CHAPTER 2
The upbringing of density functional theory

2.1 Formulism of density functional theory

Development of human civilization has always been dependent on evolution of devices used. The progress of our civilization therefore depends on the devices used today.[1] To have advanced technology, demands have been rising to predict new materials and design the material properties for which understanding material's properties have become important.[2] Prior to birth of density functional theory, the process of calculating properties of material beyond helium was seen as a challenging task.

In this section, we briefly discuss the versatility of density functional theory based computational methods in studying materials' properties. The advancement in computer and algorithms has made characterization and designing of new materials possible through computer simulations.[3] A range of computational methods can be applied to investigate the fundamental properties of various types of materials and to design new materials for advanced technologies.[4-7] In addition the computational physics bridges the gap between traditional experimental and theoretical methodologies.

A major challenge in theoretical physics and chemistry was the description of structure and dynamics of many-electron systems particularly in finding the solution of Schrödinger's equation. Materials are composed of nuclei and electrons and the behaviour of nucleus can be treated classically due to their massive nature as compared to electrons. The wave function of nucleus is strongly localized and hardly overlaps whereas electrons exhibit quantum mechanical behaviour with overlapping orbitals. The electrons not only interact with the stationary nuclei through the attractive Coulomb force but also with each other by means of the repulsive

Coulomb force. This makes the electronic structure calculations a many-body problem. In the middle of the sixties, on the basis of quantum mechanics, Hohenberg, Kohn and Sham established density functional theory of the quantum ground state. First principles methods based on density functional theory have been realized for its unprecedented predicting power because they do not require experimental input where all physical quantities are computed self consistently by solving quantum mechanical equation. Ever since the formulation of density functional theory, it has grown vast in popularity, and resulted in large amount of computational work in molecular and solid-state physics making it a mainstay for electronic structure calculations.[8-10] Using DFT, one can approach any interacting problem by mapping it to a solvable non-interacting problem. The use of approximate functionals were shown to provide a useful balance between computational cost and accuracy. Nowadays, with the use of sufficiently powerful computers, one can perform electronic structure calculations for about 100 atoms per unit cell. The main advantage of first-principles methods is that they can be carried out without knowing any experimental data of the system. The first- principles calculations in this thesis are mainly done within density functional theory (DFT).

In general, a solid is regarded as a many electron system with non-distinguishable mutual interaction in a lattice composed of nuclei. In principle, the effective potential in Schrödinger's equation includes: Coulomb potential due to the electronic charge distribution which is termed as Hartree potential, exchange potential arising due to the interaction described by the Pauli exclusion principle and correlation potential due to the effect of a given electron on the overall charge distribution. Following density functional theory, electron density distribution function

$n(r)$ is used instead of many electron wave function $\Psi\ (r_1, r_2, r_3\ldots\ldots, r_n)$ to determine the energy E for any system consisting of nuclei and electrons.[11] The solution of many body problem is reduced exactly to the solution for the ground state density distribution given by a one particle Schrödinger's equation. The formulation of Kohn sham equation using density functional theory is discussed in the following sections.

2.1.1 Many body problem

A solid can be treated as a collection of heavy nucleus and lightly bound electron particles. For a 'N' nucleus solid, there are N+ZN electromagnetically interactive particles where Z is the atomic number and the system is a many body interaction problem. The ground state energies can be evaluated by solving the the time independent Schrödinger's equation:[12]

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

where Ψ is the wave function for all particles, and E is the energy eigen value of this system and $\hat{H}$ is the many particle Hamiltonian. The simplest case is the Hydrogen atom, which has only one electron and one proton. We can solve the above equation exactly for this case and the energy of Hydrogen atom is -13.6 eV. But in conventional solids, there are large number of electrons and ions, and thus it result into complex interactions between the electrons and ions. Therefore, the Hamiltonian of the system also acquires complex form and given by

$$\boldsymbol{\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}} \tag{2.2}$$

were $\boldsymbol{\hat{T}_N}$ and $\boldsymbol{\hat{T}_e}$ are the kinetic energy operators for the nuclei and electrons respectively, $\boldsymbol{\hat{V}_{ee}}$, $\boldsymbol{\hat{V}_{eN}}$ and $\boldsymbol{\hat{V}_{NN}}$ are the potential energy due to the electron-electron interactions, electrons-nuclei interactions and nuclei-nuclei interactions respectively. The many body Schrödinger equation reads:

$$\boldsymbol{H\psi} = [-\frac{\hbar^2}{2m_e}\sum_{i}\frac{\partial^2}{\partial\bar{r}_i{}^2} - \frac{\hbar^2}{2M}\sum_{l}\frac{\partial^2}{\partial\bar{R}_l{}^2} + \frac{1}{2}\sum_{\substack{l,l'\\ l\neq l'}}\frac{e^2}{4\pi\varepsilon_0}\frac{Z_lZ_{l'}}{|\bar{R}_l-\bar{R}_l{}'|}$$

$$+\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\bar{r}_i-\bar{r}_j|} - \sum_i\sum_l\frac{e^2}{4\pi\varepsilon_0}\frac{Z_l}{|\bar{r}_i-\bar{R}_l|}]\psi = \boldsymbol{E\psi} \qquad (2.3)$$

where *i* and *l* are indices running for electron and nuclei, m_e and M stands for the mass of electron and nuclei, $\boldsymbol{Z_l}$ and $\boldsymbol{Z_{l'}}$ define the charges on different nuclei, $\bar{\boldsymbol{r}}_i - \bar{\boldsymbol{r}}_j$, $\bar{\boldsymbol{R}}_l - \bar{\boldsymbol{R}}_l'$ and $\bar{\boldsymbol{r}}_i - \bar{\boldsymbol{R}}_l$ represent distances between electron-electron, nuclei-nuclei and electron-nuclei respectively. The solution of the equation 2.1 is the eigen state and energy eigen value which is the total energy of the system from which the ground state properties of materials at equilibrium condition can be obtained. The Hamiltonian in equation 2.3 involves atomic mass and charge of electron, atomic number and mass of nuclei, therefore the solution of equation 2.1 does not require any adjustable parameter owing to which the method is known as first-principles calculation. In practice, for smaller system such as hydrogen the equation 2.1 is easily solvable, but is difficult to solve for large systems and for that several approximations were proposed.

2.2 Wave function based methods to solve many body problem

2.2.1 The Born-Oppenheimer approximation

The nuclei are heavier and move slowly than the electrons, Born and Oppenheimer[13] assumed that the nuclei can be treated as static with reference to moving electrons and hence their kinetic energy can be neglected and wave function can be separated in two parts namely electronic part and ionic part leading to many body wave function:[13]

$$\boldsymbol{\psi} = \chi_l(\bar{R})\, \boldsymbol{\phi}_i(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) \tag{2.4}$$

Here $\chi_l(\bar{R})$ represents ionic, while $\phi_i(\bar{r},\, \bar{R})$ stands for electronic wave function. Following equations are separated ionic and electronic parts of wave function:

$$\left[-\frac{\hbar^2}{2M}\sum_l \frac{\partial^2}{\partial \bar{R}_l{}^2} + \boldsymbol{V}_{NN}(\bar{\boldsymbol{R}}) + \boldsymbol{E}_E(\bar{\boldsymbol{R}})\right] \chi_l(\vec{\boldsymbol{R}}) = \boldsymbol{E}\chi_l(\bar{R}) \tag{2.5}$$

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \bar{\bar{r}}_i{}^2} + \boldsymbol{V}_{Ne}(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) + \boldsymbol{V}_{ee}(\bar{\boldsymbol{r}})\right] \boldsymbol{\phi}_i(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) = \boldsymbol{E}_e\, \boldsymbol{\phi}_i(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) \tag{2.6}$$

Here, in the above two equations derived from equation 2.2, where the first term of equation 2.2 vanishes under Born-Oppenheimer (BO) approximation and the last term will be a constant.[14] The residual Hamiltonian will now be read as:

$$\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{T}}_e + \widehat{\boldsymbol{V}}_{ee} + \widehat{\boldsymbol{V}}_{eN} + \text{ Constant} \tag{2.7}$$

The Hamiltonian operator ($\widehat{\boldsymbol{H}}$) can be modified as a sum of kinetic energy of electrons, the electron-electron interaction ($\widehat{\boldsymbol{V}}_{ee}$) and the interaction with the external potential ($\widehat{\boldsymbol{V}}_{ext}$):

$$\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{T}}_e + \widehat{\boldsymbol{V}}_{ee} + \widehat{\boldsymbol{V}}_{ext} \tag{2.8}$$

where the electron kinetic energy operator $\hat{T}_e$ for the electrons is:

$$\hat{T}_e = \frac{-\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \bar{\bar{r}}_i{}^2} \tag{2.9}$$

and the potential energy $\hat{\boldsymbol{V}}_{\boldsymbol{ee}}$ due to electron-electron interactions is:

$$\hat{\boldsymbol{V}}_{\boldsymbol{ee}} = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} \tag{2.10}$$

The external potential of interest is the electron-nuclei interaction and is given by

$$\hat{\boldsymbol{V}}_{\boldsymbol{ext}} = \sum_{i,I} V_I(|r_i - R_I|) \tag{2.11}$$

were r_i is the coordinate of ith electron and $\hat{\boldsymbol{V}}_{\boldsymbol{ext}}$ is the external potential.

2.2.2 Hartree approximation

In Hartree approximation, the electron-electron interaction has its footing on the classical electrostatics where the Coulomb repulsion accounts in some form. In classical electrostatics, a distribution of electronic charge n(r) produces an electrostatic potential through Poisson's equation:

$$\boldsymbol{\nabla^2 \varphi(r) = 4\pi n(r)} \tag{2.12}$$

The electrons experiencing this potential will have a potential energy called Hartree potential which satisfies the Poisson’s equation:[15]

$$\boldsymbol{\nabla^2 V_H(r) = -4\pi n(r)} \tag{2.13}$$

The solution of equation 2.9 in Hartree units, will have the form: a potential energy $\boldsymbol{V_H(r) = -\varphi(r)}$, which is called the Hartree potential

$$\boldsymbol{E_H[n] = \frac{1}{2}\frac{n(r)n(r')}{|r-r'|}d^3r d^3r'} \tag{2.14}$$

With the inclusion of Hartree potential one can write the complete Schrödinger’s equation for electronic part as follows:

$$-\frac{\hbar^2}{2m_e}\nabla_i{}^2\phi_i - \frac{1}{4\pi\varepsilon_0}\sum\nolimits_l \frac{Ze^2}{|\bar{r}_i-\bar{R}_l|}\phi_i + \frac{1}{4\pi\varepsilon_0}\sum\nolimits_{j\neq i}\int\frac{e^2|\Psi_j|^2}{|\bar{r}_i-\bar{r}_j|}d^3r_j = \in_i \phi_i \qquad (2.15)$$

The first term on the left-hand side of the equation is the kinetic energy of electrons, 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. Equation 2.11 is known as Hartree equation and solution is given using variational principle which provides ground state energy by minimization of expectation value of energy E.

$$E = \frac{\langle\Psi_H|H|\Psi_H\rangle}{\langle\Psi_H|\Psi_H\rangle} \qquad (2.16)$$

Hartree reduced many body problem into one electron problem which is also known as independent electron approximation which neglected correlations between electrons and the asymmetric wave function nature for electrons.

2.2.3 Hartree-Fock (HF) approximation

Being Fermions and following of Pauli's exclusion principle, the asymmetric nature of wave function and the effect of correlation for electrons cannot be ignored. Hatree and Fock considered the asymmetric wave function given by the following equation:

$$\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_i},\sigma_i,\ \dots,\overline{r_j},\sigma_j,\dots) = -\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_i},\sigma_i,\ \dots,\overline{r_j},\sigma_j,\dots) \qquad (2.17)$$

In HF approximation, minimization of equation 2.15 is done by considering the above asymmetric wave function in the determinant form known as Slater's determinant.[16]

$$\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_N},\sigma_N) = \begin{vmatrix} \Psi_1(\overline{r_1},\sigma_1) & \Psi_1(\overline{r_2},\sigma_2)\dots & \Psi_1(\overline{r_N},\sigma_N) \\ \Psi_2(\overline{r_2},\sigma_2) & \Psi_2(\overline{r_2},\sigma_2)\dots & \Psi_2(\overline{r_N},\sigma_N) \\ \Psi_N(\overline{r_N},\sigma_N) & \Psi_N(\overline{r_N},\sigma_N)\dots & \Psi_N(\overline{r_N},\sigma_N) \end{vmatrix} \qquad (2.18)$$

The determinant of the wave function can be written as

$$\boldsymbol{\Psi}_{HF} = \frac{1}{N!}\sum_{P}(-1)^{p}P\,\boldsymbol{\Psi}_{1}(x_{1})\,\boldsymbol{\Psi}_{2}(x_{2})\ldots\boldsymbol{\Psi}_{N}(x_{N}) \tag{2.19}$$

where, $x = (\bar{r}, \sigma)$, P is the permutation number and p is number of interchanges for making up this permutation. Substituting the Slater determinant of many body wave function in equation 2.15 gives expectation value of Hamiltonian as

$$\begin{aligned} E = {} & \sum_{i}\int \Psi^{*}(\vec{r})\left[-\frac{\hbar^{2}}{2m_{e}}\sum_{i}\nabla_{i}^{2} + V_{l}(\vec{r})\right]\Psi(\vec{r})d^{3}r\frac{1}{2}\sum_{i}\sum_{i\neq j}\iint\frac{e^{2}}{4\pi\varepsilon_{0}}\frac{|\Psi_{i}(x_{i})||\Psi_{j}(x_{j})|^{2}}{|\vec{r}-\vec{r}'|}d^{3}rd^{3}r' \\ & -\frac{1}{2}\sum_{i,j}\sum_{j\neq i}\iint\frac{e^{2}}{4\pi\varepsilon_{0}}\frac{\Psi_{i}^{*}(\vec{r})\Psi_{j}^{*}(\vec{r}')\,\Psi_{i}(\vec{r}')\,\Psi_{j}(\vec{r})}{|\vec{r}-\vec{r}'|}d^{3}rd^{3}r' \end{aligned} \tag{2.20}$$

where the last term is the consequence of Pauli's exclusion principle known as exchange energy. Minimization of equation 2.17 leads to Hartree-Fock equation;

$$\begin{aligned} & \left[-\frac{\hbar^{2}}{2m_{e}}\sum_{i}\nabla^{2} - V_{l}(\vec{r}) + V_{H}(\vec{r})\right]\Psi_{i}(\vec{r}) - \frac{1}{2}\sum_{i,j}\sum_{j\neq i}\iint\frac{e^{2}}{4\pi\varepsilon_{0}}\frac{\Psi_{j}^{*}(\vec{r}')\,\Psi_{i}(\vec{r}')\,\Psi_{j}(\vec{r})}{|\vec{r}-\vec{r}'|}d^{3}rd^{3}r' \\ & = \in_{i}\Psi_{i}(\vec{r}) \end{aligned} \tag{2.21}$$

This is an improvement over Hartree method due to the involvement of exchange energy considering the asymmetric nature of wave-function. However, total energy $\in_{i}$ involves minimization over sum of N particle Slater's determinant (equation 2.15). This type of determinant is quite large; hence this approximation is computationally quite costly for large as well as small systems.

2.3 Density based method: Density functional theory

The ultimate aim is to evaluate the ground state energy of many electron system by solving many body Schrödinger's equation given in equation 2.3. For a system with N number of electrons, there exist 3N variables leading to complex solution of equation 2.3. The density functional theory relies on density-based method where the interaction energy and potentials depend only on the density of electrons which reduces the computational cost by a large amount.

2.3.1 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.[17,18] 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 by following equation can be written in terms of electron density $n(\bar{r})$ as:

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

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

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

where E is the Total energy. The total number of particles can be obtained by the minimization of above energy with constraint recognized by Lagrange multiplier as:

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

The equation 2.23 can be solved self consistently. Here, Thomas-Fermi theory does not include the exchange energy. Dirac extended this method to include the exchange interaction and correlation functional.[19,20] However, the shell structure and behaviour of atoms of complex systems were not considered in Thomas-Fermi theory.

2.3.2 Hohenberg and Kohn theorem

In 1964 Hohenberg and Kohn formulated two theorems[21] which form the foundation of density functional theory calculations. Schematic of Hohenberg and Kohn (HK) theorems is shown in Figure 2.1.22 The first theorem is stated as follows;

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* $n(r)$*"*[21,23]

According to Theorem I, the ground state of a system is unique functional of density. Thus, given the charge density, the Hamiltonian operator could be uniquely determined and the wave function Ψ and all materials properties can be computed. The proof of Theorem 1 is presented below:

Consider two different external potentials $V_{ext}^{(1)}(r)$ and $V_{ext}^{(2)}(r)$ differing by more than a constant and leading to different ground state wave functions, $\Psi^{(1)}$ and $\Psi^{(2)}$ respectively. Let us assume same ground state density n(r) for both potentials. The two external potentials lead to two different Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$. Since $\Psi^{(2)}$ is not the ground state of $\hat{H}^{(1)}$.

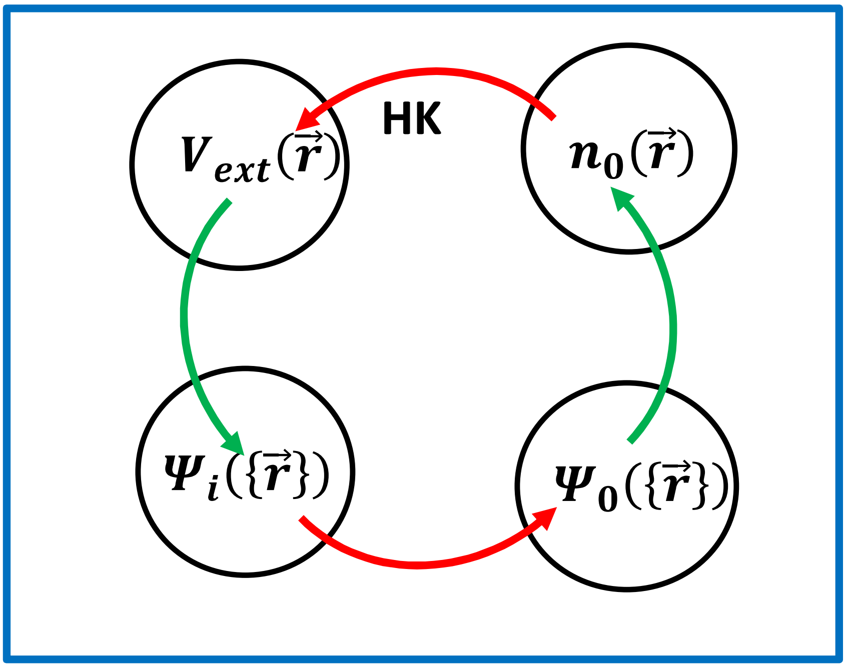

Figure 2.1: Schematic representation of first Hohenberg and Kohn theorem. Here, the HK theorem completes the circle, while arrow shows the solution of Schrödinger equation. Image adapted from ref.[22]

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

The last term can be rewritten as:

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

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

so that

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

It is reasonable to interchange the labels 1 and 2.

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

Adding equations (2.25) and (2.26) gives

$$E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)} \tag{2.30}$$

Which contradicts our assumption and proves that there can only be one external potential $V_{ext}(r)$ that produces the ground state density $n(r)$, and conversely that the external potential $V_{ext}(r)$ is uniquely determined by the ground state density.

The second theorem is stated as follows;

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."*

We may now consider a system with the ground state density $n^{(1)}(r)$ corresponding to the external potential $V_{ext}^{(1)}(r)$. The universal functional can be written as:

$$E[n] = F[n] + \int V_{ext}(r) n(r) d^3r \tag{2.31}$$

$$\text{where } F[n] = T[n] + E[n]_{int} \tag{2.32}$$

Further, the universal functional is equal to the expectation value of the ground state Hamiltonian which has wave function $\Psi^{(1)}$ and corresponding density $n^{(1)}(r)$

$$E^{(1)} = E\left[n^{(1)}\right] = \left\langle \Psi^{(1)} \middle| \widehat{H}^{(1)} \middle| \Psi^{(1)} \right\rangle \tag{2.33}$$

Therefore a different density, $n^{(2)}(r)$ corresponds to a different wave function $\Psi^{(2)}$, implying that the $E^{(2)}$ of this state is greater than $E^{(1)}$, since

$$E^{(1)} = \left\langle \Psi^{(1)} \middle| \hat{H}^{(1)} \middle| \Psi^{(1)} \right\rangle < \left\langle \Psi^{(2)} \middle| \hat{H}^{(1)} \middle| \Psi^{(2)} \right\rangle = E^{(2)} \tag{2.34}$$

Thus, the energy given by equation (2.31) evaluated for the correct ground state density $n_0(r)$ is indeed lower than that corresponding to any other density $n(r)$. The above variational principle is known as the second Hohenberg-Kohn theorem. The universal functional F[n] yields the lowest energy if and only if the input density is the true ground-state density n_0.

2.3.3 The Kohn-Sham equation

The Hohenberg-Kohn theorems[4] allow to express the energy into two parts, the system dependent $\int V_{ext}(r)n(r)d^3r$ and the unknown functional $F[n]$ as expressed in equation 2.28. Kohn and Sham devised proposed unknown $F[n]$. The Kohn-Sham perturbed DFT into a practical tool by construction of an auxiliary system of non-interacting quasiparticles that have the density same as that of true interacting problem. By formulating good approximations to these functional, direct minimizations of the energy would be possible.

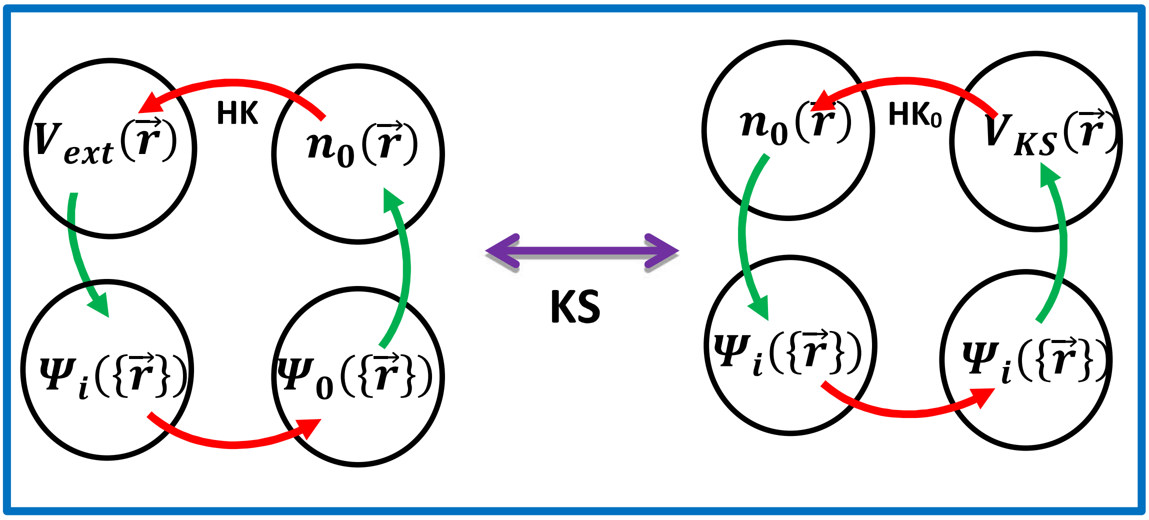

Figure 2.2: The connection between many body and the independent particle system is provided by Kohn – Sham, where HK_0 defines Hohenberg and Kohn theorem applied to non-interacting system.

If there exists a system of non-interacting electrons with the same density as of interacting system, according to Hohenberg-Kohn theorem, the total energy for the interacting system can be written as:

$$E[n]=T[n]+V[n]+\int V_{ext}(r)n(r)d^3r \tag{2.35}$$

where T[n], V[n] and $V_{ext}(r)$ are the kinetic energy functional, Coulomb potential functional and external potential respectively. Since the single particle system and the interacting system are assumed to have the same density, adding and subtracting $T_s[n]$ (the non-interacting kinetic energy) and $E_H[n]$ (the Hartree energy) to (2.24), gives

$$E_{KS}[n]=T_s[n]+E_H[n]+\{T[n]-T_s[n]+V[n]-E_H[n]\}+\int V_{ext}(r)n(r)d^3r \tag{2.36}$$

$$E_{KS}[n]=T_s[n]+E_H[n]+E_{xc}[n]+\int V_{ext}(r)n(r)d^3r \tag{2.37}$$

where the exchange-correlation energy is defined as:

$$E_{xc}[n]=T[n]-T_s[n]+V[n]-E_H[n] \tag{2.38}$$

Here the difference in kinetic energy $T[n]-T_s[n]$ is the kinetic contribution to correlation and the difference $V[n]-E_H[n]$ is the electrostatic and Hartree-Fock exchange contribution to correlation. Though the exchange correlation potential spans all important quantum many-body effects, the evaluation of exact exchange correlation functional is very challenging. Therefore, approximations are done by simple functionals as discussed in Section 2.5.

The Hartree energy $E_H[n]$ in equation 2.27 is the classical electrostatic energy for a charge distribution *n(r)* given by equation 2.10. The non-interacting kinetic energy T_s*, density* *n(r)* and particle count *N* of the non-interacting system can be evaluated from the single particle wave functions as:

$$T_s[n] = -\frac{1}{2}\sum_i^N \langle \psi_i | \nabla^2 | \psi_i \rangle \tag{2.39}$$

$$n(r) = \sum_i^N |\psi_i(r)|^2 \tag{2.40}$$

$$N = \int n(r) d^3 r \tag{2.41}$$

T_s[n] is explicitly expressed as a functional of the orbital's whereas all other terms are functionals of the density, then solution of equation 2.39 is the problem of minimization with respect to density *n(r)*.

$$\frac{\delta E_{KS}}{\delta \psi_i^*(r)} = \frac{\delta T_s[n]}{\delta \psi_i^*(r)} + \left[\frac{\delta E_{ext}[n]}{\delta n(r)} + \frac{\delta E_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)}\right]\frac{\delta n(r)}{\delta \Psi_i^*(r)} = 0 \tag{2.42}$$

From equation (2.35) and (2.37):

$$\frac{\delta T_s[n]}{\delta \psi_i^*(r)} = -\frac{1}{2}\nabla^2 \psi_i(r) \quad \text{and} \quad \frac{\delta n(r)}{\delta \psi_i^*(r)} = \psi_i(r) \tag{2.43}$$

which leads to the Schrödinger like equations:

$$(H_{KS} - \varepsilon_i)\psi_i(r) = 0 \tag{2.44}$$

where the ε_i are the eigen values, and H_{KS} is the effective Hamiltonian

$$H_{KS}(r) = -\frac{1}{2}\nabla^2 + V_{KS}(r) \tag{2.45}$$

$$V_{KS}[r] = V_{ext}[r] + V_H[r] + V_{xc}[r] \tag{2.46}$$

Equations (2.44)-(2.46) are the well-known Kohn-Sham equations, where the total energy E_{KS} and density n(r) are given by (2.36) and (2.40). 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 $E_{xc}[n]$ is known.

2.4 Exchange and correlation functionals

Formulating approximations for exchange correlation energy (E_{xc}) has been an active field of research in density functional theory. Different flavours of functionals are developed for particular cases where they have been validated by comparison with experimental data. Among them, the most widely used approximations are the local density approximation (LDA) and the generalized gradient approximation (GGA). The exchange correlation functionals are calculated as:

$$\boldsymbol{E_{xc} = \int n(r)\, V_x(r) F_{xc}(\ldots\ldots)d^3r} \tag{2.47}$$

where F_{xc} is the enhancement and its parameters depend on whether the functional is LDA or GGA or any other high level functionals.

2.4.1 Local density approximation (LDA)

In local density approximation (LDA), the functional is assumed to have dependency on electron density of homogeneous electron gas (HEG).[24] It is the most widely used approximation for exchange-correlation energy. It is assumed that the infinitesimal volume of a system has same exchange correlation energy as that of homogeneous electron gas at the same density. The exchange and correlation energy under LDA is defined as:

$$E_{xc}^{LDA}[n] = \int^{\int^{3}} n(r)\varepsilon_{xc}^{hom(n)} \tag{2.48}$$

Taking spin into account one can have spin polarized generalization of the approximation (LSDA) which is given as:

$$E_{xc}^{LSDA}\left[n^{\uparrow}, n^{\downarrow}\right] = \int^{\int^{3}} n(r)\varepsilon_{xc}^{hom}\left(n^{\uparrow}, n^{\downarrow}\right) \tag{2.49}$$

$$E_{xc}^{LSDA}\left[n^{\uparrow}, n^{\downarrow}\right] = \int n(r)\left[\varepsilon_{x}^{\text{hom}}\left(n^{\uparrow}, n^{\downarrow}\right) + \varepsilon_{c}^{\text{hom}}\left(n^{\uparrow}, n^{\downarrow}\right)\right] d^{3}r \tag{2.50}$$

Homogeneous electron gas is a system analogous to ideal metal in neutral state with electrons moving in background of positive charge distribution. The electron density $n = N/\Omega$ is assumed to remain constant everywhere. LDA yields correct geometrical parameters while bulk moduli and phonon frequencies are accurate upto few percent. However, the density varies rapidly in realistic systems for which LDA does not yield correct physical properties. The form of the exchange and correlation energy functionals are known exactly or at least to very high accuracy for homogeneous electron gas model.

The exchange-correlation (XC) functional is the sum of a correlation functional and an exchange functional:

$$\varepsilon_{xc}^{\text{hom}}(n) = \varepsilon_{x}^{\text{hom}}(n) + \varepsilon_{c}^{\text{hom}}(n) \tag{2.51}$$

The per electron exchange energy for homogeneous system is:

$$\varepsilon_x^{\text{hom}}(n) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n(r)^{1/3} \tag{2.52}$$

$$n = \left(\frac{4\pi}{3} r_s^3\right)^{-1} \tag{2.53}$$

In LDA, the exchange of uniform electron gas of a density equal to the density at the point where the exchange is to be assessed is used:

$$E_{xc}^{LDA}[n] = -\frac{3}{4\pi}\left(3\pi^2\right)^{1/3} \int n^{4/3}(r)\,d^3r \tag{2.54}$$

However, a serious limitation of LDA is that it cannot provide estimation to the long-ranged van der Waals (vdW) interaction.

2.4.2 Generalized gradient approximation (GGA)

Generalized gradient approximation (GGA) is an improvement over LDA where first order gradient terms are included in such away that the exchange-correlation energy is dependent on the local densities and their gradients.[25] The functionals are defined in generalized form as:

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

$$E_{xc}^{GGA}[n^{\uparrow}, n^{\downarrow}] = \int n(r)\varepsilon_x^{\text{hom}}(n)F_{xc}\left(n^{\uparrow}, n^{\downarrow}, \left|\nabla n^{\uparrow}\right|, \left|\nabla n^{\downarrow}\right|\right)d^3r \tag{2.56}$$

where F_{xc} is dimensionless quantity and $\varepsilon_x^{\text{hom}}(n)$ is the exchange energy.

The GGA has gained much attention owing to its moderate computational cost and simplicity. Among many functionals, the three most popular functionals were suggested by Becke,[25] Perdew and Wang (PW)[26] and Perdew, Burke and Enzerhof (PBE).[27] Many studies have demonstrated that the GGA improves the LDA error in calculating cohesive energies of solids and molecules[28] and gives more accurate equilibrium lattice parameters compared to LDA.[29,30]

2.5 Density functional perturbation theory (DFPT)

To describe the chemical structure and binding of atoms and molecules, the understanding of vibrational frequencies and displacement patterns is very important. Techniques such as Infrared, Raman and Inelastic scattering are used to measure vibrational frequency. 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.[31-33]

In DFPT, V, E, H, ψ_{kn}, n(r), etc. are subjected to perturbation. The external potential υ_{ext} is expanded as

$$\upsilon_{ext} = \upsilon_{ext}^{0} + \lambda\upsilon_{ext}^{(1)} + \lambda^2\upsilon_{ext}^{(2)} + \lambda^3\upsilon_{ext}^{3} + \ldots\ldots \tag{2.57}$$

Similar expansion is done for E, H, ψ_{kn}, n(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. One can write energy as functional of density as:

$$E[\psi] = \min_{\psi^{(1)}} \textstyle\sum_{i\in occ}\langle\psi_i|T + V_{ext}|\psi_i\rangle + E_{Hxc}[n] \tag{2.58}$$

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

$$+\frac{1}{2}\frac{\delta^{2}{}_{EHxc}}{\delta n(r)\delta n(r')}\bigg| n^{(0)} n^{(1)}(r) n^{(1)}(r') d^3r d^3r' + \int \frac{d}{d\lambda}\frac{\delta E_{Hxc}}{\delta n(r)}\bigg|_{n^{(0)}} n^{(1)}(r) d^3(r) \frac{1}{2}\frac{d^2 E_{Hxc}}{d\lambda^2}\bigg|_{n^{(0)}} \qquad (2.59)$$

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

$$\left\langle \psi_i^{(0)} \middle| \psi_j^{(j)} \right\rangle = 0 \qquad (2.60)$$

The dynamical matrix is Hermitian and its eigenvalues $\omega_j^{\,2}(\boldsymbol{q})$ are real, and eigenvectors $\xi_j(\boldsymbol{q})$ are orthonormal. In addition, the phonon band structure $\omega_j(\boldsymbol{q})$ directly corresponds to density of states which provides the information of phonons in whole Brillouin zone (BZ).[34-39]

To obtain the information of the whole phonon spectrum, the scanning of Brillouin-zone is important. These scanning consists in $D_{\alpha\beta}\begin{pmatrix}\boldsymbol{q}\\ kk'\end{pmatrix}$-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 $n_1, n_2, n_3 = -N,., N$. In total, this includes $N_i = (2N+1)^{40}$ points in Brillouin zone. The phonon density of states (DOS) is determined by summation over all the phonon states and is defined by[34,39,40]

$$g(\omega) = D'\int_{BZ}\sum_j \delta\left(\omega-\omega_j(\boldsymbol{q})\right)dq = D'\int_{BZ}\sum_{jp}\delta\left(\omega-\omega_j(\boldsymbol{q})\right)dq_p \qquad (2.61)$$

Here, D' is a normalization constant such that $\int g(\omega)d\omega = 1$; and g($\omega$)d$\omega$ is the fraction of phonons with energies ranging from ω to ω + dω. The mesh index (‘p’) is characterized by ‘$\boldsymbol{q}$’

in the discretized irreducible Brillouin zone, where d$\boldsymbol{q}_p$ provides the weighting factor corresponding to the volume of p^{th} mesh in $\boldsymbol{q}$-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. It is defined as follow:

$$g(\omega) \;=\; D'\sum_{jp}\delta\left(\omega-\omega_j(q)\right)\frac{|\xi_j(q)|^2}{\sum_{jp}|\xi_j(q)|^2} \tag{2.62}$$

2.6 Dispersion correction to density functional theory

The Kohn Sham formulation of DFT is to study the electronic structure of materials inorder to provide reasonable prediction for distinct properties of molecules and solids. However, various approximations such as LDA, GGA and hybrid functional failed to account long-range van der Waals (vdW) interaction.[41-43] The vdW interaction plays an important role in initial stage of physical absorption, crystal growth and chemical reaction. To assess the vdW interaction, efforts have been devoted to formulate recipes for the non-local exchange-correlation term.[19]

The vdW correction to total energy is given by

$$\boldsymbol{E_{DFT-D} = E_{KS-DFT} + E_{disp}} \tag{2.63}$$

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[44]

$$\boldsymbol{E_{disp} = -s_6 \sum_{i=1}^{(N_{at}-1)} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij})} \tag{2.64}$$

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

$$\boldsymbol{f_{dmp}(R_{ij}) = \frac{1}{1+e^{-d(R_{ij}/R_{0ij}-1)}}} \tag{2.65}$$

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

$$\boldsymbol{C_6^{ij} = \sqrt{C_6^i C_6^j}} \tag{2.66}$$

$$\boldsymbol{R_{0ij} = R_{0i} + R_{0j}} \tag{2.67}$$

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

2.7 Elastic properties

Response of crystals to the external forces is determined by the elastic properties of materials characterized by Young's modulus, shear modulus, bulk modulus and Poisson's ratio. Elastic constants which reveal the bonding character of atoms, atomic planes and structural stability of materials, are also linked thermodynamically to the specific heat, thermal expansion and Debye temperature.[45]

The total energy of strained system E_{tot}, having volume V can be expressed as:

$$E_{tot} = E_{tot}^{0} + P(V - V_0) + \Phi_{elast} \tag{2.68}$$

where E_{tot}^{0} is the total energy of crystal at initial stage with volume V_0 without strain. Φ_{elast} is the elastic energy and P is the pressure defined by:

$$P = -\left(\frac{\partial E_{tot}^{0}}{\partial V}\right)(V_0) \tag{2.69}$$

The strained lattice vector $\vec{a}$ is related to the unstrained lattice ($\vec{a}_0$) by $\vec{a} = \left(I + \bar{\varepsilon}\right).\vec{a}_0$, where I is the identity matrix and $\bar{\varepsilon}$ is the strain tensor. The elastic constants (C_{ijkl}) can be defined using elastic energy Φ_{elast} following Hooke's law as:

$$\Phi_{elast} = \frac{V}{2} C_{ijkl}\varepsilon_{ij}\varepsilon_{kl} \qquad (i, j, k, l = 1, 2, 3) \tag{2.70}$$

or, in the Voigt's two suffix notation:

$$\Phi_{elast} = \frac{V}{2} C_{ij}\varepsilon_{i}\varepsilon_{j} \qquad (i, j = 1, 2, 3, 4, 5, 6) \tag{2.71}$$

Since in Equation (2.68), the (V-V_0) term follows linear relationship with strain, it is possible to derive elastic constants from the second order derivatives of E_{tot}:

$$C_{ij} = \frac{1}{V_0}\frac{\partial^2 E_{tot}}{\partial \varepsilon_i \partial \varepsilon_j} \tag{2.72}$$

Elastic tensor of cubic crystal has only three independent elastic constants, C_{11}, C_{12} and C_{44}:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{12} & & & \\ C_{12} & C_{11} & C_{12} & & & \\ C_{12} & C_{12} & C_{11} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{44} \end{pmatrix} \tag{2.73}$$

All the three elastic constants of cubic crystal can be determined by solving three equations implying that three types of strain must be applied to the crystal. Bulk modulus of crystal can be evaluated by fitting $E_{tot}(V)$ with the third order Birch-Murnaghan equation of state[46] where the E_{tot} is computed for different values of strain. Bulk modulus is finally derived using:

$$B(V_0) = \frac{1}{3}(C_{11} + 2C_{12}) = V_0\left(\frac{\partial^2 E_{tot}}{\partial V^2}\right)(V_0) \tag{2.74}$$

To evaluate the elastic tensors, volume conservative tetragonal strains are applied where one varies the axial ratio $\frac{c}{a} = 1 + e$ leading to the strain tensor:

$$\bar{\varepsilon} = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_1 & 0 \\ 0 & 0 & \frac{1}{(1+\varepsilon_1)^2} - 1 \end{pmatrix} \text{ or in Voigt notation } \begin{pmatrix} \varepsilon_1 \\ \varepsilon_1 \\ \frac{1}{(1+\varepsilon_1)^2} - 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{2.75}$$

where $\varepsilon_1 = (1+e)^{-1/3} - 1$. The elastic energy resulting from tetragonal strain to second order in ε_1 can be written as:

$$\frac{\Phi_{tetra}}{V_0} = 3(C_{11} - C_{12})\varepsilon_1^2 + o(\varepsilon_1^3) \tag{2.76}$$

$E_{tot}(\varepsilon_1)$ is fitted to a N degree polynomial P which is decided by the number of deformed structures ($N \leq$ (Number of data) - 1). The value of $(C_{11}\text{-}C_{12})$ is obtained from computation of second of derivative of P:

$$P''(\varepsilon_1 = 0) = 6V_0(C_{11} - C_{12}) \tag{2.77}$$

The mechanical stability of a system can be studied by evaluating elastic constants from the ground state total energy calculations. A given crystal cannot exist in a stable or metastable phase if their elastic constants do not follow the stability criteria determined by themselves. The mechanical stability criteria for cubic crystals at ambient conditions are:[47,48]

$$C_{11} + 2C_{12} > 0,\ C_{44} > 0,\ C_{11} - C_{12} > 0 \text{ and } C_{12} < B < C_{11} \tag{2.78}$$

and the isotropic bulk modulus (B) is given by:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{2.79}$$

The Born criteria for 2D hexagonal structure are:[49]

$$C_{11} > 0.0,\ C_{11}\text{-}C_{12} > 0.0 \text{ and } C_{66} > 0.0 \tag{2.80}$$

The elastic modulus characterized by the Young's modulus (E), shear modulus (G_H), Poisson's ratio (σ) and anisotropic ratio (A) play an important part in determining the strength of the material[50] and are calculated using following relations:

$$E = \frac{9BG_H}{3B+G_H} \tag{2.81}$$

$$G_H = \frac{G_V+G_R}{2} \tag{2.82}$$

where Voigt shear modulus is:

$$G_V = \frac{C_{11}-C_{12}+3C_{44}}{5} \tag{2.82}$$

and Reuss shear modulus is:

$$G_R = \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})} \tag{2.84}$$

$$\sigma = \frac{3B-2G}{2(3B+G)} \tag{2.85}$$

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