CHAPTER 2

THEORETICAL APPROACH AND COMPUTATIONAL METHODOLOGY

2.1 Introduction to Density Functional Theory

In this chapter we discuss the brief formulation of Density Functional Theory (DFT)[1] to predict the ground state/fundamental properties of materials. DFT has been recognized as one of the most frequently used successful technique and a quantum mechanical tool for studying and predicting the properties of periodic bulk solids and material interfaces.[2,3] Also, DFT has gained a lot of attention due to its prediction power as in direct research/experimental investigation it is quite difficult due to the associated expenditure of chemicals and technical difficulties like the study of materials under extreme pressures and temperatures or in case of the study of the toxic substances or nuclear radiation associated studies, etc.[4,5] DFT is superior due to the quantum mechanical approach as compared to classical approach; this is because the classical approach fails to describe the interaction of quantum systems such as electrons in a periodic system, electron-phonon interactions, quasi-particle dispersions, non-equilibrium states, etc. The quantum approach to investigate the interaction and behaviour of electron in materials deals with solving the many body time independent Schrödinger equation. But, the problem with this method is that we have to consider 3N degrees of freedom of the many-body electronic wave-function. This can be modified by representing the many-body electronic wave-function in terms of the electron density. This approximation drastically reduces the degrees of freedom of the many-body wave-function from 3N to just three (3), making the calculations computationally quicker and easier.

During 1960's combined efforts by, Hohenberg, Kohn and Sham led to the development of the *first-principles* method based on DFT investigating the ground state of a quantum system.[6,7] Ever since then, the DFT has revolutionized the material science through its prediction power of material properties. This is achieved computationally by solving the self-consistent field-based approach using the Schrödinger-like equation.

2.2 The Schrödinger Equation and Many-Body Problem

The description of structure and dynamics of many-electron system particularly for obtaining the solution of the Schrödinger equation was considered as a major challenge for theoretical physicists prior to the development of DFT. To understand the behaviour of a system governed under the quantum mechanical rule-set, we need to determine the wave-function (r) of the quantum particle at every point r $= xu_x + yu_y + zu_z$ in the region of interest, and this can be achieved by solving the Schrödinger equation.[8] The Schrödinger equation for an electron moving in a weak periodic potential could be solved under the nearly free-electron approximation to obtain energy eigenvalues as a function of the momentum $\boldsymbol{k}$, which is known as the electronic band structure.[9] The time-independent Schrödinger equation is represented by:

$$H\psi(r) = E\psi(r) \tag{2.1}$$

$$(kinetic\ energy\ +\ potential\ energy)\psi(r) = E\psi(r)$$

Where, H is the Hamiltonian operator which is the sum of the kinetic and potential energy, E is the energy eigenvalue for the stationary state described by the wave-function $\psi(r)$. Therefore, for an electron in a potential energy landscape V(r), the L.H.S. of the above equation can be re-written as;

$$H\psi(r) = \left\{\frac{P^2}{2m} + V(r)\right\}\psi(r) = E\psi(r) \tag{2.2}$$

Here, m is the mass of electron and the momentum operator P, which can be expressed as follows:

$$P = -i\hbar\nabla \tag{2.3}$$

When we wish to study the many-particle systems such as, collection of electrons and ionic nuclei together, we need to introduce a so called *many-body* wave-function, Ψ, which depends on the positions of each electron and each nucleus in the system. In the case of N electrons with position coordinates $r_1, r_2, \ldots, r_N$ and M nuclei with position coordinates $R_1, R_2, \ldots, R_M$, we can represent the many-body wave-function as Ψ $(r_1, r_2, \ldots, r_N, R_1, R_2, \ldots, R_M)$. Moreover, the solution of such many body ground states is quite difficult due to the mathematical complexity. This can be reduced to the solution for the ground state density distribution given by a single particle Schrödinger equation using the approximation which is discussed in the proceeding section. Apart from the kinetic energy term (T), the Hamiltonian in the Schrödinger equation also includes the potential energy term (V), also addressed as the effective potential arising from the Coulomb interaction between the electrons V_{ee}, electrons and the nuclei V_{eN} and between the nuclei V_{NN}. The Hamiltonian is then represented as:

$$H = T_N + T_e + V_{ee} + V_{eN} + V_{NN} \tag{2.4}$$

Here, T_N and T_e are the operators of kinetic energy for the nuclei and electrons, respectively. It is very difficult to solve this problem exactly, hence, one must find the acceptable approximation.

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

$$\left. + \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\bar{r}_i - \bar{r}_j|} - \sum_i \sum_l \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l}{|\bar{r}_i - \bar{R}_l|} \right]\Psi = E\Psi \qquad (2.5)$$

Where, *i* and *l* are indices running for electron and nuclei, m_e and M stand for the mass of electron and nuclei, Z_l and $Z_{l'}$ define the charges on different nuclei, $\bar{r}_i - \bar{r}_j$, $\bar{R}_l - \bar{R}_l'$ and $\bar{r}_i - \bar{R}_l$ represent the distances between electron-electron, nuclei-nuclei and electron-nuclei, respectively. The solution of the equation (2.5) is the eigen state and energy eigen value which is the total-energy of the system. Once the total-energy of the system is determined, the ground state properties of the material at equilibrium condition can be obtained. The Hamiltonian in equation (2.4) consists of atomic mass, mass of nuclei, atomic number and charge of electron. This method is known as the *first-principles* calculation as the solution of equation (2.5) does not require any adjustable parameter. In reality, the equation (2.1) is easily solvable for smaller system such as hydrogen and helium but for larger systems containing many electrons is difficult to solve, therefore, several approximations to this theory were proposed which are discussed in detail in the proceeding sections.

2.3 A Journey from Wave-Function to Density

2.3.1 The Born-Oppenheimer Approximation

The first approximation was made by Born and Oppenheimer[10] for the many-body time-independent Schrödinger equation wherein, the kinetic energy of nucleus is neglected since they are much heavier than the electrons thereby reducing the average kinetic energy of the nuclei much lower than the electronic one. This approximation led to the decoupling of electronic and ionic motions. Therefore, the first term of equation (2.4) disappears under this approximation and the last term that is potential of nuclei becomes constant. The major contributing terms in equation (2.4) are the kinetic energy of the electrons (T_e) and, the potential energy due to electron-electron and electron-nuclei interactions; while the potential generated due to the nuclei-nuclei interaction is treated as a constant. Hence, equation (2.4) becomes[11]:

$$H = T_e + V_{ee} + V_{eN} + \text{Constant} \tag{2.6}$$

The modified Hamiltonian operator can be expressed as the sum of three terms; the kinetic energy of electrons, the electron-electron interaction and the interaction of electrons with the nuclei treated as an external potential (V_{ext}). Hence, the Equation (2.6) can be re-written as:

$$H = T_e + V_{ee} + V_{ext} \tag{2.7}$$

Here, the electron kinetic energy operator for the electrons is $T_e = \frac{-\hbar^2}{2m_e}\sum_i \nabla_i^2$, and the potential due to electron-electron interactions and atomic nuclei and electron are $\hat{V}_{ee} = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}$ and $\hat{V}_{ext} = \sum_{i,I} V_I(|r_i - R_I|)$, respectively.

Here, r_i represents the coordinates of electron i and V is the external potential. The average total-energy for a state specified by a particular Ψ, not necessarily one of the eigen functions of the Equation (2.1), is the expectation value of H, that is

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle + \int V_{ext}(r) n(r) d^3 r \tag{2.8}$$

The notation $\langle \Psi \rangle$ emphasizes the fact that the energy is a *functional* of the wave-function. The external potential justifies the effect of nucleus over electrons which are relatively fixed, this leads to the independent electron approximation.

2.3.2 Independent Electron Approximation

Independent electron approximation is bifurcated into two basic classical approaches that is, (i) Hartree and, (ii) Hartree-Fock (HF) methods.[12]

2.3.2.1 Hartree Approximation

Simplest way of writing the many body wave-function Ψ as a product of single particle functions suggested by Hartree is presented below:

$$\Psi(\boldsymbol{r_1},\boldsymbol{r_2},r_3\ldots,\boldsymbol{rn}) = \Psi(r_1)\ \Psi(r_1)\ \Psi(r_3)\ldots\ \Psi(\boldsymbol{rn}) \tag{2.9}$$

These single particle wave-functions $\Psi_i(r_i)$ satisfy the single particle Schrödinger equation together with potential term due to the average field of the other electrons.

$$\left(\frac{-\hbar^2}{2m_e}\sum_i \nabla_i^2 + \hat{V}_{ext} + \Phi_i\right)\Psi_i(\boldsymbol{r_i}) = \epsilon_i \Psi_i(\boldsymbol{r_i}) \tag{2.10}$$

Where, the Coulomb potential is given by the Poisson's equation[6]

$$\nabla^2 \Phi_i = 4\pi e^2 \sum_{\substack{j=1 \\ i\neq j}}^{N} \left|\Psi_j\right|^2 \tag{2.11}$$

and, V_{ext} is the potential due to the nuclei-nuclei interaction.

2.3.2.2 Hartree-Fock Approximation

Since electrons are Fermions, it was necessary to address them under the Fermi-Dirac statistics. This is incorporated by replacing the product wave-function by a single determinantal function.[13,14] As the Fermions follow the Pauli's exclusion principle, the asymmetric nature of the wave-function and the effect of correlation for electrons could not be ignored. Hence, Hatree and Fock considered the asymmetric wave-function given by the following equation:

$$\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_i},\sigma_i,\ \dots,\overline{r_j},\sigma_j,\dots) = -\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_i},\sigma_i,\ \dots,\overline{r_j},\sigma_j,\dots) \qquad (2.12)$$

In the HF approximation, minimization of equation (2.10) is done by considering the above asymmetric wave-function in the determinant form known as Slater's determinant.[15]

$$\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_N},\sigma_N) = \begin{vmatrix} \Psi_1(\overline{r_1},\sigma_1) & \Psi_1(\overline{r_2},\sigma_2)\dots & \Psi_1(\overline{r_N},\sigma_N) \\ \Psi_2(\overline{r_2},\sigma_2) & \Psi_2(\overline{r_2},\sigma_2)\dots & \Psi_2(\overline{r_N},\sigma_N) \\ \Psi_N(\overline{r_N},\sigma_N) & \Psi_N(\overline{r_N},\sigma_N)\dots & \Psi_N(\overline{r_N},\sigma_N) \end{vmatrix} \qquad (2.13)$$

The determinant of the wave-function can hence be written as,

$$\Psi_{HF} = \frac{1}{N!}\textstyle\sum_P (-1)^p P\ \Psi_1(x_1)\ \Psi_2(x_2)\dots\ \Psi_N(x_N) \qquad (2.14)$$

where, $x = (\bar{r},\sigma)$, P is the permutation number and p represent the number of interchanges for making up this permutation. Substituting the Slater determinant of many-body wave-function in equation (2.10) gives expectation value of Hamiltonian as,

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

(2.15)

where the last term is the consequence of Pauli's exclusion principle known as exchange energy. Minimization of equation (2.15) leads to Hartree-Fock equation given below:

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \nabla^2 - V_l(\vec{r}) + V_H(\vec{r})\right]\Psi_i(\vec{r}) - \frac{1}{2}\sum_{i,j}\sum_{j\neq i}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{\Psi_j{}^*(\vec{r}')\ \Psi_i(\vec{r}')\ \Psi_j(\vec{r})}{|\vec{r}-\vec{r}'|}d^3rd^3r'$$
$$= \ \in_i \Psi_i(\vec{r}) \qquad (2.16)$$

This is an improvement over Hartree method due to the involvement of exchange energy considering the asymmetric nature of the wave-function. However, total-energy $\in_i$ involves minimization over sum of N particle Slater's determinant (Equation (2.12)). This type of determinant is quite large; hence this approximation is computationally quite costly for large as well as small systems.

2.4 Thomas-Fermi Theory

The first approach for solving many body systems to calculate ground state energy using density-based theory originated from the Thomas Fermi (TF) theory.[16,17] In 1927, Thomas and Fermi proposed that the electron density can be used as basic variable instead of single particle wave-function or orbitals and the total-energy of the system can be written as a functional of electron density. The kinetic energy of N interacting electrons is given by the following equation which is written in terms of the electron density n($\bar{r}$) as:

$$T_{TF} = C_k \int n(\bar{r})^{\frac{5}{3}} d^3r \tag{2.22}$$

The total-energy can then be written as a functional of electron density by adding the kinetic energy, electrostatic energy and external potential as a functional of electron density

$$E = T_{TF} + \int V_{IE}(\bar{r})\, n(\bar{r}) d^3r + \frac{1}{2} \iint \frac{e^2}{4\pi\varepsilon_0} \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r}-\vec{r}'|} d^3r d^3r' \tag{2.23}$$

Here, E is the total-energy of the system. The total number of particles can be obtained by the minimization of above energy with a constraint recognized by Lagrange multiplier as:

$$\frac{5}{3} C_k n(\bar{r})^{\frac{2}{3}} + \int \frac{e^2}{4\pi\varepsilon_0} \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' = \mu; \quad \mu = \frac{5}{3} C_k n(\bar{r})^{\frac{2}{3}} + V(\bar{r}) \tag{2.24}$$

The equation 2.23 can be solved self-consistently. The Thomas-Fermi theory does not include the exchange energy. Dirac extended this approximation via including the exchange interaction and the correlation functional.[18,19] However, the shell structure and behavior of the atoms of complex systems were not considered in Thomas-Fermi theory. This was addressed in the approximation by Hohenberg and Kohn.

2.5 Hohenberg and Kohn Theorem

Hohenberg and Kohn established the connection between the electron density and the many body Schrödinger equation. In 1964, they introduced two theorems which is considered the initiative of density functional theory and developed the proof for the following two theorems.[20]

Theorem I: *"The ground state density $n(r)$ of a bound system of interacting electrons in some external potential $V_{ext}(r)$ determines this potential uniquely".*[20,21]

The above statement states that the electron density uniquely determines the Hamiltonian operator (Equation (2.4)) as the ground state is a unique functional of density. The Hamiltonian can be computed from the density simply by integration over the entire space which is specified by the external potential and the total number of electrons N. In a nut-shell, the charge density and the Hamiltonian operator could be uniquely determined corresponding to the wave-functions Ψ (for all states).

To prove this theorem,[20] we will consider two different external potentials $V_{ext}^{(1)}(r)$ and $V_{ext}^{(2)}(r)$ which correspond to different ground state wave-functions, $\Psi^{(1)}$ and $\Psi^{(2)}$ both of which have the same ground state density $n(r)$. Therefore, these two external potentials lead to two different Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$. This means that $\Psi^{(2)}$ is not the ground state of $\hat{H}^{(1)}$; hence, we have,

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle \tag{2.25}$$

The last term can be re-written as:

$$\langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle \tag{2.26}$$

$$= E^{(2)} + \int \left[V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r) \right] n(r) d^3r \tag{2.27}$$

From equations (2.25) and (2.27), we have

$$E^{(1)} < E^{(2)} + \int \left[V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r) \right] n(r) d^3r \tag{2.28}$$

The $\hat{H}^{(1)}$ or $\hat{H}^{(2)}$ are just the notations, therefore, we can swap the labels 1 and 2 and we will have the following relation:

$$E^{(2)} < E^{(1)} + \int \left[V_{ext}^{(2)}(r) - V_{ext}^{(1)}(r) \right] n(r) d^3r \tag{2.29}$$

Then adding equation (2.28) and (2.29) produces contradiction,

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$$

The assumption that the two different external potentials $V_{ext}^{(1)}(r)$ and $V_{ext}^{(2)}(r)$ which actually correspond to the different ground states of wave-functions $\Psi^{(1)}$ and $\Psi^{(2)}$, both have the same ground state density $n(r)$; which is not possible. This means that there can only be one external potential $V_{ext}(r)$ that can produce the corresponding ground state density $n(r)$, and conversely, that the ground state density $n(r)$ uniquely determines the external potential $V_{ext}(r)$.

The Hohenberg-Kohn theorem can be generalized, as the nature of the quantum particles; i.e., the Fermions or Bosons and interacting or non-interacting are not considered.

Theorem II: *"The functional that delivers the ground state energy of the system, describes the lowest energy if and only if the input density is the true ground state density".*

This theorem is another form of the *variational principle* in terms of the density instead of wave-function. It is implied that[20]

$$E_0[n_0] = min_n\, E\,[n] = min_n\, T\,[n] + E_{ee}[n] + E_{e_N}[n] \qquad (2.30)$$

and

$$E_{HK}[n] = T[n] + E[n] + \int V_{ext}(r)n(r)d^3r_{int} \qquad (2.31)$$

where ($\int V_{ext}(r)n(r)d^3r$) is system dependent while other part is universally constant that can be define H-K functional $F_{HK}[n]$) as:

$$F_{HK}[n] = T[n] + E[n]_{int} \qquad (2.32)$$

Substituting equation (2.32) in equation (2.31) becomes

$$E_{HK}[n] = F_{HK}[n] + \int V_{ext}(r)n(r)d^3r \qquad (2.33)$$

If $F_{HK}[n]$ were known exactly, then we can have the exact solution of the Schrödinger equation without need of such approximations.

Consider a system with the ground state density $n^{(1)}(r)$ corresponding to the external potential $V_{ext}^{(1)}(r)$. The expectation value of the Hamiltonian with the unique ground state and wave-function $\Psi^{(1)}$ is equal to the H-K functional have the form given below:

$$E^{(1)} = E_{HK}\left[n^{(1)}\right] = \left\langle \Psi^{(1)} \middle| \hat{H}^{(1)} \middle| \Psi^{(1)} \right\rangle \tag{2.34}$$

Therefore, the density, $n^{(2)}(r)$ corresponds to a different wave-function $\Psi^{(2\ )}$ having energy $E^{(2)}$ of this state is always greater than ground state energy $E^{(1)}$:

$$E^{(1)} = \left\langle \Psi^{(1)} \middle| \hat{H}^{(1)} \middle| \Psi^{(1)} \right\rangle < \left\langle \Psi^{(2)} \middle| \hat{H}^{(1)} \middle| \Psi^{(2)} \right\rangle = E^{(2)} \tag{2.35}$$

The H-K functional evaluated the correct ground state density $n_0(r)$ which is indeed lower than the value of this expression for any other density $n(r)$ given by equation (2.33). Therefore, density based *variational principle* is also known as the second Hohenberg-Kohn theorem.

2.6 The Kohn-Sham Equation

Hohenberg and Kohn[20] theorem play unique role for the foundation of density functional theory.[22] The Hohenberg-Kohn theorems divides the energy into two parts, one is the system dependent that is $\int V_{ext}(r)n(r)d^3r$ and other is the unknown functional $F_{HK}[n]$. Major problem is to find the unknown functional $F_{HK}[n]$ to have exact solutions. Kohn and Sham devised a better way to handle the unknown $F_{HK}[n]$. The Kohn-Sham approach considered auxiliary system of non-interacting quasiparticles that have the same density as the true interacting problem, i.e., there exists some single particle potential $V_{eff}(r)$ which when applied to non-interacting electrons, yields the same ground state density as the fully interacting problem.

The total energy for the interacting system can be written as:[20]

$$E[n] = T[n] + V[n] + \int V_{ext}(r)n(r)d^3r \tag{2.36}$$

where T[n] is the interacting kinetic energy functional and V[n] is the Coulomb potential functional for the interacting system, and $V_{ext}(r)$ is the external potential.

Here, we have assumed the non-interacting system while the interacting system have the same density. Therefore, we can add and subtract the non-interacting kinetic energy ($T_s[n]$) and the Hartree energy ($E_H[n]$) to (2.36) respectively which is give as:

$$E_{KS}[n] = T_s[n] + E_H[n] + \{T[n] - T_s[n] + V[n] - E_H[n]\} + \int V_{ext}(r)n(r)d^3r \tag{2.38}$$

$$E_{KS}[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(r)n(r)d^3r \tag{2.39}$$

The exchange-correlation energy is defined as:

$$E_{xc}[n] = T[n] - T_s[n] + V[n] - E_H[n] \tag{2.40}$$

The exchange-correlation energy ($E_{xc}[n]$) is also universal functional as it depend on the external potential. The kinetic contribution to the correlation and the Hartree-Fock exchange and the electrostatic contribution to the correlation are given by ($T[n]-T_s[n]$) and $V[n]-E_H[n]$ respectively.

The Hartree energy $E_H[n]$ is the classical electrostatic energy for a charge distribution $n(r)$ given as:

$$E_H[n] = \frac{1}{2}\iint \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' \tag{2.41}$$

The non-interacting kinetic energy T_s is then evaluated from the single particle wave-functions,

$$T_s[n] = -\frac{1}{2}\sum_i^N \langle \psi_i | \nabla^2 | \psi_i \rangle \tag{2.42}$$

and the density $n(r)$ and particle count N of the non-interacting system can be straightforwardly calculated as:

$$n(r) = \sum_i^N |\psi_i(r)|^2 \tag{2.43}$$

with

$$N = \int n(r) d^3 r \tag{2.44}$$

The minimization of the ground state can with respect to density *n(r)* of the effective potential *V_{eff}(r)* is the solution of KS auxiliary system is given below.

$$\frac{\delta E_{KS}}{\delta \psi_i^*(r)} = \frac{\delta T_S[n]}{\delta \psi_i^*(r)} + \left[\frac{\delta E_{ext}[n]}{\delta n(r)} + \frac{\delta E_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)}\right] \frac{\delta n(r)}{\delta \Psi_i^*(r)} = 0 \tag{2.45}$$

Where, $T_s[n]$ is explicitly expressed as a functional of the orbital's while all other terms are functionals of the density. We can Schrödinger like equations after substituting equations (2.26) and (2.27) in to equation (2.29)

$$(H_{KS} - \varepsilon_i)\psi_i(r) = 0 \tag{2.46}$$

Where, $\frac{\delta T_s[n]}{\delta \psi_i^*(r)} = -\frac{1}{2}\nabla^2 \psi_i(r)$, $\frac{\delta n(r)}{\delta \psi_i^*(r)} = \psi_i(r)$, the ε_i are the eigen values and H_{KS} is the effective Hamiltonian.

The effective Hamiltonian is given by:

$$H_{KS}(r) = -\frac{1}{2}\nabla^2 + V_{KS}(r) \tag{2.47}$$

Where, $V_{KS}[r] = V_{ext}[r] + V_H[r] + V_{xc}[r]$

The Kohn-Sham equations is given equation (2.46) resulting to total energy E_{KS} and density n(r) given by (2.41) and (2.43) which is independent of any approximation to the functional $E_{xc}[n]$. If the exact functional $E_{xc}[n]$ were known then we can have the exact ground state density and energy for the interacting system.

2.7 Exchange and Correlation Functionals

In order to solve the Kohn-Sham equation, we need to specify the exchange-correlation function Exc[n] and defining it seems to be difficult to get from Hohenberg theorem.[2] To have derivation of this functional, firstly we have to considered electron density at all place to be constant that is n(r) = constant as in case of uniform gas. This approximation was developed by Kohn-Sham found to be very successful in calculating the electronic structure of atoms, molecules, and solids.[22] Afterwards, the variety of approximations for the exchange-correlation functional has been developed for different case validate with experimental data. Among them, the most widely used ones in generals are the local density approximation (LDA) and the generalized gradient approximation (GGA).

The exchange correlation functionals is define as:

$$E_{xc} = \int n(r)\, V_x(r) F_{xc}(\ldots\ldots)d^3r \tag{2.48}$$

Where, F_{xc} is the enhancement and its parameters depend on whether the functional is LDA or GGA.

2.7.1 Local Density Approximation

The local density approximation (LDA) is the simplest approximation for Exc which assumed that the electron density n(r) varies very slowly in space [23] so that each small volume-element of the system leads to locally inform in terms of homogenous electron gas at the same density. The LDA for exchange and correlation energy is defined as:

$$E_{xc}^{LDA}[n] = \int n(r)\varepsilon_{xc}^{\mathrm{hom}}(n)d^3r \tag{2.49}$$

where, ε_{xc}^{hom}(n) is the exchange–correlation energy per particle of a uniform electron gas of density and it is sum of correlation functional and an exchange functional:

$$\varepsilon_{xc}^{\text{hom}}(n) = \varepsilon_{x}^{\text{hom}}(n) + \varepsilon_{c}^{\text{hom}}(n) \tag{2.50}$$

The exchange energy per electron for homogeneous system is given as:

$$\varepsilon_{x}^{\text{hom}}(n) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n(r)^{1/3} \tag{2.51}$$

$$n = \left(\frac{4\pi}{3} r_s^3\right)^{-1} \tag{2.52}$$

Substituting equations (2.51) and (2.52) in equation (2.49) we have:

$$E_{xc}^{LDA}[n] = -\frac{3}{4\pi}\left(3\pi^2\right)^{1/3} \int n^{4/3}(r) d^3 r \tag{2.53}$$

However, this approximation cannot provide estimation to the long-ranged exchange-correlation interaction that is van der Waals (vdW) interaction. To overcome the issue of this interaction, we have to include the non-local exchange-correlation term[20] that is disused in dispersion correction. There are many draw backs of LDA such as it underestimates band gaps in semiconductors and insulators and over-binds molecules/solids.[23]

2.7.2 Generalized Gradient Approximation

There is need of approximation beyond LDA to higher accuracy, therefore instead of considering slow varying electron density in space, the exchange correlation function is considered as functional of density as well as gradient which satisfies the sum rule [23]. The GGA for exchange and correlation energy is defined as:

$$E_{xc}^{GGA}[n^{\uparrow},n^{\downarrow}] = \int n(r)\varepsilon_{xc}\left(n^{\uparrow},n^{\downarrow},\left|\nabla n^{\uparrow}\right|,\left|\nabla n^{\downarrow}\right|\right)d^{3}r \tag{2.54}$$

$$E_{xc}^{GGA}[n^{\uparrow},n^{\downarrow}] = \int n(r)\varepsilon_{x}^{\mathrm{hom}}(n)F_{xc}\left(n^{\uparrow},n^{\downarrow},\left|\nabla n^{\uparrow}\right|,\left|\nabla n^{\downarrow}\right|\right)d^{3}r \tag{2.55}$$

where $F_{xc}$is dimensionless and $\varepsilon_{x}^{hom(n)}$is the exchange energy of the unpolarized gas. The generalized gradient approximation has attracted much attention it overcomes the drawback of LDA such in calculating cohesive energies of solids/molecules[24] and gives more accurate equilibrium lattice parameters.[25,26] The Most frequently used GGA functionals are Becke,[27] Perdew and Wang (PW)[28] and Perdew, Burke and Enzerhof (PBE).[29]

2.8 Density Functional Perturbation Theory

In solid state physics, the study of phonon is essential as the phonons play an important role in many of the physical properties of solids, such as the thermal conductivity and the electrical conductivity. Density functional perturbation theory (DFPT) is a powerful theoretical technique within density functional theory framework to calculate such properties.[30–32] In this method, linear response is applied to the Khon-Sham equation to observe the change in solution of electron charge density due to small perturbation.[33,34] Therefore, v_{ext}, E, n(r), etc. are subjected to perturbation in DFPT. The external potential v_{ext} depends on some parameter λ is expanded as

$$v_{\lambda ext}(r) = v_{ext} + \lambda\frac{\partial v_{ext(r)}}{\partial\lambda} + \frac{1}{2}\lambda^{2}\frac{\partial^{2}v_{ext}(r)}{\partial\lambda^{2}} + \cdots \tag{2.56}$$

All derivatives are calculated λ =0. Similar expansion is done for charge density and energy functional which is given as:

$$n_{\lambda}(r) = n(r) + \lambda\frac{\partial n(r)}{\partial\lambda} + \frac{1}{2}\lambda^{2}\frac{\partial^{2}n(r)}{\partial\lambda^{2}} + \cdots \tag{2.57}$$

$$E_{\lambda}(r) = E(r) + \lambda \frac{\partial E(r)}{\partial \lambda} + \frac{1}{2}\lambda^2 \frac{\partial^2 E(r)}{\partial \lambda^2} + \cdots \tag{2.58}$$

Where, $\frac{\partial E(r)}{\partial \lambda} = \int n(r) \frac{\partial v_{ext(r)}}{\partial \lambda} dr$

Here, the first-order derivative E does not depend on any derivative of n(r) whereas The second-order derivative energy $\frac{\partial^2 E(r)}{\partial \lambda^2}$ depends on the first-order derivative of the charge density, $\frac{\partial n(r)}{\partial \lambda}$. Therefore, the second order energy $\frac{\partial^2 E(r)}{\partial \lambda^2}$ is used to calculate the dynamical matrix for phonon frequency calculations and Born effective charges. The expression of energy as functional of density is given as:

$$E[\psi] = \min_{\psi^{(1)}} \sum_{i \in occ} \langle \psi_i | T + V_{ext} | \psi_i \rangle + E_{Hxc}[n] \tag{2.59}$$

$$\frac{\partial^2 E(r)}{\partial \lambda^2} = \min_{\psi^{(1)}} \sum_{i \in occ} \left[\left\langle \psi_i^{(1)} \middle| H^{(0)} - \varepsilon_i^{(0)} \middle| \psi^{(1)} \right\rangle + \left\langle \psi_i^{(1)} \middle| v_{ext}^{(1)} \middle| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(0)} \middle| v_{ext}^{(1)} \middle| \psi^{(1)} \right\rangle + \left\langle \psi_i^{(0)} \middle| v_{ext}^{(2)} \middle| \psi_i^{(0)} \right\rangle \right]$$

$$+ \frac{1}{2} \frac{\delta^2{}_{EHxc}}{\delta n(r) \delta n(r')} \bigg| n^{(0)} n^{(1)}(r) n^{(1)}(r') d^3r d^3r'$$

$$+ \int \frac{d}{d\lambda} \frac{\delta E_{Hxc}}{\delta n(r)} \bigg|_{n^{(0)}} n^{(1)}(r) d^3(r) \frac{1}{2} \frac{d^2 E_{Hxc}}{d\lambda^2} \bigg|_{n^{(0)}} \tag{2.60}$$

The second order term of energy is obtained as variational with respect to first order wave-function provided first order wave-functions are orthogonal to the ground state wave-functions

$$\left\langle \psi_i^{(0)} \middle| \psi_j^{(j)} \right\rangle = 0 \tag{2.61}$$

Here, dynamical matrix is Hermitian, therefore its eigenvalues $\omega_j^2(\boldsymbol{q})$ and eigenvectors $\xi_j(\boldsymbol{q})$ are real and orthonormal respectively. The phonon band structure $\omega_j(\boldsymbol{q})$ directly corresponds to density of states that gives the details of phonons in whole Brillouin zone (BZ).[35–40] The information about the whole phonon spectrum can be obtain by scanning of whole Brillouin-zone and it consists of $D_{\alpha\beta}\begin{pmatrix} \boldsymbol{q} \\ kk' \end{pmatrix}$ -matrix diagonalization over the three-dimensional net of wave vector $\boldsymbol{q} = \left(\frac{\boldsymbol{a}^*}{n_1}, \frac{\boldsymbol{b}^*}{n_2}, \frac{\boldsymbol{c}^*}{n_3}\right)$, at n_1, n_2, n_3 = - N,., N. where it includes N_i = (2N + 1) points in Brillouin zone.[40] The phonon density of states (DOS) is determined by summation over all the phonon states and is defined by.[35,40,41]

$$g(\omega) = D'\int_{BZ}\sum_{j}\delta\left(\omega-\omega_j(\boldsymbol{q})\right)dq = D'\int_{BZ}\sum_{jp}\delta\left(\omega-\omega_j(\boldsymbol{q})\right)dq_p \qquad (2.62)$$

Where, D' is a normalization constant such that $\int g(\omega)d\omega = 1$; and g(ω)d*ω* is the fraction of phonons with energies ranging from *ω* to *ω* + d*ω*. The mesh index (‘*p*’) is characterized by ‘***q***’ in the discretized irreducible Brillouin zone, where d$\boldsymbol{q}_p$ provides the weighting factor corresponding to the volume of *p*th mesh in ***q***-space. The contribution of different atoms to phonon density of states (DOS) is known from the partial atomic density of states (PDOS) which provide essentially aids in understanding the atomic level contribution to the total phonon DOS and, can be defined as follows:

$$g(\omega) = D'\sum_{jp}\delta\left(\omega-\omega_j(q)\right)\frac{|\xi_j(q)|^2}{\sum_{jp}|\xi_j(q)|^2} \qquad (2.63)$$

2.9 Dispersion Correction to Density Functional Theory

The incorporation of van der Waals (vdW) interaction is necessary to understand the initial stage of physical absorption and chemical reaction which fails in case of DFT. Also, in case of confined materials, like layered 2D materials[42] or 2D and 1D heterostructures [43–45] it is mandatory to include the long range weak vdW interactions for accurate prediction of diverse properties like binding energy, electronic dispersion, excitonic properties, surface carrier trapping, adsorption energy, etc. As discussed in the earlier section that the approximations LDA and GGA fail to account long-range van der Waals (vdW) interaction,[46–48] thereby suggesting to include the non-local exchange-correlation term in the solution of Khon-Sham equation [18]. The vdW correction to total energy is given by

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} \tag{2.64}$$

Where, E_{DFT-D} is general Kohn Sham energy functional and the empirical vdW dispersion correction to the correlation functional E_{disp} is given by [49]

$$E_{disp} = -s_6 \sum_{i=1}^{(N_{at}-1)} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}) \tag{2.65}$$

where s_6 is global scaling factor which depends on the functionals, N_{at} is the total number of atoms, C_6^{ij} defines the dispersion coefficient for atom pair *ij*, and R_{ij} is interatomic distance. The damping function $f_{dmp}(R_{ij})$ is given by

$$f_{dmp}(R_{ij}) = \frac{1}{1 + e^{-d\left(R_{ij}/R_{0ij}-1\right)}} \tag{2.66}$$

where, R_0 is the sum of atomic vdW radii. C_6^{ij} and R_{0ij} are defined as:

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \tag{2.67}$$

$$R_{0ij} = R_{0i} + R_{0j} \tag{2.68}$$

The results are precisely tested on systems including elements up to xenon and large hydrocarbons with many hydrogen atoms showed.

2.10 Optical Properties under Random Phase Approximation

Apart from the spatial electronic dispersion curve, it is necessary to calculate the optical properties of the material for testing its applicability in the field of optoelectronics. Although, apart from being material specific, the electro-optic transport of any material is found to be approximation dependent.[50] The reports suggest the widely used random phase approximation (RPA) [51,52] almost accounts the relevant parameters affecting the optical properties of the material and thus, is reliable for computing the frequency dependent ground-state optical transport properties of the materials ranging from bulk [50,53,54] to confined dimensions [55,56] and to the materials with complex geometry.[57,58] The frequency dependent optical parameters such as complex di-electric function, refractive index, optical reflectivity, absorption co-efficient, etc., can be computed under RPA.[51,52] This approximation first provides the imaginary parts of the complex di-electric function, and then, from the Kremmer-Kronig relations, the real part of the complex di-electric function can be derived. These two parameters then can be utilized for further computation of the remaining optical properties.

For understanding the relation between the complex di-electric function with optical properties like reflectivity, loss function, absorption spectra, etc., let us consider the ***x*-*z*** plane to be the plane of incidence with z-axis to be the surface normal, then the reflectivity for light polarized parallel and perpendicular to the plane of incidence can be expressed as

$$R_{\parallel} = \left| \frac{n_x n_z cos\theta - (n_z^2 - sin^2\theta)^{\frac{1}{2}}}{n_x n_z cos\theta + (n_z^2 - sin^2\theta)^{\frac{1}{2}}} \right|^2$$

(2.70)

$$R_{\perp} = \left| \frac{cos\theta - (n_y^2 - sin^2\theta)^{\frac{1}{2}}}{cos\theta + (n_y^2 - sin^2\theta)^{\frac{1}{2}}} \right|^2$$

(2.71)

Here, the $n_i(i = x, y \text{ } or \text{ } z)$ represents complex refractive index. In the case of NWs grown in z direction, the surface normal becomes parallel to the growth axis, and hence, $n_z = n_{\parallel}$, and $n_x = n_y = n_{\perp}$, and within linear response regime, $n(\omega) = \sqrt{\varepsilon(\omega)}$. The $\varepsilon(\omega)$ is known as the frequency dependent complex di-electric function ε(ω) that cab be further expressed as the combination of the real part $\varepsilon_{\text{real}}(\omega)/\varepsilon_1(\omega)$ and the imaginary part $\varepsilon_{\text{im}}(\omega)/\varepsilon_2(\omega)$.

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

(2.72)

As the two components $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are not independent of each-other within the linear response regime, they must obey Kramer-Kronig (KK) relations,

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\mathcal{P}\int_0^{\infty} \frac{\omega' \varepsilon_2(\omega)}{\omega'^2 - \omega^2} d\omega'$$

(2.73)

$$\varepsilon_2(\omega) = -\frac{2}{\pi}\mathcal{P}\int_0^{\infty} \frac{\omega \varepsilon_1(\omega)}{\omega'^2 - \omega^2} d\omega'$$

(2.74)

With $\mathcal{P}$ being the Cauchy principle value. The imaginary part of the complex di-electric function can be computed using the relation,

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum\nolimits_{k,c,v}\int |\Psi_k^c < \hat{u}\mathrm{r} > \Psi_k^v|^2\,\delta(E_k^c - E_k^v - E)$$

(2.75)

Here, the parameter Ω is proportional to $m^2\omega^2$, with ω being the frequency and m is the effective mass of the electron. The Ψ_k^c, Ψ_k^v, E_k^c and E_k^v are respectively the wave-functions and energies of conduction band and valence band for specific point $\boldsymbol{k}$. After computing the imaginary part of the di-electric function, one can easily compute the real part via KK relation (see equation (2.73) and (2.74)). The two components of the di-electric functions can be further utilized for evaluating the optical properties like refractive index, extinction co-efficient, loss function, absorption co-efficient, etc. Provided the conditions, $\varepsilon_1 = n^2 + k^2$ and $\varepsilon_2 = 2nk$, we can define the complex index of refraction as follows:

$$\mathrm{N}(\omega) = n(\omega) + \mathrm{i}k(\omega) \tag{2.76}$$

with $n(\omega)$ and $k(\omega)$ being the refractive index and the extinction co-efficient, respectively that can be further defined as,

$$n(\omega) = \frac{1}{\sqrt{2}}[(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \varepsilon_1]^{\frac{1}{2}} \tag{2.77}$$

and

$$k(\omega) = \frac{1}{\sqrt{2}}\left[(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} - \varepsilon_1\right]^{\frac{1}{2}} \tag{2.78}$$

These two functions were utilized for further computation of the reflectivity R and the absorption co-efficient α.

$$\alpha \neq \frac{\omega k}{c} = \frac{4\pi k}{\lambda_0} \tag{2.79}$$

$$R(\omega) = \frac{[(n-1)^2+k^2]}{[(n+1)^2+k^2]} \tag{2.80}$$

λ_0, c and k being the wavelength and velocity of light and extinction co-efficient in vacuum, respectively. We have also computed the electron energy loss function L(ω) which is the measure of energy lost by the semiconductor material subjected to motion of electrons inside the homogeneous medium.

$$\mathrm{L}(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \tag{2.81}$$

2.11 Thermoelectric Properties under Boltzmann Transport Equations

The thermoelectric transport through the material is solely governed by the two famous effects; first being the Seebeck effect[59] that accounts for the conversion of thermal energy to electrical energy via temperature gradient, and, the complementary effect known as the Peltier effect, which is also known as the reverse Seebeck effect due to its reverse working principle. For the computations of thermoelectric properties, semi-classical Boltzmann transport equations (BTE) for electrons and phonon need to be solved iteratively to calculate electronic and phonon contributions to the thermoelectric properties.[60] The efficiency of any material to convert the thermal energy to electrical energy can be assessed by computing the figure of merit ZT of the material that can be expressed as under:

$$ZT_e = \left(\frac{S^2\sigma}{\kappa_e}\right)T \tag{2.82}$$

$$ZT = \left(\frac{S^2\sigma}{\kappa_e+\kappa_l}\right)T \tag{2.83}$$

Here, S represents Seebeck co-efficient, σ is electrical conductivity, T is temperature and κ_e and κ_l are the electronic and lattice/phonon contributions to the thermal conductivity, respectively. The ZT_e and ZT are respectively, the electronic and overall figure of merits of the material respectively. The electronic contributions to thermoelectric properties was computed by solving BTE utilizing BoltzTraP code[61] and the phonon contribution to the same is obtained by solving phonon Boltzmann transport equation (PBTE) considering the third order phonon scattering effects as implemented on ShengBTE code.[62] The assessment of electronic contributions to the thermoelectric transport properties is done by extrapolating the electronic band energies using Fourier expansion.[61] This was done considering the constant relaxation time approximation (CRTA), in which the Seebeck co-efficient of the system is independent of the scattering rates [63] but also has a limitation as it computes relaxation time τ dependent electrical conductivity σ and electronic thermal conductivity κ_e. As far as phonon contribution to thermal conductivity is concerned, it is noteworthy, that the second order interatomic force constants that are usually computed under harmonic approximation does not account the anharmonicity of the material; therefore, to address this issue, the third order force constants are computed. To compute the τ independent accurate values of σ and κ_e, we have computed the relaxation time τ for all the systems using the deformation potential theory proposed by Bardeen and Shokley[64] which first gives the carrier mobility μ (see Equation (2.84)) and then utilizing μ, one can estimate the value of relaxation time τ (see Equation (2.85)).

$$\mu = \frac{(8\pi)^{\frac{1}{2}} \hbar^4 e C_{ii}}{(m^*)^{\frac{5}{2}} (k_B T)^{\frac{3}{2}} E_1^2} \tag{2.84}$$

Where, μ is carrier mobility, e is electronic charge, $\hbar$ is reduced Plank's constant, C_{ii}represents the elastic constant of the system, k_B is Boltzmann co-efficient, T is temperature, m^* is the carrier effective mass and E_1 represents the deformation potential constant. For computing the deformation potential E_1, the unit cells need to get relaxed under the influence of external strain in the range of ± 3% with 0.5% step size and the respective valence band maxima (VBM)/conduction band minima (CBM) energies need to be computed for hole/electron dependent properties. The valence band maxima (E^{VBM})/conduction band minima (E^{CBM}) energies are usually not exact, and hence need to be aligned properly for accurate prediction of the electronic dispersion dependent properties.[64] Hence, together with E^{VBM} or E^{CBM}, it is necessary to compute the respective lowest energy eigen values (E^{Core}) of the corresponding structures under the influence of external strain. To align the E^{VBM}/ E^{CBM} with respect to lowest energy level (E^{Core}) can be achieved by taking the difference between E^{VBM}/E^{CBM} and E^{Core}. This aligned energy eigen values when plotted with respect to applied strain, gives the value of the deformation potential by implementing the formula $d(E^{VBM/CBM} - E^{Core})/dv$. Here, v is volume strain = $\Delta V/V_0$ with $\Delta V = V - V_0$; V and V_0 being the volumes of unit cell under strained and equilibrium conditions, respectively. The aligned energy eigen values were plotted as a function of $\Delta V/V_0$ which was then fitted and the slope $(\delta(E^{VBM} - E^{Core})/\delta(\Delta V/V_0))$ was extracted, defined here as deformation potential constant E_1. After computing the magnitudes of C_{ii}, and E_1, the mobility μ can be evaluated from Equation 2.84, and utilizing μ, we can compute the respective relaxation time τ of the material which represents the time between the two successive collisions of electron and ions.

$$\tau = \frac{\mu m^*}{e} \tag{2.85}$$

In case of inorganic semiconductors, the thermally activated electrons and holes play a key role in transport, and usually possess much higher coherent wavelengths than the lattice constant of the respective material with the magnitude lying close to the acoustic phonon mode at the center of the first Brillouin zone (BZ).[65] Apart from the bulk materials, it is observed that on imposition of dimensional confinement, akin to the major transport and dynamics governing properties, the electron-acoustic phonon coupling achieves domination over other factors and governs the scattering mechanism.[66,67] The deformation potential theory as proposed by Bardeen and Shockley[64] has been proven to account dimension dependence of the carrier mobility [68–71] that can be evaluated by the equations given below:

$$\mu_{2D} = \frac{2e\hbar^3 C}{3k_B T|m^*|^2 E_1^2} \tag{2.86}$$

$$\mu_{1D} = \frac{e\hbar^2 C}{(2\pi k_B T)^{\frac{1}{2}}|m^*|^{\frac{3}{2}} E_1^2} \tag{2.87}$$

The equations (2.86) and (2.87) under the deformation potential approximation can be utilized for evaluating the confinement dependent carrier mobilities and relaxation time and τ independent computation of the thermoelectric properties of the relevant material can be done in more efficient way.

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