DFT is the quantum mechanical computational approach used in physics, chemistry, and material science etc. for predicting the ground state properties of many electrons system. The precision of the physical and chemical properties mainly depends on the accuracy of the selected exchange-correlation functional, which leads to predict the accurate electron density. Various DFT based packages have been explored and also tried to overcome the limitation in last three decades. The recent developments in the DFT are able to compute the accurate and wide range of properties by post-processing of data. The DFT results help the development of new materials and also in understanding the detailed insight of experimental results. The importance of DFT study can be understood by the fact that the number of publications on DFT study exponentially increasing in every year, shown in Figure 3.1.
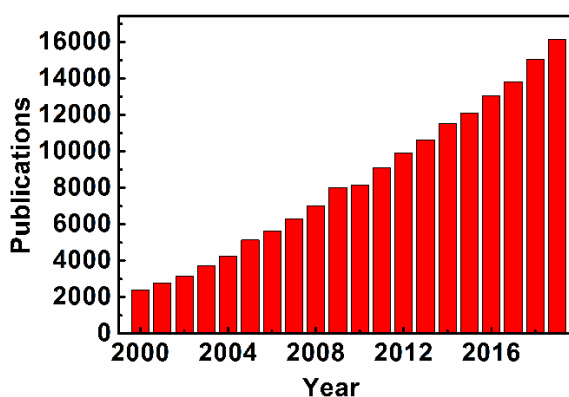

Figure 3.1 Density functional theory based per year publications from 2000 to 2019 (Source: Web of Science)

3.1 Many-Body Problem

The interactions between the electrons and nuclei play a vital role in computing the properties of an atom or a molecule. Such interactions can be defined with the help of quantum mechanics. In quantum mechanics, wave functions are used for the mathematical description of a quantum state. This complex interaction can be used in the form of different exchange potentials and the many electrons wave function can be solved using the Schrödinger equation.

$$\hat{H}\,\Psi(r_1, r_2, r_3 \ldots, R_a, R_b, R_c \ldots \ldots) = E\,\Psi(r_1, r_2, r_3 \ldots, R_a, R_b, R_c \ldots \ldots) \quad (2.1)$$

Where r_i denotes the position of electrons and R_j is the position of nucleus. $\hat{H}$ symbolizes the Hamiltonian operator which is the sum of kinetic energy of the nuclei and the interaction between them; E signifies the total energy and Ψ denotes the many-body wave function. A material consists of various types of interaction including, electron-electron (r_{ij}), electron-nucleus (R_{ia}) and nucleus-nucleus interactions (R_{ab}), as schematically represented in Figure 3.2. If someone is only interested in the ground state energy, then the time can be neglected and the energy can be found out by solving the time independent Schrödinger equation.
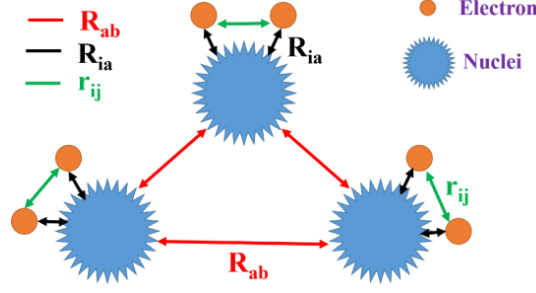
Figure 3.2 Schematic representation of Schrödinger system for electrons and nuclei interaction

Considering all the possible interactions, the total Hamiltonian is written as:

$$\hat{H} = \left(\hat{T}_N + \hat{V}_{N-N}\right) + \left(\hat{T}_{el} + \hat{V}_{el-el}\right) + \hat{V}_{el-N} + \hat{V}_{ext} \tag{2.2}$$

Where $\hat{T}_N$ and $\hat{T}_{el}$ are the kinetic energy of nuclei and electrons, respectively. $\hat{V}_{N-N}$, $\hat{V}_{el-el}$ and $\hat{V}_{el-N}$ are the columbic repulsion between nuclei - nuclei, electron - electron and nuclei– electron, respectively. Kinetic and potential energies are expressed as:

$$\hat{T}_N = \sum_a\left(-\frac{-\hbar^2}{2M_{ion,a}}\nabla_a^2\right),$$

$$\hat{V}_{N-N} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{a,b}\frac{Z_aZ_be^2}{|R_a-R_b|} \tag{2.3}$$

Where a and b refer to the nuclei present in materials.

$$\hat{T}_{el} = \sum_i\left(\frac{-\hbar^2}{2m}\nabla_i^2\right)$$

$$\hat{V}_{el-el} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{i,j}\frac{e^2}{|r_i-r_j|} \tag{2.4}$$

$$\hat{V}_{el-N} = \frac{1}{4\pi\epsilon_0}\sum_{i,a}\frac{-Z_ae^2}{|r_i-R_a|} \tag{2.5}$$

The mass of nuclei is much higher than the electron. The nuclei and electrons possess the equal amount of force, which ensure that the electron can move with relatively much higher speed with respect to the nuclei. That's why nuclei are considered as frozen. This decoupling of electron and nucleus is called as Born Oppenheimer approximation [Born and Oppenheimer et al, 1927]. By considering such constraint, the kinetic energy of nuclei and potential energy of nuclei-nuclei interaction are not considered. Due to so called "frozen nucleus", the wave function depends only on electronic configurations.

The electronic part of Hamiltonian for a fixed/frozen nuclei is given as:

$$\hat{H}_{el} = \sum_i\left(\frac{-\hbar^2}{2m}\nabla_i^2\right) + \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{i,j}\frac{e^2}{|r_i-r_j|} + \frac{1}{4\pi\epsilon_0}\sum_{i,a}\frac{-Z_ae^2}{|r_i-R_a|} \tag{2.6}$$

$$\hat{H}_{el} = \hat{T}_{el} + \hat{V}_{el-el} + \hat{V}_{el-N} \tag{2.7}$$

The exact solution of the Schrödinger equation with all possible interactions is possible for hydrogen atom and helium atom. However, the molecules or crystals consist of large number of atoms, where each atom contains large numbers of electrons. Thus, it becomes challenging to consider the interaction of electron with other electrons at the same time. Such systems are not solvable exactly by treating the complex interactions. So, some approximations are needed to solve for the same and are covered briefly in the following sections.

3.2 Density functional theory

In DFT, electron density is considered as the basic variable for solving the n electron system. Electron density reduces the 3n dimensional equation to n separate 3 dimensional equations. It is defined as the number of electrons per unit volume. The electron density in DFT is written as:

$$\rho(r) = \sum_i|\phi_i|^2 = 2\sum_i^{occ}|\phi_i|^2 \tag{2.8}$$

In DFT, the orbital ϕ_i is used instead of Ψ_i for denoting the electron density. ϕ_i is known as the Kohn-Sham (KS) orbital. Integrating the electron density all over the space gives total number of electrons:

$$\int \rho(r)dr = n \tag{2.9}$$

3.2.1 Hohenberg-Kohn Theorem

Hohenberg and Kohn [Hohenberg and Kohn et al, 1964] proposed that the electron density plays an important role in the electronic calculations. Hohenberg-Kohn proposed two important theorems as:

Theorem 1: The external potential V_{ext} is uniquely determined from electron density, $(\rho[r])$ within the limits of an additive constant.

Theorem 2: Energy functional $(E[\rho])$ can be defined in terms of electron density $(\rho[r])$ for any external potential.

The minimum value of $E[\rho]$ is the ground state energy, and corresponding electron density is known as ground-state electron density. A new method in terms of $\rho(r)$ was introduced by Hohenberg and Kohn to determine the ground state energy. The energy in DFT is written in functional form of $\rho(r)$ as:

$$E_v(\rho) = T(\rho) + V_{ee}(\rho) + V_{ne}(\rho) \tag{2.10}$$
$$= F_{HK}[\rho] + \int \rho(r)V(r)dr \tag{2.11}$$

$F_{HK}(\rho)$ represents the sum of kinetic and electron–electron interaction energy. $V(r)$ is the external potential. Its dependence on external potential is denoted by v in the subscript of E. To determine the ground state energy, second theorem is used. A function (G here) is formed using the Lagrange method of undetermined multipliers and minimized to get the ground state energy of the system.

$$\delta\left\{E_v[\rho] - \mu\left[\int \rho(r)dr - n\right]\right\} = \delta G = 0$$

μ being the Lagrange multiplier. Euler Lagrange equation gives:

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(r)} = V(r) + \frac{\delta F^{HK}[\rho(r)]}{\delta \rho(r)} \tag{2.12}$$

V(r) being the external potential. $F^{HK}[\rho(r)]$ known as the universal functional and is independent of the external potential. Its exact form for a system of interacting electrons is not known yet.

3.2.2 Kohn-Sham Theorem

The idea of the Kohn-Sham scheme is to replace many-electron interaction problems to the non-interacting electron with the same ground state energy equal to the original interacting many-electrons. The non-interacting electrons were considered to be moving in an effective potential, known as KS potential, V_{KS}. Due to the non-interacting condition, the electron-electron interaction vanishes. Hartree atomic units (e=1, m=1, $\hbar$=1, [$1/(4\pi \in)$] =1) are used for further discussion. The Kohn-Sham Hamiltonian becomes:

$$H_{KS} = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_i V_{KS}(r_i) \tag{2.13}$$

For a non-magnetic material containing n number of electrons, n/2 orbital will be occupied with each containing two electrons of opposite spins. The wave function for KS system using the Slater determinant is written as:

$$\Psi_{KS} = \frac{1}{\sqrt{\left(\frac{n}{2}\right)!}}\left|\phi_1\phi_2\phi_3 \ldots \phi_{\frac{n}{2}}\right| \tag{2.14}$$

ϕ_i is the KS orbital wave function. The Schrödinger equation is modified as:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(r)\right]\phi_i(r) = E_i\phi_i(r) \tag{2.15}$$

Using the above equations, kinetic energy in KS system is written as:

$$T_{KS} = 2\left\langle\Psi_{KS}\left|\sum_i^{n/2} -\frac{1}{2}\nabla_i^2\right|\Psi_{ks}\right\rangle$$

$$= 2 \sum_{i}^{n/2} \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle$$

$$= 2 \sum_{i}^{n/2} \int \phi_i^*(r) \left(-\frac{1}{2}\nabla^2 \right) \phi_i(r) dr \tag{2.16}$$

Charge density in KS system using the single orbital is written as:

$$\rho_{KS} = 2 \sum_{i}^{n/2} \phi_i^*(r)\phi_i(r) \tag{2.17}$$

Due to non-interacting electrons in KS system, energy functional is given by:

$$E[\rho_{KS}] = T_{KS}[\rho_{KS}] + \int V_{KS}(r)\rho_{KS}(r)dr \tag{2.18}$$

The above expression should be minimized for all densities to get the ground state energy. This can be done using the Lagrange method of undetermined multipliers and minimizing a functional G (here).

$$G[\rho_{KS}] = T_{KS}[\rho_{KS}] + \int V_{KS}(r)\rho_{KS}(r)dr - \mu[\int \rho_{KS}(r)dr - n] \tag{2.19}$$

As already discussed above, μ is the Lagrange multiplier and the functional minimization $\delta G[\rho_{KS}] = 0$ will result in:

$$\mu = V_{KS}(r) + \frac{\delta T_{KS}[\rho_{KS}]}{\delta \rho_{KS}(r)} \tag{2.20}$$

We know that the properties of an interacting system are different from that of the non-interacting system. The correlation between these two can be expressed as in terms of KE:

$$T[\rho] = T_{KS}[\rho] + (T[\rho] - T_{KS}[\rho]) \tag{2.21}$$

The term in the bracket shows the deviation. In the same way, electron-electron interaction energy for an interacting system is written as the sum of a classical and non-classical term representing charge energy distribution and exchange and correlation energy, respectively.

$$V_{ee}[\rho] = J_{ee}[\rho] + (V_{ee}[\rho] - J_{ee}[\rho]) \tag{2.22}$$

J_{ee} is calculated as:

$$J_{ee}[\rho] = \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \tag{2.23}$$

Using the above equations, the energy functional of the interacting system in terms of KS scheme is written as:

$$E[\rho] = T_{KS}[\rho] + J_{ee}[\rho] + \int \rho(r)V(r)dr + (T[\rho] - T_{KS}[\rho] + V_{ee}[\rho] - J_{ee}[\rho])$$

$$= T_{KS}[\rho] + J_{ee}[\rho] + \int \rho(r)V(r)dr + (E_{XC}[\rho]) \tag{2.24}$$

The E_{XC} is the exchange-correlation functional, consisting of two parts: i) difference in kinetic energies of interacting and non-interacting system and ii) non-continuum part due to electron-electron interaction. The exact form of this functional is not known yet. The accuracy of our result using the KS scheme will depend on the accuracy of this functional.

Now to get the ground state energy, this $E[\rho]$ functional should be minimised. A similar method of Lagrange undetermined multiplier will be followed which will give the Euler-Lagrange equation as:

$$\mu = V_{eff} + \frac{\delta T_{KS}[\rho]}{\delta \rho(r)} \tag{2.25}$$

$$V_{eff}(r) = V(r) + \int \frac{\rho(r')}{|r - r'|} dr' + V_{XC}(r)$$

$$= V(r) + V_H(r) + V_{XC}(r) \tag{2.26}$$

Here, V(r) is nuclear potential, $V_H(r)$ is the Hartree potential which is due to the distribution of electron charge and $V_{XC}(r)$ is the exchange-correlation potential. So, the density of ground state of system can be calculated by replacing V_{KS} by V_{eff}. The final equation will be as follows:

$$\left[-\frac{1}{2}\nabla^2 + V_{eff} \right] \phi_i(r) = E_i \phi_i(r) \tag{2.27}$$

In the next section, we will be discussing the approximations used for the exchange-correlation functional.

3.3 Exchange-Correlation Functional

As mentioned earlier, the accuracy of ground-state properties depends on how accurately we can approximate the exchange-correlation functional. The two most widely used approximations are described briefly in the following subsections:
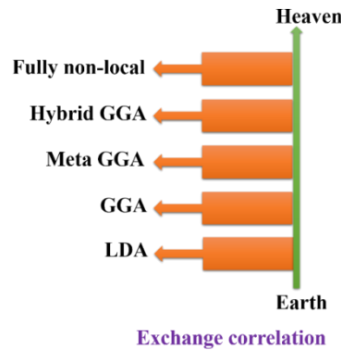

Figure 3.3 Jacob's ladder of exchange correlation functional

3.3.1 Local Density Approximation (LDA)

The exchange correlation (XC) term in the local density approximation is approximated by homogeneous electron gas model, in which electrons are distributed evenly with a uniform positive external potential, and the overall charge neutrality is preserved. In LDA, the XC energy per electron at a point r is considered the same as that for a homogeneous electron gas (HEG) that has the same electron density at the point r. The Local Density Approximation XC functional can be written as (Kohn & Sham, 1965a).

$$E_{XC}^{LDA}[\rho(r)] = \int \rho(r) E_{XC}^{heg}\{\rho(r)\} d^3r \tag{2.28}$$

Where E_{XC}^{heg} refers to the XC energy possessed by an electron in a homogenous gas of electron (*heg*) density $\rho(r)$. Exchange correlation energy is the summation of the exchange and correlation energy, can be expressed using the equation given below

$$= \int \rho(r) \left[E_X^{Heg}\{\rho(r)\} + E_C^{Heg}\{\rho(r)\} \right] d^3r$$

The above equation can be modified to include the spin, and the approximation now will be called Local spin density approximation (LSDA).

$$E_{XC}^{LDA}[\rho \downarrow, \rho \uparrow] = \int \rho(r) E_{XC}^{heg}\{\rho \downarrow (r), \rho \uparrow (r)\} d^3r \tag{2.29}$$

This method has produced results with a quite good accuracy and successfully used to understand the materials' properties. However, there are certain drawbacks associated with it:

   i)   It usually underestimates the lattice parameter,
   ii)   Calculated adsorption energy and diffusion barrier are too high and low, respectively,
   iii)   Usually underestimates spin moments, and
   iv)   Does not produce accurate results for materials having weaker hydrogen bonds.

3.3.2 Generalized Gradient Approximation (GGA)

Generally, the real systems are not homogenous and have a varying electron density. For more accurate XC functional, both the density ρ, and its gradient are considered in define GGA approximation. As a result, it returns better results compared to LDA (Langreth & Mehl, 1983).

$$E_{XC}^{GGA}[\rho \downarrow, \rho \uparrow] = \int \rho(r) E_{XC}^{GGA}[\rho \downarrow, \rho \uparrow, \nabla\rho \downarrow, \nabla\rho \uparrow] dr \tag{2.30}$$

There are certain other approximations such as meta-GGA which even takes the second order derivative into account to produce better results for semiconductor materials. Unlike the LDA method, there is no simple functional that can be used to represent the GGA energy functional. It is usually fitted to be in accordance with various constraints. Hybrid GGA further improve the accuracy. The bonding description of GGA is far better than LDA. Earlier Sun and co-workers (Sun et al., 2016)investigated the new parameterization, which makes Meta-GGA more accurate

than GGA and equivalent to hybrid functional. Jacob's ladder of exchange correlation energy for predicting the more accurate physical and chemical properties is shown in Figure 2.3. The accuracy of exchange correlation energy is increase from ground to heaven and computational time follows the reverse trend (Perdew, 2001).

3.4 Self-Consistent Field calculation

The first step for calculation is to guess the initial electron density and compute the effective potential, which is the addition of $V(r)$, $V_H(r)$ and $V_{XC}(r)$. Then Kohn-Sham equation is solved to find the single-particle wave functions. The new electron density is constructed based on calculated single-particle wave function and compared with the old electron density. If the new and old electron density is the same, then we considered the optimized ground-state electron density. In addition, if both the electron densities are not the same, then we used the mixed electron density (X% of initial electron density and Y% of final electron density) and repeat the whole process and compare the new and old electron density again. This process is repeated until the convergence is achieved. The schematic diagram of SCF cycle is shown in Figure 3.4.
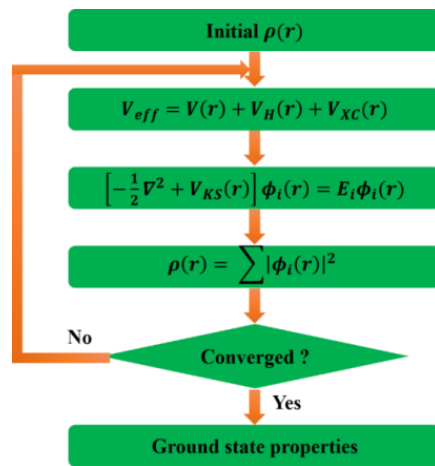

Figure 3.4 Flow chart of self-consistent field cycle iteration

3.4.1 Crystal Structure

The crystal structure in the DFT is defined through the unit cell, in which atoms are arranged in a specific position to possess the symmetry. The lattice vector R is written as

$$R = m_1 \boldsymbol{b_1} + m_2 \boldsymbol{b_2} + m_3 \boldsymbol{b_3}$$

Where, m_1, m_2 and m_3 are the integer numbers and $\boldsymbol{b_1}$, $\boldsymbol{b_2}$ and $\boldsymbol{b_3}$ are the reciprocal lattice vectors, which are computed from the direct lattice vectors. The crystal structure is the periodic arrangement of the atoms, and this periodicity may be in one, two, and three dimensions for 1D, 2D and 3D systems.

3.4.2 Bloch's Theorem

In a periodic system, the Kohn-Sham potential for a unit cell is also periodic because of the periodicity of crystalline materials i.e.,

$$u(r) = u(r+R) \tag{2.31}$$

In a similar way, the electron density is also periodic because of equation 2.31 is dependence on the position:

$$\rho(r) = \rho(r+R)$$

The electron density is periodic but wave functions are not periodic in general because of the complex number in the phase factor. Bloch resolve the periodicity problem by mapping the same plane waves on to the repeating pattern of solids, which made the system periodic with the introduction of a periodic function, $u_k(r)$:

$$\psi_k(r) = u_k(r)\exp(ik.r) \tag{2.32}$$

The wave function of the periodic potential can be expressed as:

$$\psi_k(r+R) = u_k(r+R)\exp[ik.(r+R)]$$

$$\psi_k(r+R) = \psi_k(r)\exp(ik.R) \tag{2.33}$$

The periodic wave function differs from the plane wave function of free electrons. The electrons in an atom are considered as perturbed free electrons. The periodic function, $u_k(r)$ in Fourier series can be expressed through reciprocal lattice vector G and Fourier expansion coefficient $c_k(G)$ as:

$$u_k(r) = \sum_G c_k(G)\exp(iG.r) \tag{2.34}$$

The wave function is modified as

$$\psi_k(r) = \sum_G c_k(\boldsymbol{G})\exp(i\boldsymbol{G}.\boldsymbol{r})\exp(i\boldsymbol{K}.\boldsymbol{r})$$

$$= \sum_G c_k(\boldsymbol{G})\exp[i(\boldsymbol{G}+\boldsymbol{K}).\boldsymbol{r}] \tag{2.35}$$

This equation reduces the infinite number problem to a finite number of problems.

3.4.3 Basis Sets

The KS-DFT method poses numerous difficulties because of different shapes in the core and valence region that's why the wave function is not the same everywhere. The wave functions are described through the basis sets. Various types of basis sets including, plane wave, a linear combination of atomic orbitals, linear augmented plane wave, and linear muffin orbital waves, are developed and employed in computations. Plane-wave is the most widely used basis sets for solving the Kohn-Sham equation. The Kohn-Sham orbitals are written as the linear combination of plane waves as:

$$\psi_k(r) = \frac{1}{\sqrt{\Omega}}\sum_G c_k(\boldsymbol{G})\exp[i(\boldsymbol{G}+\boldsymbol{K}).\boldsymbol{r}] \tag{2.36}$$

Where, $\frac{1}{\sqrt{\Omega}}$ is the renormalization factor. The Kohn-Sham equations are modified as

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(r)\right]\psi_k(r) = E_k\psi_k(r)$$

Substitute $\psi_k(r)$ in the above equation

$$\sum_{G'}\left[\frac{1}{2}|\boldsymbol{K}+\boldsymbol{G}|^2 + V_{KS}(\boldsymbol{G}-\boldsymbol{G}')\right]c_k(\boldsymbol{G}) = E_k c_k(G) \tag{2.37}$$

The solution of the above equation is obtained by diagonalization of the Hamiltonian matrix. The size of the matrix can be determined in terms of the cutoff energy $E_{cut} = \frac{1}{2}|\boldsymbol{K}+\boldsymbol{G}|^2$.

3.4.4 Pseudopotentials

The key consideration for the pseudopotentials is to separate the atomic electrons into two parts according to the significant contribution in the ground state properties. The nucleus and core electrons are considered frozen. These electrons are localized and oscillate because of strong Coulomb interaction by nuclei, shown in Figure 3.5. They are not contributing significantly to materials properties because of their negligible influence on the bond formation. The core electrons are strongly bound with the nuclei and remain fixed in most of the circumstances. Moreover, the valence electrons are considered because of their participation in the formation of bonds and other ground-state properties. The consideration of nucleus and core electrons as frozen, significantly reduces the number of electrons in the atoms present in the crystal structure used for calculation. This approach reduced the computational time for predicting the ground state properties. In a pseudopotential approach, the core of an atom is removed, and deal with only active valence electrons, shown in Figure 3.5.
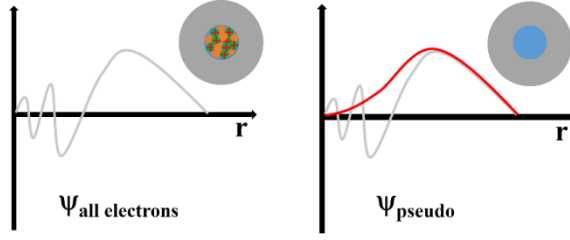
Figure 3.5 Schematic representation of approximation of full potential to pseudopotentials

3.4.5 Force and Energy Minimization

In this thesis, we have optimized all the crystal structures before computing the properties. The optimization of crystal structures is performed using the Hellmann-Feynman theorem (Feynman, 1939; Hellmann, 1933) to get the atoms in the ground state.

$$F_I = -\frac{\partial E}{\partial R_I} \tag{2.38}$$

Hellmann-Feynman equation modified as:

$$F_I = -\langle\Psi\left|\frac{\partial\hat{H}}{\partial R_I}\right|\Psi\rangle - \langle\frac{\partial\Psi}{\partial R_I}\left|\hat{H}\right|\Psi\rangle - \langle\Psi\left|\hat{H}\right|\frac{\partial\Psi}{\partial R_I}\rangle \tag{2.39}$$

Where, Ψ is the Kohn-Sham wave functions. The second and third term in above equation becomes zero.

$$F_I = -\langle\Psi\left|\frac{\partial\hat{H}}{\partial R_I}\right|\Psi\rangle \tag{2.40}$$

This force theorem is used to calculate the relax atomic positions.

3.5 Software Packages

3.5.1 Quantum ESPRESSO and WIEN2k

In this thesis, we have used the DFT based Quantum ESPRESSO [(Giannozzi et al., 2009a)] and WIEN2k software (Blaha & Madsen, 2016) package for ground-state properties. Quantum ESPRESSO is based on the plane wave pseudopotentials and allows to compute the properties. The GGA-PBE exchange-correlation functional used for the calculation of structural and electronic properties. The Monkhorst-Pack scheme used for sampling of the Brillouin zone. The structural parameters are optimized until the forces and energy are well converged. The van der Waals interaction is chosen by considering the DFT-D2 approximation (Grimme, 2006). The tetrahedron method is used for calculating the density of state calculation. WIEN2k is based on the full potential linearized augmented plane wave for computing the electronic and optical properties. The muffin tin radius (R_{mt}) is chosen sufficiently large to avoid the charge leakage. The energy cutoff parameter $R_{mt}K_{max}$ is selected sufficiently high to get the accurate results. The modified Becke-Johnson (mBJ) exchange-correlation is used for computing the accurate optoelectronic properties (Tran & Blaha, 2009).

3.5.2 BoltzTrap Package

BoltzTrap package is based on the semi-classical Boltzmann transport equation. It is useful for calculating the thermoelectric properties of the materials except for the lattice thermal conductivity [(Madsen & Singh, 2006)]. The electrical current due to the existence of the electric field, magnetic field, and temperature are described through the conductivity tensor.

$$j_i = \sigma_{ij}E_j + \sigma_{ijh}E_jB_k + v_{ij}\nabla_jT \tag{2.41}$$

Where, j_i, σ_{ij}, and σ_{ijk} are the electric current, and conductivity tensors. E_j, B_k, v_{ij} and ∇_jT are the electric field, magnetic field, group velocity, and temperature gradient, respectively.

Group velocity can be defined through the slope of the energy bands:

$$v_\alpha(i, \vec{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon(i, \vec{k})}{\partial k_\alpha} \tag{2.42}$$

The inverse mass tensor is using the energy band dispersion as:

$$M_{\beta\mu}^{-1}(i, \vec{k}) = \frac{1}{\hbar} \frac{\partial^2 \varepsilon(i, \vec{k})}{\partial k_\beta \partial k_\mu} \tag{2.43}$$

Conductivity tensor is written as:

$$\sigma_{\alpha\beta}(i, \vec{k}) = e^2 \tau v_\alpha(i, \vec{k}) v_\beta(i, \vec{k})$$
$$\sigma_{\alpha\beta\gamma}(i, \vec{k}) = e^3 \tau^2 \varsigma_{\gamma u v} v_\alpha(i, \vec{k}) v_\beta(i, \vec{k}) M_{\beta\mu}^{-1} \tag{2.44}$$

Where, $\varsigma_{\gamma u v}$ is the Levi-Civita symbol and v_α is the group velocity
Density of states based on the conductivity tensor is given as:

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N} \sum_{i,k} \sigma_{\alpha\beta}(i, k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon} \tag{2.45}$$

Where N is the number of k points used for sampling.
The transport tensor can be calculated through the conductivity tensor:

$$\sigma_{\alpha\beta}(T; \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f_\mu(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \tag{2.46}$$

$$v_{\alpha\beta}(T; \mu) = \frac{1}{eT\Omega} \int \sigma_{\alpha\beta}(\varepsilon)(e - \mu) \left[-\frac{\partial f_\mu(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \tag{2.47}$$

$$k_{\alpha\beta}^{elec}(T; \mu) = \frac{1}{e^2 T\Omega} \int \sigma_{\alpha\beta}(\varepsilon)(e - \mu)^2 \left[-\frac{\partial f_\mu(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \tag{2.48}$$

$$\sigma_{\alpha\beta\gamma}(T; \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta\gamma}(\varepsilon) \left[-\frac{\partial f_\mu(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \tag{2.49}$$

Where, $k_{\alpha\beta}^{elec}$, Ω, μ, $\sigma_{\alpha\beta}(\varepsilon)$ and $f_\mu(T; \varepsilon)$ are electronic thermal conductivity, volume of unit cell, chemical potentials, density of states and distribution, respectively. The Seebeck coefficient and Hall coefficient are written as

$$S_{ij} = E_j(\nabla_j T)^{-1} = (\sigma^{-1})_{\sigma i} v_{\alpha j} \tag{2.50}$$

$$R_{ijk} = \frac{E_j^{ind}}{j_i^{appl} B_k^{appl}} = (\sigma^{-1})_{\sigma j} \sigma_{\alpha\beta k} (\sigma^{-1})_{i\beta} \tag{2.51}$$

The lattice thermal conductivity is computed through the *Phono3py package* (Togo & Tanaka, 2015). It requires second and third-order force constant. The force constants are computed through supercell and finite displacement method. The second-order harmonic force constant is written as:

$$\phi_{\alpha\beta}(lk, l'k') = \frac{\partial^2 \phi}{\partial u_\alpha(lk) \partial_\beta(l'k')} \tag{2.52}$$

Third-order cubic anharmonic force method is given by:

$$\phi_{\alpha\beta\gamma}(lk, l'k', l''k'') = \frac{\partial^3 \phi}{\partial u_\alpha(lk) \partial_\beta(l'k') \partial_\gamma(l'k'')} \tag{2.53}$$

The finite difference method is used for approximation of first and second order force constant. The second-order force constant:

$$\phi_{\alpha\beta}(lk, l'k') \approx -\frac{F_\beta[l'k'; u(lk)]}{u_\alpha(lk)} \tag{2.54}$$

Where, $u_\alpha(lk)$ is the atomic displacement and $F_\beta[l'k'; u(lk)]$ is the atomic force measured at $r(l'k')$ due to the displacement $u(lk)]$ in the supercell.
Third-order cubic anharmonic force constant

$$\phi_{\alpha\beta\gamma}(lk, l'k', l''k'') \approx -\frac{F_\gamma[l''k''; u(lk), u(l'k')]}{u_\alpha(lk) u_\beta(l'k')} \tag{2.55}$$

$F_\gamma[l''k''; u(lk), u(l'k')]$ is determined by displacing the pairs of atoms in the supercell. A displacement length of 0.09 Å is used for computing the force constants.
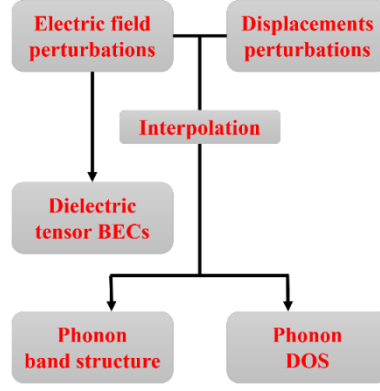
Figure 3.6 Flow chart diagram of Density Functional Perturbation Theory

3.5.3 Density Functional Perturbation Theory (DFPT)

Density Functional Perturbation Theory is an efficient approach to predict the lattice dynamic properties of materials. In the present work, we have used the DFPT to predict the dynamic stability of monolayers. Phonon band structure are related to the second order derivative of energies with atomic displacements. The flow chart diagram of DFPT is shown in Figure 3.6.

3.5.4 SCAPS Simulator

SCAPS is the one-dimensional solar cell capacitance simulator developed at the university of Gent Belgium (Burgelman, Decock, Niemegeers, Verschraegen, & Degrave, 2018). This is a public domain software, used for predicting the photovoltaic performance of the homo/hetero structure solar cells. It solves the one-dimensional coupled semiconductor equations with certain boundary conditions:

$$\frac{\partial}{\partial x}\left(\varepsilon_0\varepsilon_r\frac{\partial\varphi}{\partial x}\right) = -q\left(p - n + N_D^+ - N_A^- + \frac{\rho_{def}}{q}\right) \tag{2.56}$$

$$-\frac{\partial J_n}{\partial x} - U_n + G_n = \frac{\partial n}{\partial t} \tag{2.57}$$

$$-\frac{\partial J_p}{\partial x} - U_p + G_p = \frac{\partial p}{\partial t} \tag{2.58}$$

$$J_n = -\frac{\mu_n n}{q}\frac{\partial E_{Fn}}{\partial x} \tag{2.59}$$

$$J_p = \frac{\mu_p p}{q}\frac{\partial E_{Fp}}{\partial x} \tag{2.60}$$

Here ε_0 and ε_r are the permittivity values in vacuum and materials, respectively; φ is the electrostatic potential, q is the electronic charge, p and n are hole and electron concentrations, respectively, N_D^+ and N_A^- are the ionized donor and acceptor density, ρ_{def} is the charge defect density, J_n and J_p are the current density due to electron and hole respectively, μ_n and μ_p are the mobility of electron and hole respectively; U_n and U_p are the recombination rate of electron and hole respectively; G_n and G_p are the generation rate of electron and hole respectively; $\frac{\partial n}{\partial t}$ and $\frac{\partial p}{\partial t}$ rate of change of electron and hole concentration respectively; E_{Fn} and E_{Fp} electron and hole Fermi level, respectively.