Chapter 2

Theoretical Framework And Computational Methodology

2.1 Introduction to Density Functional Theory

The formulation of Density Functional Theory (DFT) [1], which predicts the fundamental properties of materials, is discussed briefly in this chapter. DFT is widely recognized as a successful technique and a quantum mechanical tool used for studying and predicting the properties of periodic bulk solids and material interfaces [2,3]. It has gained considerable attention due to its predictive power, especially in cases where direct experimental investigation is difficult due to factors such as cost, technical challenges associated with extreme conditions (e.g., high pressures, temperatures), in the study of toxic substances or nuclear radiation [4,5]. Compared to the classical approach, DFT offers superiority by employing a quantum mechanical approach to describe the interaction of quantum systems such as electrons in a periodic system, electron-phonon interactions, quasi-particle dispersions, and non-equilibrium states. In the quantum approach, the behavior of electrons in materials is investigated by solving the many-body-time-independent Schrödinger equation. However, this method encounters a challenge in considering the 3N degrees of freedom of the many-body electronic wave function. To overcome this, the many-body electronic wave function is approximated in terms of the electron density, significantly reducing the 3N variables to 3 coordinates (x, y, z) only. This modification enables quicker and easier computational calculations. In 1964, Hohenberg and Kohn introduced two theorems which serves as exact theoretical framework for DFT [6,7].

2.1.1 *Many-body Problem*

The properties of crystalline solids at atomic level are governed by quantum mechanics. Nuclei and electrons are the fundamental constituents of any material which suggests that all the properties are determined with the interactions that occur between electrons and ions. The interactions between the electrons and ions are understood through the quantum mechanical approach as they do not obey classical mechanics. The behaviour of electrons and ions governed under the quantum mechanical approach can be understood by solving the time independent Schrödinger equation. The time-dependent Schrödinger equation is written as [8],

$$\hat{H}\psi = E\psi \tag{2.1}$$

The Hamiltonian in equation (2.1) is written as,

$$\hat{H} = \frac{p^2}{2m} + V(\vec{r}) \tag{2.2}$$

Here, $\hat{H}$ is the Hamiltonian of the system which is the sum of kinetic and potential energy, E is the energy eigen value characterize by wave function $\psi(r)$.

The simplest case is that of the hydrogen atom which consists of one proton and one electron. By solving the above-mentioned equation for hydrogen atom, we get the exact energy as-13.6 eV. But material consists of large number of atoms thus increasing the number of protons and electrons for which the single electron Schrödinger equation does not hold true. Thus, for a system of many electrons and protons we have to find the solution for many-body Schrödinger equation to estimate the interactions between the same. The many-body equation consists of many-body wavefunction depending on the position of each electrons $(\vec{r_1}, \vec{r_2}, \ \vec{r_3}, \dots\dots\dots \vec{r_i})$ and nuclei $(\vec{R_1}, \vec{R_2}, \ \vec{R_3}, \dots\dots\dots \vec{R_I})$.

Accordingly, the many-body Schrödinger equation [9] is written as,

$$\hat{H}\psi(\vec{r}, \vec{R}) = E\psi(\vec{r_1}, \vec{r_2}, \ \vec{r_3}, \dots\dots\dots \vec{r_i}; \vec{R_1}, \vec{R_2}, \ \vec{R_3}, \dots\dots\dots \vec{R_I}) \tag{2.3}$$

Now, the Hamiltonian $\hat{H}$ can be represented as

$$\hat{H} = \hat{T}_E + \hat{T}_I + \hat{V}_{II} + \hat{V}_{EE} + \hat{V}_{IE} \tag{2.4}$$

Where, $\widehat{\mathrm{T}}_{\mathrm{E}} + \widehat{\mathrm{T}}_{\mathrm{I}}$ is kinetic energy and $\widehat{\mathrm{V}}_{\mathrm{II}} + \widehat{\mathrm{V}}_{\mathrm{EE}} + \widehat{\mathrm{V}}_{\mathrm{IE}}$ represents potential energies to include ion-ion, electron-electron and electron-ion interactions. This can also be written as,

$$\widehat{\mathrm{H}} = -\frac{\hbar^2}{2\mathrm{m_e}}\sum_{\mathrm{i}}\frac{\partial^2}{\partial\bar{\mathrm{r}}_{\mathrm{i}}{}^2} - \frac{\hbar^2}{2\mathrm{M}}\sum_{\mathrm{l}}\frac{\partial^2}{\partial\bar{\mathrm{R}}_{\mathrm{l}}{}^2} + \frac{1}{2}\sum_{\substack{\mathrm{l,l'}\\ \mathrm{l\neq l'}}}\frac{\mathrm{e}^2}{4\pi\varepsilon_0}\frac{\mathrm{Z_l Z_{l'}}}{|\bar{\mathrm{R}}_{\mathrm{l}}-\bar{\mathrm{R}}_{\mathrm{l'}}|} + \frac{1}{2}\sum_{\substack{\mathrm{i,j}\\ \mathrm{i\neq j}}}\frac{\mathrm{e}^2}{4\pi\varepsilon_0}\frac{1}{|\bar{\mathrm{r}}_{\mathrm{i}}-\bar{\mathrm{r}}_{\mathrm{j}}|} - \sum_{\mathrm{i}}\sum_{\mathrm{l}}\frac{\mathrm{e}^2}{4\pi\varepsilon_0}\frac{\mathrm{Z_l}}{|\bar{\mathrm{r}}_{\mathrm{i}}-\bar{\mathrm{R}}_{\mathrm{l}}|} \tag{2.5}$$

here, i and l run for electron and nuclei, m_e ……, M, $Z_l Z_{l'}$…….

m_e is mass of electron

M is mass of nuclei

$Z_l Z_l$ defines charges on different nuclei

$\bar{r}_i - \bar{r}_j$ distance between electron-electron

$\bar{r}_i - \bar{R}_l$ distance between electron-nuclei

By solving equation (2.4) we can obtain the ground state energy of the system through which the properties can be computed at equilibrium. For the solution of the equation (2.5) we need electronic charge, atomic number and mass and the calculation is based on laws of physics and nature's constants. This type of calculations where no adjustable parameters are required as input is known as *first principles* calculations. Over the years, several approximations to this theory have been put forth which are discussed in subsequent sections.

2.2 Wave Function Based Methods to Solve Many-body Problem

2.2.1 *Born-Oppenheimer Approximation*

The Born-Oppenheimer (BO) approximation allows to decouple electronic and ionic motions. Electrons being 10^3-10^4 times lighter than the ions, tend to move faster than the ions.

Thus, while solving the many-body Schrödinger equation, ions are considered at fixed position while electrons move around the ions adiabatically. According to this approximation [10] many-body wave function (equation 2.3) is decomposed in ionic and electronic part

$$\psi = \chi_i(\vec{R})\psi_E(\bar{r},\bar{R}) \tag{2.6}$$

here, $\chi_i(\vec{R})$ is ionic wave function, $\chi_1(\vec{R}), \chi_2(\vec{R}), \chi_3(\vec{R}) \ldots\ldots\ldots$

$\psi_E(\bar{r},\bar{R})$ is electronic wave function

The electronic part of equation (2.6) is given by,

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \bar{r}_i{}^2} + V_{IE}(\bar{r},\bar{R}) + V_{EE}(\bar{r})\right]\psi_E(\bar{r},\bar{R}) = E_E\ \psi_E(\bar{r},\bar{R}) \tag{2.7}$$

$\psi_E(\bar{r},\bar{R})$ is many-body electron wave function satisfying Schrödinger equation with fixed ionic position

Ionic part is given by

$$\left[-\frac{\hbar^2}{2M}\sum_l \frac{\partial^2}{\partial \bar{R}_l{}^2} + V_{II}(\bar{R}) + E_E(\bar{R})\right]\chi_l(\vec{R}) = E\,\chi_l(\vec{R}) \tag{2.8}$$

Ions due to its heavy mass are considered stationary making the ionic kinetic energy term vanish and also ion-ion repulsion potential becomes constant. This approximation is better for semiconductors and insulators as the electrons cannot excite to higher levels due to steady ions whereas it is inconclusive in case of metals. However, Hamiltonian with electronic part is still difficult to solve and thus further approximation is required.

2.2.2 *Hartree Approximation*

The Coulomb interactions governed by classical electrostatics between the electrons need to be discussed for simplification of many-body systems. The calculations were simplified by

Hartree, as he modified the issue into the independent electron approximation [11,12]. He regarded the n-electron system as a collection of separate one-electron systems, with no interactions between them. In this scenario, each electron encounters an averaged electrostatic potential created by the presence of the other electrons. Hartree considered the electronic motion and assumed that the wave function is the product of the single particle function [13].

$$\Psi_H = \Psi(\bar{r_1}, \sigma_1)\Psi(\bar{r_2}, \sigma_2) \ldots \Psi(\overline{r_N}, \sigma_N) \tag{2.9}$$

here, $\Psi(\bar{r_1}, \sigma_i)$ is wave function of single electron i with spin σ. Variational principle is used for ground state energy, which states expectation value of the energy is

$$E = \langle \Psi_H | H | \Psi_H \rangle \geq E_0 \tag{2.10}$$

Using Hamiltonian from equation 2.7, the wave function from equation 2.9 we get the equation known as Hartree equation.

$$-\frac{\hbar^2}{2m_e}\nabla_i{}^2\Psi_i - \frac{1}{4\pi\varepsilon_0}\sum\nolimits_l \frac{Ze^2}{|\bar{r}_i - \bar{R}_l|}\Psi_i + \frac{1}{4\pi\varepsilon_0}\sum\nolimits_{j\neq i}\int \frac{e^2|\Psi_j|^2}{|\bar{r}_i - \bar{r}_j|} d^3r_j = \epsilon_i \Psi_i \tag{2.11}$$

In left hand side of the equation, first term is the kinetic energy, while the 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. Also, Hartee did not consider the asymmetric wave function for electrons; as the electrons are classified as fermions, and according to the Pauli's exclusion principle the asymmetric nature should be considered.

2.2.3 *Hartree-Fock Approximation*

It is imperative to discuss the behaviour of fermions in the framework of Fermi-Dirac statistics. In order to include asymmetric nature, unlike to product wave function, determinantal for function is used, and is written as,

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

If the wavefunction is represented as Slater's determinant [14] then it satisfies the antisymmetric requirement.

$$\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_N},\sigma_N)=\frac{1}{N!}\begin{vmatrix}\Psi_1(\overline{r_1},\sigma_1) & \Psi_1(\overline{r_2},\sigma_2)\dots & \Psi_1(\overline{r_N},\sigma_N)\\ \Psi_2(\overline{r_2},\sigma_2) & \Psi_2(\overline{r_2},\sigma_2)\dots & \Psi_2(\overline{r_N},\sigma_N)\\ \Psi_N(\overline{r_N},\sigma_N) & \Psi_N(\overline{r_N},\sigma_N)\dots & \Psi_N(\overline{r_N},\sigma_N)\end{vmatrix}$$

The determinant of the wavefunction is given by,

$$\Psi_{HF}=\frac{1}{N!}\sum\nolimits_P(-1)^p P\ \Psi_1(x_1)\ \Psi_2(x_2)\dots\ \Psi_N(x_N) \tag{2.13}$$

here, x = $(\bar{r},\sigma)$

$\frac{1}{N!}$ is the normalization factor

P = number of permutation

p = number of interchanges making the permutation

Using the variational principle we obtain,

$$E=\sum_i\int\Psi^*(\vec{r})\left[-\frac{\hbar^2}{2m_e}\sum_i\nabla_i^2+V_I(\vec{r})\right]\Psi(\vec{r})d^3r$$

$$+\frac{1}{2}\sum_i\sum_{i\neq j}\iint\frac{e^2}{4\pi\varepsilon_0}\frac{|\Psi_i(x_i)||\Psi_j(x_j)|^2}{|\vec{r}-\vec{r}'|}d^3rd^3r'$$

$$-\frac{1}{2}\sum\nolimits_{i,j}\sum\nolimits_{j\neq i}\iint\frac{e^2}{4\pi\varepsilon_0}\frac{\Psi_i{}^*(\vec{r})\Psi_j{}^*(\vec{r}')\,\Psi_i(\vec{r}')\,\Psi_j(\vec{r})}{|\vec{r}-\vec{r}'|}d^3rd^3r' \tag{2.14}$$

The first term of above equation is consisting the kinetic energy and interaction of external potential, while 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 2.13 leads to canonical form of Hartree-Fock equation

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \nabla^2 - V_l(\vec{r}) + V_H(\vec{r})\right]\Psi_i(\vec{r})$$

$$-\frac{1}{2}\sum_{i,j}\sum_{j\neq i}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{\Psi_j^{*}(\vec{r}')\,\Psi_i(\vec{r}')\,\Psi_j(\vec{r})}{|\vec{r}-\vec{r}'|}d^3r d^3r' = \in_i \Psi_i(\vec{r}) \tag{2.15}$$

Involvement of exchange energy by taking asymmetric nature of wave function improves Hartree method. However, total energy $\in_i$ contains minimization over sum of N particle Slater’s determinant and this type of determinant are quite large; hence this approximation becomes computationally very costly for large as well as small systems.

2.3 Density Based Methods: Density Functional Theory

DFT is the most successful approach for the calculation of ground state energy to determine the properties of a material. Here, for many-body problem of N electrons there are possible 3N variables which are reduced to 3 coordinates when considering density of electrons as the base of our study. In the subsequent sections, we will discuss the Thomas-Fermi theory that describes atoms, molecules or solids in terms of density followed by Hohenberg-Kohn theorems that give us the ground state energy in terms of density and lastly the Kohn-Sham equation, which is the many-body Schrödinger equation in terms of electron density.

2.3.1. Thomas-Fermi Theory

The first approach to solve many body systems and obtain the ground state energy using density was introduced by Thomas and Fermi in 1927 [15,16]. In this method, the basic variable is electron density instead of single particle wave function or orbitals. They have considered density of non-interacting electron in homogeneous gas equal to the local density at a given point. Thomas-Fermi (TF) theory can approximate the kinetic energy and potential of N interacting electrons by following equation

$$T_{TF} = C_k \int \eta(\bar{r})^{\frac{5}{3}} d^3r \tag{2.16}$$

where, $C_k = \frac{3}{10}\frac{\hbar^2}{m_e}(3\pi^2)^{\frac{2}{3}}$ and $\eta(\bar{r})$ is the density of electrons

T_{TF} is the local approximation to the kinetic energy that can be obtained by adding all free electron energy states up to Fermi wave vector.

The TF theory gives total energy as a functional by adding kinetic energy, electrostatic energy and interaction of external potential as a functional of electron density which is represented in equation (2.17).

$$E = T_{TF} + \int V_{IE}(\bar{r})\, \eta(\bar{r}) d^3r + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{\eta(\vec{r}')\,\eta(\vec{r})}{|\vec{r}-\vec{r}'|} d^3r d^3r' \tag{2.17}$$

This energy is known as TF energy and TF equation can be obtained by minimization of above energy with constraint recognized by Lagrange multiplier μ which gives the proper number of particles.

$$\frac{5}{3}C_k\eta(\bar{r})^{\frac{2}{3}} + \int \frac{e^2}{4\pi\varepsilon_0}\frac{\eta(\bar{r}')}{|\bar{r}-\bar{r}'|} d^3r' = \mu$$

$$\mu = \frac{5}{3}C_k\eta(\bar{r})^{\frac{2}{3}} + V(\bar{r}) \tag{2.18}$$

This is the basic equation of TF theory and it can be solved self consistently. TF does not include the exchange energy in the equation (2.18). Further, this method has been extended by Dirac to include the exchange interaction and to include the correlation to kinetic energy functional but fails to establish shell structure and does not describe the behaviour of electrons for atoms to complex systems.

2.3.2. Hohenberg and Kohn Theorems

In 1964, Hohenberg and Kohn (HK) formulated two theorems [17] which forms the foundation of DFT calculations. Schematic of HK theorem is shown in ***Figure 2.1*** [18]. The first theorem states that;

Theorem I: *"For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density* $\eta(\mathbf{r})$*."* [17,19]

The above theorem states that ground state can be determined by density. The density thus corresponds to a unique potential which can be used to describe a unique Hamiltonian. The proof of the theorem is as follows:

Proof: Consider two potentials $V_{ext}^{(1)}(r)$ and $V_{ext}^{(2)}(r)$ which differ from each other by more than a constant. The two potentials have the same ground state density n(r). Thus, the two potentials provide us two separate wave functions $\psi_{ext}^{(1)}(r)$ and $\psi_{ext}^{(2)}(r)$.

According to variational principle, wave function $\psi_{ext}^{(1)}(r)$ gives the lowest energy for $H_{ext}^{(1)}(r)$ and $\psi_{ext}^{(2)}(r)$ is not the ground state for $H_{ext}^{(1)}(r)$. Thus,

$$E^{(1)} = \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle < \langle \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle \tag{2.19}$$

If we consider non-degenerate system, the last term of above equation becomes,

$$\langle \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle = \langle \psi^{(2)} | \hat{H}^{(2)} | \psi^{(2)} \rangle + \langle \psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \psi^{(2)} \rangle \tag{2.20}$$

$$= E^{(2)} + \int [\, V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r)]\, \eta(r) d^3r \tag{2.21}$$

So that

$$E^{(1)} < E^{(2)} + \int [\, V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r)]\, \eta(r) d^3r \tag{2.22}$$

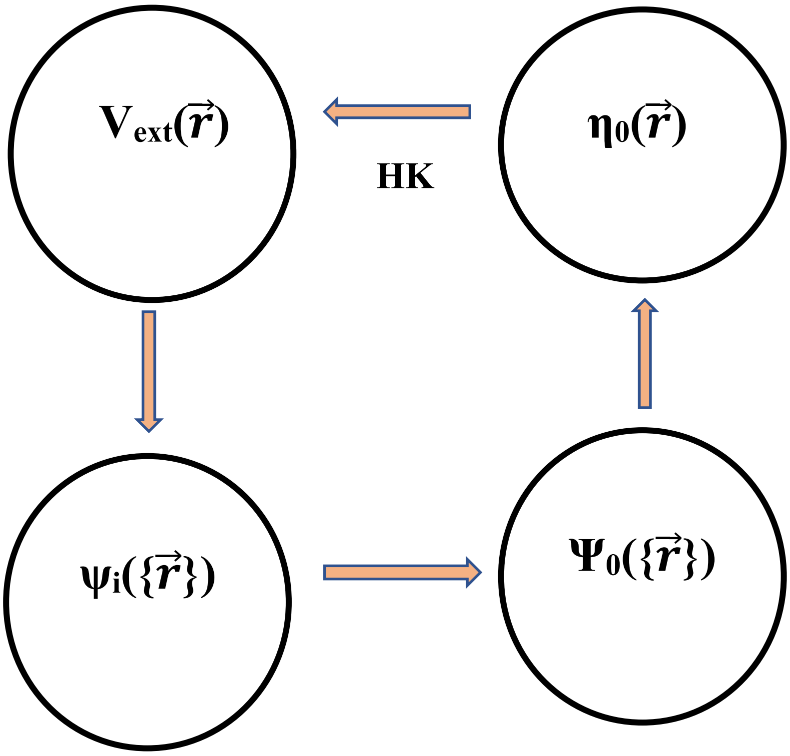

Figure 2.1: Schematic representation of first HK theorem. Here, the HK theorem completes the circle, while other smaller arrow shows the solution of Schrödinger equation. Image adapted from ref. [18]

Now, interchanging the labels 1 and 2 is reasonable.

$$E^{(2)} < E^{(1)} + \int [V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r)]\, \eta(r) d^3r \tag{2.23}$$

Adding equations 2.18 and 2.19 we get,

$$E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)} \tag{2.24}$$

This is contradictory which confirms the fact that there can only be one external potential $V_{ext}(r)$ that produces the ground state density $\eta(r)$, and conversely that the ground state density $\eta(r)$ uniquely determines the external potential $V_{ext}(r)$. The second theorem states that,

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.*

Proof: Now we consider a system with the ground state density $\eta^{(1)}(r)$ which corresponds to external potential $V_{ext}^{(1)}(r)$. The universal functional can be written as,

$$E[\eta] = F[\eta] + \int V_{ext}(r)\eta(r)d^3r \tag{2.25}$$

Where, $F[\eta] = T[\eta] + E[\eta]_{int}$ (2.26)

Further, it is known that universal functional equals the expectation value of ground state Hamiltonian with wave function $\psi^{(1)}$ and the corresponding density as $\eta^{(1)}(r)$.

$$E^{(1)} = E\left[\eta^{(1)}\right] = \left\langle \psi^{(1)} \middle| \hat{H}^{(1)} \middle| \psi^{(1)} \right\rangle \tag{2.27}$$

By the variational principle, a different density $\eta^{(2)}(r)$ will give higher energy

$$E^{(1)} = E\left[\eta^{(1)}\right] = \left\langle \psi^{(1)} \middle| \hat{H}^{(1)} \middle| \psi^{(1)} \right\rangle < \left\langle \psi^{(2)} \middle| \hat{H}^{(1)} \middle| \psi^{(2)} \right\rangle = E^{(2)} \tag{2.28}$$

The H-K functional evaluated the correct ground state density $\eta_0(r)$ which is indeed lower than the value of this expression for any other density $\eta(r)$ given by equation (2.25). Therefore, density based variational principle is also known as the second Hohenberg-Kohn theorem.

2.3.3. Kohn-Sham Equation: Density Functional Theory

In the above discussion we have referred number of approximations that have simplified the many-body Schrödinger equation but none of them guided us on how to solve it and obtain the value of charge density. HK estimated the kinetic energy of electrons and exchange correlation energy same as TF theory. In 1998, noble prize was awarded to Walter Kohn for the Kohn-Sham (KS) ansatz [20] in which they have replaced a many-body interacting system in external potential with a non-interacting auxiliary system and further assumed that they possess same ground state electron density and hence same ground state properties. KS came up with the approach that replaces N-electrons with fictious system of one electron. ***Figure 2.2*** summarizes the KS approach.

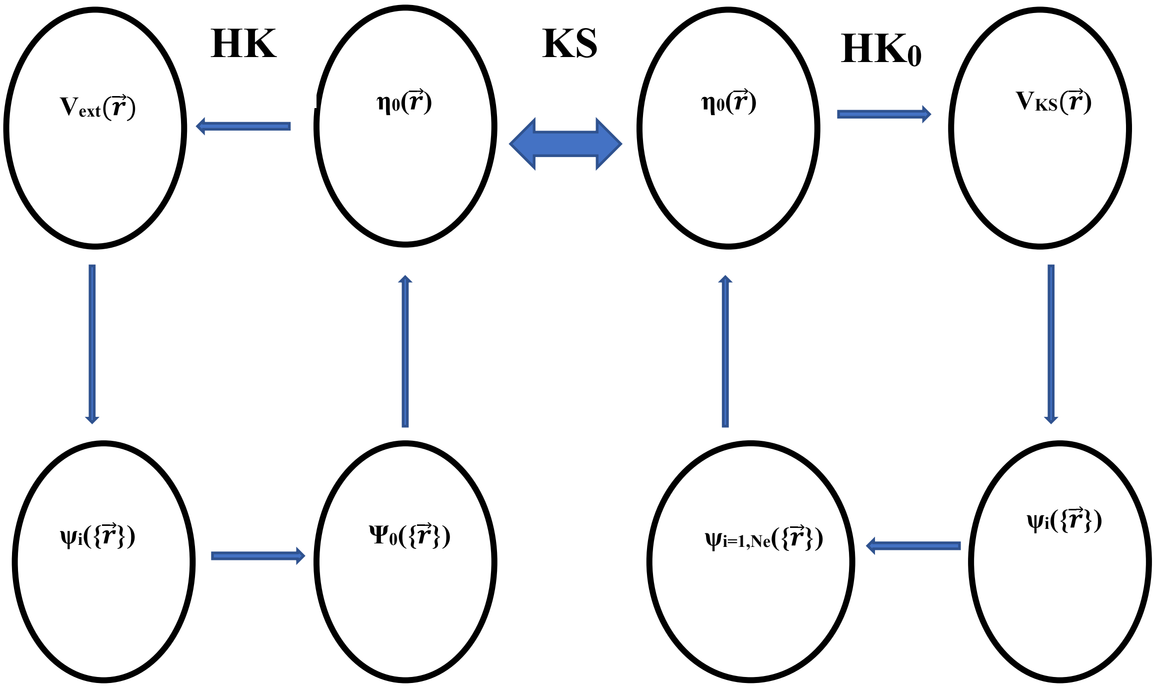

Figure 2.2: Same as Figure 2.1 but for Kohn-Sham ansatz. HK_0 defines Hohenberg and Kohn theorem applied to non-interacting system. The connection between many-body and the independent particle systems provided by Kohn-Sham that labelled as double arrow. Image is adapted from ref. [21]

The Hohenberg – Kohn theorem describes that total energy for a system can be expressed as,

$$E[\eta] = T[\eta] + V[\eta] + \int V_{ext}(r)\eta(r)d^3r \tag{2.29}$$

where, $T[\eta]$ is the kinetic energy functional

$V[\eta]$ is the Coulomb potential functional

V_{ext} is the external potential

Assuming that single particle system and interacting-particle system have same density. Adding and subtracting $T_s[\eta]$ (the non-interacting kinetic energy) and $E_H[\eta]$ (the Hartree energy) to equation (2.29), giving

$$E_{KS}[\eta] = T_s[\eta] + E_H[\eta] + \{T[\eta] - T_s[\eta] + V[\eta] - E_H[\eta]\} + \int V_{ext}(r)\eta(r)d^3r \quad (2.30)$$

$$E_{KS}[\eta] = T_s[\eta] + E_H[\eta] + E_{XC}[\eta] + \int V_{ext}(r)\eta(r)d^3r \quad (2.31)$$

where the exchange correlation term is defined as,

$$E_{XC}[\eta] = T[\eta] - T_s[\eta] + V[\eta] - E_H[\eta] \quad (2.32)$$

here, $E_{xc}[\eta]$ is a universal functional, which does not depend on the external potential $T[\eta]-T_s[\eta]$ is the kinetic contribution to correlation

$V[\eta]-E_H[\eta]$ arises from the Hartree-Fock exchange and the electrostatic contribution to correlation

The Hartree energy $E_H[\eta]$ is the classical electrostatic energy for a charge distribution $\eta(r)$

$$E_H[\eta] = \frac{1}{2}\int\int \frac{\eta(r)\eta(r')}{|r-r'|}d^3rd^3r' \quad (2.33)$$

The non-interacting kinetic energy T_s is evaluated from the single particle wave functions and is given as;

$$T_s[\eta] = -\frac{1}{2}\sum_i^N\langle\psi_i|\nabla^2|\psi_i\rangle \quad (2.34)$$

The density $\eta(r)$ and particle count N of the non-interacting system is straightforwardly calculated as,

$$\eta(r) = \sum_i^N|\psi_i(r)|^2 \quad (2.35)$$

$$N = \int \eta(r)d^3r \quad (2.36)$$

$T_s[\eta]$ is explicitly expressed as a functional of the orbitals that are also known as KS orbitals but all other terms are considered to be functionals of the density, then the solution is minimization in terms of $\eta(r)$.

$$\frac{\delta E_{KS}}{\delta \psi_i^*(r)} = \frac{\delta T_s[\eta]}{\delta \psi_i^*(r)} + \left[\frac{\delta E_{ext}[\eta]}{\delta \eta(r)} + \frac{\delta E_H[\eta]}{\delta \eta(r)} + \frac{\delta E_{xc}[\eta]}{\delta \eta(r)}\right]\frac{\delta \eta(r)}{\delta \psi_i^*(r)} = 0 \tag{2.37}$$

Also, from equations 2.29 and 2.30, we can write;

$$\frac{\delta T_s[\eta]}{\delta \psi_i^*(r)} = -\frac{1}{2}\nabla^2\psi_i(r) \qquad \text{and} \qquad \frac{\delta \eta(r)}{\delta \psi_i^*(r)} = \psi_i(r) \tag{2.38}$$

This further leads us to Schrödinger like equations:

$$(H_{KS} - \varepsilon_i)\psi_i(r) = 0 \tag{2.39}$$

where, ε_i are the eigen values

H_{KS} is the effective Hamiltonian

$$H_{KS}(r) = -\frac{1}{2}\nabla^2 + V_{KS}(r) \tag{2.40}$$

here,

$$V_{KS}[r] = V_{ext}[r] + V_H[r] + V_{xc}[r] \tag{2.41}$$

Equations (2.39)- (2.41) are the well-known Kohn-Sham equations, where the total energy E_{KS} and density η(r) are given by equations (2.30) and (2.35). These are independent particle equations and the potential can be found using the density, self consistently. The exact ground state density and energy can be obtained if exact functional $E_{xc}[\eta]$ is known.

2.4 Self-Consistency in Kohn-Sham Equation

In the above section, we have discussed various theories to solve the Schrödinger equation. Also, we have derived the Kohn-Sham equations to calculate density as well as ground state energy. The KS equation can be solved as eigen value problem. The solution can be obtained by varying the density of electrons and effective potential till desired self-consistency is achieved. In ***Figure 2.3***, we have shown the schematic flow chart to obtain the solution for the KS equation. Hartree potential and exchange correlation potential depends on electron density and this density yield correlation energy where initial guess of density is made. The unknown wavefunction $\psi_i(\vec{r})$ yields the new density and also the effective potential calculation is conducted. To achieve the self-consistency, initial guess is made. The initial guess is made by specifying nuclear coordinates. If the calculated new density is same as the old density, we can consider that desired self-consistency is achieved or else new effective potential is obtained from new electron density. After this process, when we achieve the ground state density, the energy is calculated.

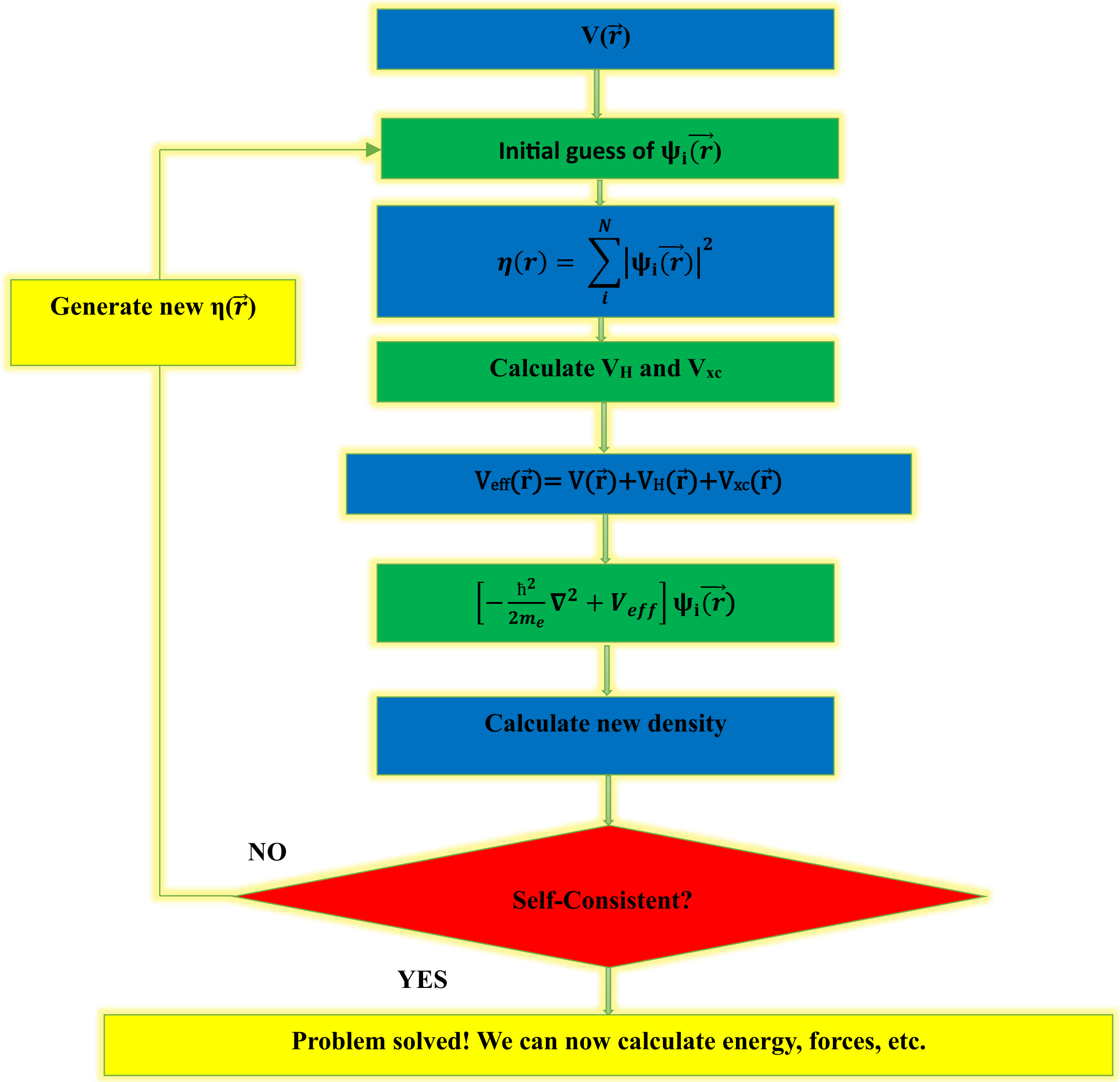

Figure 2.3: Schematic flowchart for finding self-consistent solutions of the Kohn-Sham equations. [From Quantum Espresso Tutorial]

2.5 Exchange and Correlation Functional

DFT solves many-body problem using KS equation where we need to approximate exchange and correlation potential. The exchange energy of electrons is defined as,

$$E_X[\eta] = \langle \psi[\eta] | V_{EE} | \psi[\eta] \rangle - U[\eta] \tag{2.42}$$

The repulsion between electrons which can be calculated using Kohn-Sham wavefunction which further gives us Hartree contribution and an exchange contribution. Slater determinant is used to represent the KS orbitals whereas the Fock orbitals gives exchange energy [22]. The exchange energy obtained is completely different than HF approximation. The differences between HF exchange and KS-DFT exchange are subtle. They can be thought of as having two different sources.

1) The KS exchange is defined for a given density, and so the exact exchange of a system is the exchange of the KS orbitals evaluated on the exact density. The HF exchange is evaluated on the HF orbitals for the system.
2) To eliminate the density difference, we can compare KS $E_X[\eta^{HF}]$ with that from HF. The remaining difference is due to the local potential for the KS orbitals.

The correlation energy is defined as,

$$E_c[\eta] = F[\eta] - T_s[\eta] - U[\eta] - E_X[\eta] \tag{2.43}$$

To obtain the solution to many-body problem and describe the properties of various systems there are some approximations to account exchange and correlation potential, which are discussed in subsequent sections.

2.5.1 *Local Density Approximation*

The accuracy to obtain sustaining results using KS equation, largely depends on the exchange-correlation functional. Kohn and Sham noticed that electrons in solids can often be considered to be close homogeneous electron gas, meaning that the effects of exchange and correlation are local. This approximation is known as the Local Density Approximation (LDA) which was proposed by Kohn and Sham. In LDA, we consider that at any point the contribution of each small volume to the exchange correlation energy is equivalent to the contribution of homogeneous electron gas that has the same density. The LDA exchange-correlation energy and functional are defined as,

$$\mathrm{E}_{\mathrm{xc}}^{\mathrm{LDA}}[\eta(\mathrm{r})] = \int \mathrm{dr}\, \eta(\mathrm{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{LDA}}[\eta(\mathrm{r})] \tag{2.44}$$

$$\mathrm{V}_{\mathrm{xc}}[\eta(\mathrm{r})] = \left(\mathrm{E}_{\mathrm{xc}}[\eta] + \eta \frac{\delta \mathrm{E}_{\mathrm{xc}}[\eta]}{\delta \mathrm{n}}\right)_{\eta=\eta(\mathrm{r})} \tag{2.45}$$

Quantum Monte Carlo Simulations [23] were used by Ceperly and Alder to obtain the functional for homogeneous electron gas which were further parameterized by Perdew and Zunger [24] and by Ortiz and Ballone [25]. LDA presents accurate results for the system in which electrons are placed in infinite region of space, with uniform positive external potential which is chosen for charge neutrality. The exchange-correlation energy sum rule in LDA is very well satisfied as exchange overestimates and correlation underestimates the values. However, LDA does not satisfy asymptotic behaviour of potential and also underestimates the band gap in semiconductors and insulators [26].

2.5.2 *Generalized Gradient Approximation*

As discussed in the above section, LDA fails to present results for complex systems as the electron density may vary with the volume element. To resolve this issue, gradient correction in density is required that is implemented in Generalized gradient approximation (GGA) [27]. Here, not just the density but also gradient of density is used in evaluation of exchange-correlation energy that is expressed as,

$$E_{xc}^{GGA}[\eta(r)] = \int dr\, \eta(r)\varepsilon_{xc}^{GGA}(\eta(r), \nabla\eta(r), \dots) \tag{2.46}$$

There are many parameterizations of the GGA based on semi-empirical and the first-principles. The widely used includes the one by Perdew, Burke and Ernzerhof which is derived from first-principles calculations [28]. It is found that the electron correlation part for finite systems is improved by gradient corrections. The gradient in the charge density can be denoted as,

$$E_{xc}[\eta] = \int \varepsilon_{xc}(\eta)\,|_{\eta=\eta(r)}\eta(r)F_{xc}[\eta(r), \nabla\eta(r)]dr \tag{2.47}$$

For simplicity in practical calculations, E_{xc} and F_{xc} must be parameterized analytic functions. GGA provides satisfactory results for small molecules but fails in case of uniform electron gas in metals. It gives us better bond dissociation energy and transition-state barrier as compared to LDA. The Perdew-Wang 1991 (PW91) [29] functional is an analytic fit to this numerical GGA, designed to satisfy several further exact conditions.

2.5.3 Pseudopotentials

In DFT single particle orbitals are given as linear combination of basis functions i.e.

$$\psi_i = \sum_{\alpha} C_{i\alpha}\emptyset_{\alpha}$$

The two most popular classes of basis functions are plane waves and Gaussian. The plane waves are preferred more in case of bulk materials and surfaces calculations as they are orthogonal to each other and are independent of atomic positions. In calculations, plane waves are used with periodic boundary conditions. Increasing the cutoff energy E_{cut} that defines the number of plane waves increases the accuracy but also the computational cost. Also, large number of plane waves are needed to represent the wave functions of core electrons because of their oscillatory nature. Due to this reason pseudopotentials are used which reduces the number of plane waves in turn making the calculations more efficient.

It is evident that the core states remain unchanged in molecules or atoms, thus the core electrons are combined with nucleus which generates effective potential on the valence electrons. Pseudopotentials are used to include properties of valence electrons in an atomic calculation. The potential designed are smooth with wave functions within a cutoff radius r_c. Here, outside the core region, the pseudo wave function matches exactly the "true" valence wave function whereas inside the core region the former is smoother than the latter which is depicted in ***Figure 2.4***. Each orbital channel (s, p, d, and f) has unique pseudopotentials defined for it. The pseudopotentials eliminate the core electrons lowering the memory requirement for simulations and they also incorporate relativistic effects at lower cost. There are mainly two kinds of pseudopotentials: Non-Conserving and Ultrasoft. There are few requirements of *ab-initio* pseudopotential given by Hamann, Schluter and Chiang [30]. They are as follows,

1) All electrons and pseudo valence eigen values agree for the chosen atomic reference configuration.
2) All electron and pseudo valence wave functions agree beyond a chosen core radius r_c.
3) The logarithmic derivatives of all the electron and pseudo wave functions agree at r_c.
4) The integrated charge inside r_c for each wave function agrees.
5) The first energy derivative of the logarithmic derivatives of all the electron and pseudo wave functions agrees at r_c.

The ultra-soft pseudopotentials fulfill the goal of accurate calculations by a transformation which expresses the problem in terms of a smooth and an auxiliary function around each ion core.

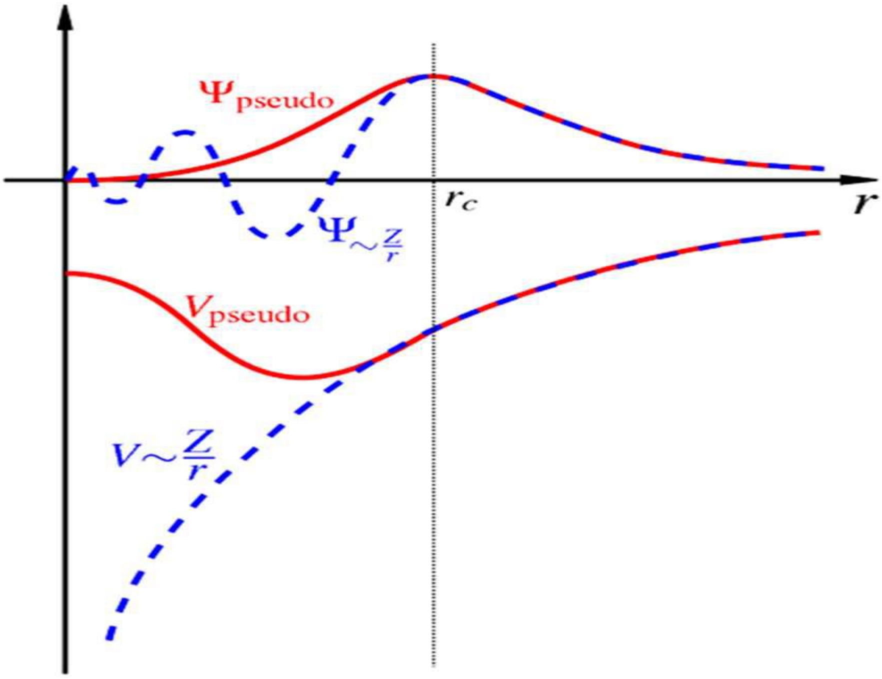

Figure 2.4: Comparison of wavefunction in Coulomb potential of nucleus (blue) and pseudopotential (red) inside and outside the cutoff region. Pseudo and real wave functions match after the cutoff radius. Image is adapted from ref. [21]

2.6 Density Functional Perturbation Theory

The understanding of vibrational frequencies and displacement patterns is crucial to describe the chemical structure and binding of atoms. Vibrational frequency is measured via Infrared, Raman and Inelastic scattering techniques. The lattice dynamical behaviour of a material affects the polarizability, phonons, Raman and Infrared spectrum, superconductivity and temperature dependent optical spectra. Density functional perturbation theory (DFPT) is a powerful theoretical technique within density functional theory framework to calculate such properties which calculate response function, phonon frequencies and Born effective charges [31-33]. By applying linear response to KS equation, we examine the alteration in electron density solution caused by perturbation. The external potential V is expanded in terms of taylor series as,

$$\mathrm{v_{ext}} = \mathrm{v_{ext}^{0}} + \lambda \mathrm{v_{ext}^{(1)}} + \lambda^2 \mathrm{v_{ext}^{(2)}} + \lambda^3 \mathrm{v_{ext}^{(3)}} + \cdots \tag{2.48}$$

$$\mathrm{E}[\psi] = \min_{\psi^{(1)}} \textstyle\sum_{\mathrm{iocc}} \langle \psi_{\mathrm{i}} | \mathrm{T} + \mathrm{V_{ext}} | \psi_{\mathrm{i}} \rangle + \mathrm{E_{Hxc}}[\eta] \tag{2.49}$$

The similar expansion is done for E, H, ψ_{kn}, $\eta(r)$, etc. The second order energy $E^{(2)}$ is an important parameter which is used to calculate the dynamical matrix for phonon frequency calculations and Born effective charges. Energy as a functional of density is written as,

$$E^{(2)} = \min_{\psi^{(1)}} \sum_{i \in occ} \left[\left\langle \psi_i^{(1)} \middle| H^{(0)} - \varepsilon_i^{(0)} \middle| \psi^{(1)} \right\rangle + \left\langle \psi_i^{(1)} \middle| \upsilon_{ext}^{(1)} \middle| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(0)} \middle| \upsilon_{ext}^{(1)} \middle| \psi^{(1)} \right\rangle + \left\langle \psi_i^{(0)} \middle| \upsilon_{ext}^{(2)} \middle| \psi_i^{(0)} \right\rangle \right]$$
$$+ \frac{1}{2} \iint \left. \frac{\delta^2{}_{EHxc}}{\delta n(r) \delta n(r')} \right|_{n^{(0)}} n^{(1)}(r) n^{(1)}(r') d^3r d^3r' + \int \frac{d}{d\lambda} \left. \frac{\delta E_{Hxc}}{\delta n(r)} \right|_{n^{(0)}} n^{(1)}(r) d^3(r) \frac{1}{2} \left. \frac{d^2 E_{Hxc}}{d\lambda^2} \right|_{n^{(0)}} \tag{2.50}$$

Where 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 ground state wave functions

$$\left\langle \psi_{\mathrm{i}}^{(0)} \middle| \psi_{\mathrm{j}}^{(\mathrm{j})} \right\rangle = 0 \tag{2.51}$$

The dynamical matrix is Hermitian and its eigenvalues $\omega_j^2(q)$ are real, and eigenvectors $\xi_j(q)$ are orthonormal. In addition, the phonon band structure ω_j (q) directly corresponds to density of states which provides the information of phonons in whole Brillouin zone (BZ). To obtain the information of the whole phonon spectrum, the scanning of BZ is important. These scanning consists in $D_{\alpha\beta}\left(\frac{q}{kk\prime}\right)$ -matrix diagonalization over the three-dimensional net of wave vector $q = \left(\frac{a^*}{n_1}, \frac{b^*}{n_2}, \frac{c^*}{n_3}\right)$, at n_1, n_2, n_3 = -N, .., N. In total, this includes $N_i = (2N + 1)^3$ points in BZ. The phonon density of states (DOS) is determined by summation over all the phonon states and is defined by

$$g(\omega) = D' \int_{BZ} \sum_j \delta\left(\omega - \omega_j(q)\right) dq = D' \int_{BZ} \sum_{jp} \delta\left(\omega - \omega_j(q)\right) dq_p \qquad (2.52)$$

Here, D' is a normalization constant such that $\int g(\omega)\, d\omega = 1$; and g(ω) dω is the fraction of phonons with energies ranging from ω to ω+dω. The mesh index ('p') is characterized by '**q**' in the discretized irreducible BZ, where d$\mathbf{q}_p$ provides the weighing factor corresponding to the volume of pth 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 provides essentially aids in understanding the atomic level contribution to the total phonon DOS. It is defined as follow:

$$g(\omega) = D' \sum_{jp} \delta\left(\omega - \omega_j(q)\right) \frac{|\xi_j(q)|^2}{\sum_{jp}|\xi_j(q)|^2} \qquad (2.53)$$

2.7 Dispersion Correction to Density Functional Theory

Kohn-Sham formulation of DFT is used to study the electronic structure of materials as it resonates accurate predictions for distinct properties of solids and molecules. To estimate the value of exchange correlation term, there are several approximations namely, LDA, GGA, hybrid functionals. Despite providing satisfactory results in various cases, GGA and hybrid functionals fail to describe the long-range electron correlations that are responsible for van der Waals (vdW) forces which is important to understand the adsorption behaviour of atoms and molecules on the surface and interfaces [34-36]. The total energy in case of vdW correction is given by,

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} \tag{2.54}$$

where E_{DFT-D} is general KS self-consistency energy

E_{disp} is the empirical vdW dispersion correction to the correlational functional given by [35]

$$E_{disp} = -s_6 \sum_{i=1}^{(N_{at}-1)} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}) \tag{2.55}$$

here, N_{at} is the number of atoms in the system

C_6^{ij} defines the dispersion coefficient for atom pair ij

S_6 depends on the functionals that are used, known as global scaling factor

R_{ij} is an interatomic distance

Damping function f_{dmp} (R_{ij}) is used to avoid near singularities for small R, that is given by

$$f_{dmp}(R_{ij}) = \frac{1}{1+e^{-d\left(\frac{R_{ij}}{R_{0ij}-1}\right)}} \tag{2.56}$$

where R_0 is the sum of atomic vdW radii

The value of C_6^{ij} and R_{0ij} is calculated by the following relation,

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \qquad R_{0ij} = R_{0i} + R_{0j} \tag{2.57}$$

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

2.8 Computational Packages

This section briefly describes the Quantum Espresso that has been used throughout our work to conduct various calculations.

2.8.1 Quantum Espresso

In 2001, a group of esteemed scientists, including Stefano Baroni, Paolo Giannozzi, Andrea Dal Corso, and others, initiated a collaborative project with the potential to bring about a remarkable transformation. This undertaking, recognized as Quantum Espresso (QE), played a pivotal role in the DFT computations carried out in this thesis [32,37]. It is an open-source package that is freely accessible to researchers worldwide under the terms of the GNU General Public License. This package was utilized for all aspects of the thesis, encompassing structural optimization, assessments of relative energy, electronic properties, magnetic characteristics, adsorption behaviours, and notably, the evaluation of catalytic activity. In this thesis, all graphical depictions of structures, DOS and PDOS plots were generated utilizing the XCrySDen [38] and Vesta visualization software [39].

2.9 Summary

In this chapter, we thoroughly discuss the comprehensive computational techniques that have been applied in this thesis. Initially, we have introduced the concept of many-body systems and proceed to investigate various approximative approaches utilized for solving the many-body Schrödinger equation, which specifically focuses on Density Functional Theory (DFT). Furthermore, we have explained the exchange-correlation functionals. Finally, we offer a concise summary of the computational software utilized to evaluate the diverse material properties scrutinized in this thesis.

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