicting bond dissociation energy and the transition-state barrier, GGA is better than LDA however there are exceptional cases. To satisfy several further exact conditions, Perdew-Wang 1991 (PW91)[81] designed functional which is an analytic fit to this numerical GGA. Plane waves and pseudopotentials which form a very natural alliance are a hallmark of the method.

2.6 Self-consistent calculations

The basic concepts of DFT and the Kohn-Sham equations anticipates a theoretical apparatus to calculate the E, and the *n(r)* of materials in their ground state. However, the theoretical apparatus is basically a numerical method of changing density of electrons and effective potential to achieve the self-consistency. Knowing the effective potential, the KS equation can be solved. Hartree potential and exchange correlation potential depends on electron density and this density yield correlation energy where initial guess of density is made. An approximation to initial guess for electron density is adding up densities of isolated atoms arranged in corresponding material.

2.7 Numerical Implementation of DFT

This section presents some selected aspects of the numerical implementation of a DFT codes which are related to our study. The error size associated with a number of approximations is often a compromise between computational time and accuracy. To solve the Kohn-Sham equation numerically the wave-functions must be represented as a liner combination of a finite number of basis functions. The choice of the basis functions determines the achievable accuracy and computational efficiency. DFT calculations implemented in different computational codes use mostly one of three types of basis sets namely, (1) Linear Combinations of atomic orbital (LCAOs), (2) Linearized augmented plane waves (LAPWs) and (3) Plane Waves (PWs) in combination with pseudo potentials for describing the electron-ion interaction. Different computational packages uses different methods.

The DFT code used throughout this work is Vienna ab-initio Simulation Package (VASP). VASP uses plane wave basis set for solving KS equation. The discussion of numerical implementation is limited to methods used in VASP code with a brief background of each concept.

2.7.1 Boundary Conditions

As per Bloch's theorem, the wave function of an electron placed in a periodic potential has a periodicity of the crystalline lattice. The Kohn-Sham orbitals, $\Psi_k^n\,(r)$, can be written as product of plane wave $e^{ik.r}$and a periodic function $u_k^n(r)$ that has periodicity of the lattice.

$$\Psi_k^i\,(r) = u_k^n(r)\,e^{ik.r} \qquad (2.30)$$

where k is a vector in first Brillouin zone and n is band index. Because of the periodicity of the lattice periodic boundary conditions can be utilized to treat infinite periodic systems such as bulk crystals. For non-periodic structures these periodic boundary condition can still be useful by forming supercells. The system of interest is modelled within a finite cell which is repeated in all directions to form super lattice. In this way, molecules, nanotubes, atomic chains and surfaces can be modelled by introducing sufficiently large vacuum region in the supercell such that the system under consideration does not interact with the periodic image. $u_k^n(r)$ can be expanded as a set of plane waves.

2.7.2 Description of ions

Framing the non-interacting KS-equations has substantial numerical difficulties: (i) In any condensed matter system, the kinetic energy of electrons near the nucleus is higher compared to the bonding region between atoms. As a result, the wave functions of the electrons near the nucleus oscillate rapidly requiring a very fine grid for an accurate numerical representation. On the other hand, the demand of large kinetic energy cut off makes the KS-equation stiff. Which means that the shape of the wave function will have little effect of any change in the chemical environment. Thus, the core region requires small basis set. (ii) In the bonding region, situation is reversed. Since the kinetic energy is low the wave functions are smoothly varying. This responds strongly to a change in environment which in turn requires large and flexible basis set.

Involving above two points for basis set construction is a nontrivial task. To address this matter several strategies are used. These strategies generally involve selection of correct basis set and the treatment of electron-ion interaction. The choice of basis set are broadly classified into three groups, (a) Linear Combination of Atomic Orbitals (LCAO), (b) Linearised Augmented Plane Waves, and (c) Plane Wave basis set in combination with pseudo potentials. LCAO have been most preferred choice to quantum chemists. The wave functions in these methods are represented by a few atomic like orbitals in the region near atoms, and bonding of atoms are described by the overlapping tails.

Plane Wave basis set is often used with pseudo potential method to describe electron-ion interaction. Plane wave basis sets offer following advantages: (i) Ease of convergence test with respect to the completeness of basis set by extending the cut-off energy, (i.e. the highest kinetic energy in the PW basis). (ii) It is easy to switch from real-space representation to momentum-space via Fast Fourier Transform where the kinetic energy T is diagonal. (iii) Force on the atoms and stresses on the unit cell may be calculated directly via the Hellmann-Feynman theorem, without applying corrections for the site-dependence of the basis set. In order to achieve convergence with a manageable size of basis set sometimes the strong ion-electrons are replaced by a sufficiently weak pseudo potential.

Pseudo potential assumes the core electrons to be chemically inert and treats it to be frozen. This reduces the number of wave functions to a great extent. This leads to a major reduction in the number of wave functions. Further, in order to achieve an acceptable convergence of plane-wave basis set, the nodal character of valence orbitals has to be eliminated. Using a pseudo potential to describe ion-electron interaction removes this nodal character. However, it raises the question of the accuracy and transferability of pseudo potential resulting in the necessity to linearize the valence-core exchange-correlation interactions. These problems can be solved within the projector-augmented wave (PAW) method.[82] PAW method was originally introduced by Bloch.[83] PAW method provides benefits of both pseudo potential method as well as full-potential linearized augmented-plane wave (FLAPW) method, that is efficiency and accuracy. PAW method takes in to account the nodal feature of the valence orbitals ensuring the orthogonality between valence and core wave functions. The basic concept of PAW method is described briefly below,

The all-electron (AE) valence wave functions Ψ_n^{AE} are reconstructed from the pseudo (PS) wave function using a linear transformation.

$$|\psi_n^{AE}\rangle = |\psi_n^{PS}\rangle + \sum_i(\varphi_i^{AE}\rangle - |\varphi_i^{PS}\rangle)\langle p_i^{PS}|\psi_n^{PS}\rangle \qquad (2.31)$$

The pseudo-wave functions Ψ_n^{PS} (*n* is the band index) are the variational quantities and are expanded in plane waves.

2.7.3 Iterative schemes for calculating the Kohn–Sham ground state

The higher requirement of number of plane waves (NPW) in a plane wave basis set methods to achieve convergence is remedied by two points: (i) The efficiency of The action of Hamiltonian onto the trail wave function can be evaluated very efficiently. (ii) Modern iterative algorithms for the calculation of the Kohn-Sham ground state avoids the explicit calculation, storage and diagonalization of the NPWxNPW Hamiltonian. These methods fall into two categories:

1) Direct methods based on the minimization of the Kohn-Sham total energy functional either using the Car-Parrinello approach[84] based on a pseudo Newtonian equation of

motion for the electronic degrees of freedom or by a conjugate gradient minimization of the total energy.[85,86]

2) Iterative methods for a sequential updating the occupied and some empty eigenstates, in conjunction with an iterative improvement of the charge-density or the potential (mixing) in a self-consistency cycle.

Recent development has showed that direct methods perform as good as self-consistent methods for semiconductors and insulators while self-consistent methods outperform direct methods in case of metallic systems.[87,88] VASP incorporates many different approaches for the iterative calculation of the lowest Kohn-Sham eigenstates. These approaches are; (i) the blocked Davidson scheme[89], (ii) the sequential conjugate-gradient (CG) algorithm proposed by Teter et al.[85] for the minimization of the total energy and adapted by Bylander et al.[90] for the iterative diagonalization of the Hamiltonian, and (iii) a variant of the minimization of the norm of the residual vector to each eigenstate combined with a direct inversion in the iterative subspace (RMM-DIIS).[91,92]

Efficiency of any iterative approach is based mainly on one criterion that is the number of operations scaling with a higher power of number of plane waves is kept at a minimum.

2.7.4 Partial Occupancy and finite temperature methods

VASP uses different methods to treat partial occupancy. Using partial occupancy one can decrease the number of k-points necessary to calculate an accurate band-structure energy. To calculate accurate band structure energy the integral over the filled parts of bands is evaluated.

$$\sum_n \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \varepsilon_{n\boldsymbol{k}} \Theta(\varepsilon_{n\boldsymbol{k}} - \mu) d\mathbf{k} \qquad (2.32)$$

where $\Theta(\mathrm{x})$is the Dirac step function This integral needs to be evaluated using discret number of k-points due to finite computer resources. [93–95]

$$\frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \rightarrow \sum_{\boldsymbol{k}} w_{\boldsymbol{k}}$$

Keeping the step function we get a sum,

$$\sum_k w_k \, \varepsilon_{nk} \Theta(\varepsilon_{nk} - \mu) \qquad (2.33)$$

The convergence of above integral is exceedingly slow with the number of k-points included. The reason for this slow convergence is the fact that the occupancy jump from 1 to 0 at Fermi-level.

For the case of semi-conductors and insulators the band is completely filled and the integral can be calculated accurately using a low number of k-points. For metals the trick is to use a smooth function f($\{\varepsilon_{nk}\}$) instead of a step function $\Theta(\varepsilon_{nk} - \mu)$. This results in much faster convergence without compromising on the accuracy of the sum. There are several methods for treating this problem. VASP uses mainly two approaches: (i) Linear tetrahedron method. (ii) Finite temperature approaches- smearing methods.

(i) Linear tetrahedron method

The basic idea of linear tetrahedron method is to interpolate the term ε_{nk} linearly between two k-points. The revised and efficient method to give effective weights f($\{\varepsilon_{nk}\}$) for each band and k-point is given by Blöchl.[96] Blöchl's corrected method also derives a correction formula to remove the quadratic error inherent in the linear tetrahedron method (linear tetrahedron method with Blöchl corrections). The drawback of this method is that it is not variational with respect to the partial occupancies if the correction terms are included. Therefore, calculated forces might be wrong by a few percent. For accurate forces calculation finite temperature method is used.

ii) Finite Temperature Methods

In finite temperature method the step function is replaced by a smooth function such as Fermi-Dirac function[97]

$$f\left(\frac{\varepsilon-\mu}{\sigma}\right) = \frac{1}{exp\left(\frac{\varepsilon-\mu}{\sigma}\right)+1} \qquad (2.34)$$

or Gauss like function.[98]

$$f\left(\frac{\varepsilon-\mu}{\sigma}\right) = \frac{1}{2}\left(1 - erf\left[\frac{\varepsilon-\mu}{\sigma}\right]\right) \qquad (2.35)$$

Nevertheless, total energy is still not variational (or minimal) in this case. It is necessary to replace the total energy by some generalized free energy.

$$F = E - \sum_{nk} w_k \sigma S(f_{nk}) \tag{2.36}$$

The calculated forces are then the derivative of free energy F. According to Fermi-Dirac statistics the free energy might be interpreted as the free energy of the electrons at some finite temperature $\sigma = k_B T$, in case of Gaussian smearing accurate extrapolation for $\sigma \rightarrow 0$ from result at finite σ is obtained using the formula:

$$E(\sigma \rightarrow 0) = E_0 = \frac{1}{2}(F + E) \tag{2.37}$$

In this way a physical quantity from finite temperature calculation is obtained. Finite temperature methods are used to get faster convergence with respect to number of k-points.

2.8 Optical Properties using VASP

The experimentally measurable optical properties such as reflectivity, transmission and absorption are used to determine dielectric function and optical conductivity. The other way round, theoretical calculation of optical constants from the frequency dependent dielectric constant is useful to predict and design nano devices in the experimental set up. At microscopic level, the complex dielectric function is closely connected with the band structure. Linear optical properties of solids can be understood by quantum mechanical treatment of solids. In such treatment contributions from various electronic bands transitions are considered. The transitions that take place from occupied states in a band to unoccupied states in the same band are called intra band processes. Such transition naturally requires intersection of the Fermi energy such that the transition involves both occupied and unoccupied states. These transitions are important for metals and semimetals. Intra-band transitions are explained using the classical Drude theory or the quantum mechanical density matrix technique. The transitions that correspond to the absorption of electromagnetic radiation by an electron in an occupied state below Fermi level and gets excited to an unoccupied state in a higher band is called inter-band transitions. The inter band transition is a quantum mechanical process and hence can be explained in the framework of quantum mechanics. VASP calculates the frequency dependent dielectric matrix after determination of the electronic ground state. The imaginary part of frequency dependent dielectric function is derived in PAW methodology[99] by summing over conduction bands. The expression for which is as follows:

$$\varepsilon^{2}_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega}\frac{1}{q^2} \lim_{q\to 0} \textstyle\sum_{c,v,k} 2\omega_k \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \times$$

$$\langle u_{ck+e_{\propto}q} | u_{vk} \rangle \langle u_{ck+e_{\propto}q} | u_{vk} \rangle^{*} \qquad (2.38)$$

where the indices *c* and *v* refers to conduction and valence band states respectively, and u_{ck} is the cell periodic part of the orbitals at the k-point . The transitions refereed in above equation corresponds to occupied to unoccupied states within the first Brillouin zone, the wave vectors are fixed k. From imaginary part of dielectric function real part of dielectric function is calculated using Kramers-Kroning relation as:

$$\varepsilon^{1}_{\alpha\beta}(\omega) = 1 + \frac{2}{\pi} P \int_{0}^{\infty} \frac{\varepsilon^{(2)}_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta}\, d\omega' \qquad (2.39)$$

where P denotes principle value. Since VASP does not incorporate the intra band transition important for metals and semi metals the intra band contribution term can be derived using classical dispersion theory. The intra band contribution term to real and imaginary part of dielectric function is obtained as

$$\varepsilon_1(\omega) = 1 + \frac{4\pi n e^2}{m}\left[\frac{\omega_0^2 - \omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2}\right] \qquad (2.40)$$

$$\varepsilon_2(\omega) = \frac{4\pi n e^2}{m}\left[\frac{\gamma}{\omega\left(\omega^2 + \gamma^2\right)}\right] \qquad (2.41)$$

where γ is referred to damping constant in the classical theory. In terms of quantum mechanical treatment γ can be taken as 1/τ , τ being the mean collision time that amounts to damping.

After obtaining frequency dependent real and imaginary part of dielectric function, Optical property aspects such as reflectivity, absorption coefficient and Electron Energy Loss Spectra (EELS) can be calculated from frequency dependent complex dielectric function, ε(ω)= $\varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The complex refractive index, Ñ(ω) = n(ω)+ ik(ω) of a material is related to ε(ω);

$$n(\omega) = \left(\frac{\sqrt{\varepsilon_1^2+\varepsilon_2^2}+\varepsilon_1}{2}\right)^{\frac{1}{2}} \tag{2.42}$$

$$k(\omega) = \left(\frac{\sqrt{\varepsilon_1^2+\varepsilon_2^2}-\varepsilon_1}{2}\right)^{1/2} \tag{2.43}$$

optical properties such as reflectivity (R), energy loss spectra (EL) and absorption coefficient (α) can be calculated using following equations.

$$R(\omega) = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \tag{2.44}$$

$$EL(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)} \tag{2.45}$$

$$\alpha(\omega) = \frac{2k\omega}{c\hbar} \tag{2.46}$$