Chapter 2:
Methodology

2.1 Introduction to Many-body Problem

The advent of quantum mechanical theory, driven by the time-independent Schrödinger equation, has emerged as an effective approach to characterize simpler systems with only one electron, like hydrogen atom. The time-independent Schrödinger equation is given as;

$$\hat{H}\psi(r) = E\psi(r) \text{ -----(2.1)}$$

where $\hat{H}$ is Hamiltonian operator which represents the sum of kinetic and potential energies, E corresponds to energy eigenvalue of the stationary state characterize by the wave function $\psi(r)$. The Hamiltonian operator in equation 2.1 is represented by;

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \text{ -----(2.2)}$$

In the case of hydrogen atom, variable separable method is employed to evaluate the solution of Schrödinger equation, which eventually yields the exact value for the ground state energy. However, for the many-body systems, wave-function denoted as $\psi(r_1, r_2, ..., r_N, R_1, R_2, ..., R_N)$, represents N electrons with position coordinates r_1, r_2, ..., r_N and N nuclei with position coordinates R_1, R_2, ..., R_N, respectively. The complexity increases with inclusion of more variables in such many-body systems. Therefore, exact solution of Schrödinger equation for many-body systems has never been found. In addition, the interactions between electron-electron, electron-ion and ion-ion comes into the picture for which the Hamiltonian is represented as;

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{e,e} + \hat{V}_{e,n} + \hat{V}_{n,n} \text{ -----(2.3)}$$

where $\hat{T}_e + \hat{T}_n$ represents kinetic energy and $\hat{V}_{e,e} + \hat{V}_{e,n} + \hat{V}_{n,n}$ represents the potential energy terms to incorporate electron-electron, electron-ion and ion-ion interactions, respectively. From the Hamiltonian describe by equation (2.3), the time-independent Schrödinger equation can be written as;

$$\hat{H}\psi(r) = \Bigg\{ -\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial r_i^2} - \frac{\hbar^2}{2M}\sum_l \frac{\partial^2}{\partial R_l^2} + \frac{1}{2}\sum_{\substack{l,l' \\ l\neq l'}} \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l Z_{l'}}{|R_l - R_{l'}|} + \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|r_i - r_j|} -$$

$$\sum_i \sum_l \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l}{|r_i - R_{l'}|}\Bigg\}\psi(r) = E\psi(r) \text{ -----(2.4)}$$

where, i and l represents the indices run over the electron and ion while the m_e and M are respective masses of electrons and ion, Z_l and $Z_{l'}$ represents charge of ions. Moreover, $|R_l - R_{l'}|$, $|r_i - r_j|$ and $|r_i - R_{l'}|$ defines the distances between ion-ion, electron-electron and electron-ion, respectively. The solution to equation (2.4) yields the eigen state and energy eigen value which gives the information about the ground state of system under consideration. Moreover, solving the equation (2.4) requires only atomic mass and charge of the electrons and ions. This particular method, known as *first-principles* calculation which does not necessitate the use of any adjustable parameters. The persistent complexities associated with it make the solution of equation (2.4) for many-body systems unattainable. Over the years, several approximations to this theory have been put forth which are discussed in subsequent sections.

2.1.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation permits the independent treatment of electronic and ionic motions by decoupling them. The core notion is that the electrons have significantly faster movement as compared to the ions, since the ions are 10^3–10^5 times heavier. Consequently, it is possible to neglect the ionic contribution in the Hamiltonian equation (2.3). This approach is known as Born-Oppenheimer Approximation.[1] Therefore, the second term of equation (2.3) vanishes and last term becomes constant. The modified equation (2.3) is written as;[2]

$$\hat{H} = \hat{T}_e + \hat{V}_{e,e} + \hat{V}_{e,n} + Constant \text{ -----(2.5)}$$

The modified Hamiltonian is described by the sum of kinetic energy of electrons, electron-electron interaction and electron-ion interaction regarded as external potential (V_{ext}). In this regard, equation (2.5) can be written as;

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial r_i^2} + \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|r_i - r_j|} + \hat{V}_{e,n} + Constant \text{ -----(2.6)}$$

where, Constant $= \frac{1}{2}\sum_{\substack{l,l'\\ l\neq l'}} \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l Z_{l'}}{|R_l - R_{l'}|}$. Despite being simplified, the electronic part of the Hamiltonian still poses a challenge to solve. Therefore, the equation necessitates further approximations for its solution which is discussed in subsequent sections.

2.1.2 Hartree Approach

The classical electrostatics governing the Coulomb interactions between the electrons need to be addressed for further simplifying the solution of many-body systems. Hartree addressed this by modifying the problem into the independent electron approximation, thereby simplifying the calculations.[3–6] He treated the n-electron system as a group of independent one-electron systems (without any interaction among them), wherein each electron experiences an averaged electrostatic potential originating from the presence of other electrons. In accordance with the Hartree approximation, the Schrödinger wave equation can be formulated as follow;

$$\left(-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial r_i^2} + \hat{V}_{ext} + \hat{V}_H\right)\psi(r) = E\psi(r) \text{ -----(2.7)}$$

here, $\hat{V}_H$ is the Hartree potential which is described by;

$$\hat{V}_H = \int \frac{\rho(r')}{|r - r'|}\, dr' \text{ -----(2.8)}$$

Since, this approach employs mean field theory, it is unable to include actual exchange-correlation interaction takes place between the electrons. Also, many-body Hartree wave function fails to incorporate antisymmetric requirement (unable to account the fermionic character of electron wave functions) which demands further approximations.[7,8]

2.1.3 Hartree-Fock Approach

Given that electrons are fermions, it is imperative to handle their analysis within the framework of Fermi-Dirac statistics. In this regard, unlike to product wave function, the determinantal function is employed in this approach.[9,10] The asymmetric wave function is represented in equation (2.9) which fulfil the Pauli exclusion principle. Also, the change in sign when two rows or columns are interchanged ensures antisymmetric nature of the wave function in order to account for the fermionic nature of electrons.

$$\psi_{HF}[(\overrightarrow{r_1},\sigma_1),(\overrightarrow{r_2},\sigma_2),\ldots,(\overrightarrow{r_N},\sigma_N)] = -\,\psi_{HF}[(\overrightarrow{r_1},\sigma_1),(\overrightarrow{r_2},\sigma_2),\ldots,(\overrightarrow{r_N},\sigma_N)] \text{ -----(2.9)}$$

The slater determinant which represents antisymmetric wave function is written as;

$$S = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\overrightarrow{r_1},\sigma_1) & \psi_1(\overrightarrow{r_2},\sigma_2) \ldots & \psi_1(\overrightarrow{r_N},\sigma_N) \\ \psi_2(\overrightarrow{r_1},\sigma_1) & \psi_2(\overrightarrow{r_2},\sigma_2) \ldots & \psi_2(\overrightarrow{r_N},\sigma_N) \\ \vdots & \vdots & \vdots \\ \psi_N(\overrightarrow{r_1},\sigma_1) & \psi_N(\overrightarrow{r_2},\sigma_2) \ldots & \psi_N(\overrightarrow{r_N},\sigma_N) \end{vmatrix} \text{ -----(2.10)}$$

here, $\frac{1}{\sqrt{N!}}$ is normalization factor. The minimization of expectation value with Lagrangian multiplier method leads to the Hartree-Fock equation which is given as follows;

$$\left(-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial r_i^2} + \hat{V}_{ext} + \hat{V}_H\right)\psi(r) - \frac{1}{2}\sum_{i,j}\sum_{j\neq i}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{\psi_j^*(r')\,\psi_j(r')\,\psi_j(r)}{|r-r'|}\partial^3 r\,\partial^3 r'$$

$$= E\psi(r) \text{ -----(2.11)}$$

This method improves upon the Hartree method by incorporating exchange energy of electrons through antisymmetric wave functions. The total energy under the Hartree-Fock approximation is the sum of kinetic energy of electrons, external energy due to interaction between nuclei and electrons, Hartree energy and exchange energy. However, total energy requires minimization for N particles Slater determinant which in turns computationally costly. Since, many-body wave functions incorporate the electron coordinates, it becomes a function of 3N variables. The solution of which is tedious and imposes high computational demands. By approximating the many-body problem into a single electronic density, density functional theory (DFT) resolves this issue which can be computationally feasible.

2.2 Density Functional Theory

The electron density, denoted as $n(\vec{r})$, could simplify the description of the electronic system significantly by relying on just three variables (x, y and z). Hohenberg and Kohn introduced DFT in 1964, which serves as a firm and exact theoretical framework for such a description. As the many-electron problem is simplified into a density dependent 3-coordinate system, the computational cost is also decreases. The framework of DFT mainly includes Thomas-Fermi theory,[11,12] Hohenberg-Kohn theorems[13] and Kohn-Sham equations[14] which is discussed in subsequent sections.

2.2.1 Thomas-Fermi Theory

The origin of density based approach for the solution of many body systems, firstly given by the Thomas and Fermi in 1927, which is known as Thomas-Fermi theory.[11,12] This theory proposes the use of electron density as basic variable rather than the single particle wave function and thus, total energy of the system can be written as functional of electron density. In the case of N interacting electrons, the kinetic energy in terms of electron density $n(\vec{r})$ is given by

$$T_{TF} = C_k \int n(\vec{r})^{\frac{5}{3}} \, d^3r \text{ -----(2.12)}$$

Therefore, total energy as a functional of $n(\vec{r})$ can be written as equation (2.13) with kinetic energy, electrostatic energy and external potential terms, respectively.

$$E = T_{TF} + \int V_{IE}(\vec{r})\, n(\vec{r})\, d^3r + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r}-\vec{r}'|}\, d^3r\, d^3\vec{r}' \text{ -----(2.13)}$$

The minimization of equation (2.13) has been done by Lagrangian multiplier method. This theory does not incorporate the contribution of exchange energy. Inclusion of exchange interaction and correlation functional was done by Dirac as extension of this approximation but failed to establish shell structure and behaviour of atoms in complex systems.

2.2.2 Hohenberg-Kohn Theorems

As we discussed in the realm of the Thomas-Fermi theory, the behaviour of electronic systems could be described in terms of the $n(\vec{r})$. In 1964, Hohenberg and Kohn gave two theorems, which serves as a firm and exact theoretical foundation of DFT.[13] The two theorems are as follow;

Theorem I:

"The external potential $\hat{V}_{ext}(\vec{r})$ is a unique functional of the electron density $n(\vec{r})$. As a result, the total ground state energy E of any many body systems is also a unique functional of $n(\vec{r})$, that is, $E = E[n]$."

According to the aforementioned statement, the Hamiltonian operator (equation (2.3)) can be uniquely derived from the electron density, given that the ground state is unique functional of density. Let us consider two different external potentials $V_{ext}^{(1)}(\vec{r})$ and $V_{ext}^{(2)}(\vec{r})$ corresponding to separate ground state wave functions say, $\psi^{(1)}$ and $\psi^{(2)}$ which have same ground state density $n(\vec{r})$. There must be two Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ corresponding to two different external potentials.

$$E^{(1)} = \langle\psi^{(1)}|\, \hat{H}^{(1)}|\psi^{(1)}\rangle < \langle\psi^{(2)}|\, \hat{H}^{(1)}|\psi^{(2)}\rangle \text{ -----(2.14)}$$

The last can also be written as;

$$\langle\psi^{(2)}|\, \hat{H}^{(1)}|\psi^{(2)}\rangle = \langle\psi^{(2)}|\, \hat{H}^{(2)}|\psi^{(2)}\rangle + \langle\psi^{(2)}|\, \hat{H}^{(1)} - \hat{H}^{(2)}|\psi^{(2)}\rangle \text{ -----(2.15)}$$

$$= E^{(2)} + \int\left[V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r})\right] n(\vec{r})\, d^3r \text{ -----(2.16)}$$

From equation (2.14) and (2.16),

$$E^{(1)} < E^{(2)} + \int\left[V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r})\right] n(\vec{r})\, d^3r \text{ -----(2.17)}$$

Also,

$$E^{(2)} < E^{(1)} + \int\left[V_{ext}^{(2)}(\vec{r}) - V_{ext}^{(1)}(\vec{r})\right] n(\vec{r})\, d^3r \text{ -----(2.18)}$$

By adding equation (2.17) and (2.18), we get

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)} \text{ -----(2.19)}$$

The above equation contradicts our assumptions and therefore we can conclude that there is only one $V_{ext}(\vec{r})$ which can uniquely produce the ground state density $n(\vec{r})$ and vice versa.

Theorem II:

"The functional $E[n]$ for the total energy has a minimum equal to the ground state energy at the ground state density."

This theorem implies that,

$$E_{HK}[n] = T[n] + E[n] + \int V_{ext}(\vec{r})\, n(\vec{r})\, d^3r \text{ -----(2.20)}$$

while, the universal functional of electron density $n(\vec{r})$ is defined as,

$$F_{HK}[n] = T[n] + E[n] \text{ -----(2.21)}$$

Substituting equation (2.21) in (2.20) we get,

$$E_{HK}[n] = F_{HK}[n] + \int V_{ext}(\vec{r})\, n(\vec{r})\, d^3r \text{ -----(2.22)}$$

Hence, for known $F_{HK}[n]$, we can calculate exact solution of the Schrödinger equation without any approximations used. Suppose we have a system that exhibits a ground state density $n^1(\vec{r})$ corresponds to the external potential $V_{ext}^1(\vec{r})$ than the expectation value of the Hamiltonian has the form,

$$E^{(1)} = E_{HK}[n^1] = \langle \psi^{(1)} |\, \hat{H}^{(1)} | \psi^{(1)} \rangle \text{ -----(2.23)}$$

Hence, the electron density $n^1(\vec{r})$ for the ground state energy is lower than any other electron density $n^2(\vec{r})$ which leads to the equation (2.24).

$$E^{(1)} = \langle \psi^{(1)} |\, \hat{H}^{(1)} | \psi^{(1)} \rangle < \langle \psi^{(2)} |\, \hat{H}^{(1)} | \psi^{(2)} \rangle = E^{(2)} \text{ -----(2.24)}$$

This *variational principle* based on density is also known as the Hohenberg-Kohn theorem wherein, lowest energy state is obtained by the universal functional only when the input electron density is equivalent to the ground state electron density.

2.2.3 Kohn-Sham Approach

The unique significance of the Hohenberg and Kohn[14] theorem lies in its contribution to establishing the fundamental principles of density functional theory.[15] To find the functional $F_{HK}[n]$ which gives the exact solution is the major challenge in the Hohenberg-Kohn theorems. In this regard, Kohn and Sham (KS) came up with a better approach in which they replace N-electrons to that with fictious system of one electron.[14] According to KS, there is a single particle potential $V_{eff}(r)$ capable of producing the same ground state density for non-interacting electrons as the one obtained with interacting problem. Therefore, total energy within KS approach is written as;

$$E_{KS}[n] = T_S[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\vec{r})\, n(\vec{r})\, d^3r \text{ -----(2.25)}$$

where $T_S[n]$ and $E_H[n]$ represents non-interacting kinetic energy and energy term under Hartree approximation, respectively. The $T_S[n]$ and $E_H[n]$ are defined as;

$$E_H[n] = \frac{1}{2} \iint \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r} - \vec{r}'|}\, d^3r\, d^3\vec{r}' \text{ -----(2.26)}$$

$$T_S[n] = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle \text{ -----(2.27)}$$

$$n(r) = \sum_i^N |\phi_i(r)|^2 \text{ -----(2.28)}$$

$$N = \int n(r)\, d^3r \text{ -----(2.29)}$$

Here, $T_S[n]$ was described in the context of KS orbitals. As we know, energy of the wave function changes under the position exchange of two particles as a consequence of anti-symmetric characteristics. This is termed as exchange energy (E_x). Conversely, when two electrons possess opposite spin orientations, they can share an orbital. Since they both carry negative charges, they exert a repulsive force on each other. This is known as electronic correlation and the energy is denoted as E_c. However, the exact formulation for the correlation energy is lacking, the sum of the E_x and E_c is collectively known as exchange-correlation energy, E_{xc}. The functional derivative of the E_{xc}, represented as V_{xc}, is the component that enhances the efficiency and advantages of DFT compared to the HF approximation:

$$V_{xc}[n(r)] = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \text{ -----(2.30)}$$

In practice, electrons move within an V_{eff}, which indirectly encompasses electronic interactions. The electron-electron interaction in KS equations is replaced by the interaction between electrons and a medium, which effectively represents electron-electron interactions.

The KS equation in the Schrödinger form is written as;

$$\hat{H}_{KS}\phi_i(r) = E_{KS}\,\phi_i(r) \text{ -----(2.31)}$$

and the Hamiltonian is;

$$\hat{H}_{KS} = -\frac{1}{2}\sum \nabla^2 + V_{eff} \text{ -----(2.32)}$$

where V_{eff} represents the sum of the three potential terms ($V_{ext} + V_H + V_{xc}$). By adjusting the ground state electron density of the non-interacting system to that of real interacting system, the iterative method is employed to solve the Hamiltonian in order to get system's ground state energy and density. This method is known as Self-consistent method where the initial guess is based on electron density. The determination of each potential term is based on the trial density where the energy convergence occurs. KS approach reduces many electrons problem to one electron problem and found effective but the exchange-correlation potential (V_{xc}) is still not known exactly and the suitable approximations has to be made which is discussed in next section.

2.3 Exchange-Correlation Functionals

We have now established reasonable framework to determine the electronic ground state of the system and correspondingly many required properties can be obtained using KS approach is we have the electron density on our plate. In particular, V_{xc} term in KS equation plays a vital role in terms of the accuracy of solutions. Over the time, several approximations were developed to effectively describe the exchange-correlation (XC) functionals. In general, they can categorize and comprehended using Jacob's ladder in which moving upwards in the rungs increases the computational cost for the system being examined. These functionals can be given as local, semi-local and non-local approximations. The functionals originating from the local density approximation (LDA) and the generalized gradient approximation (GGA) are the three most popular and commonly used.

2.3.1 Local Density Approximation

When evaluating approximations for the XC energy, one easy way to address the varying electron densities in a system is to assume that electrons perceive the overall landscape in the same manner as they perceive local surroundings.[16] This is similar to the homogeneous free electron gas. The XC energy in the context of LDA is given as;

$$E_{xc}^{LDA}[n(r)] = \int n(r)\,\epsilon_{xc}[n(r)]d^3r \text{ -----(2.33)}$$

where ϵ_{xc} represents the per particle XC energy for interacting free electron gas with density $n(r)$. This is local functional and shows excellent results for the systems with relatively slowly varying densities like metals. LDA satisfies the XC energy sum rule very well as exchange overestimates and correlation underestimates the values. Nevertheless, LDA does not satisfies the asymptotic behaviour of the potential and additionally underestimates the band gaps in semiconductors and insulators.[17]

2.3.2 Generalized Gradient Approximation

It is evident that the real systems lack homogeneity and display differing density distributions around electrons. To enhance the accuracy of XC functionals, GGA came from Herman's (1969) proposition which includes both local and semi-local characteristics, specifically, the electron density and its gradient at a particular point.[18] The XC functional according to GGA is defined as;

$$E_{xc}^{GGA}[n(r)] = \int n(r)\,\epsilon_{xc}[n(r), \nabla\,[n(r)]]d^3r \text{ -----(2.34)}$$

Unlike $E_{xc}^{LDA}[n(r)]$, there is no single functional equation that adequately describes the GGA data. Consequently, the practical representation of GGA takes the LDA as its foundation and incorporates an enhancement factor F(s) to directly modify the LDA energy.

$$E_{xc}^{GGA}[n(r), s] = \int n(r)\,\epsilon_{xc}^{LDA}[n(r)]F(s)d^3r \text{ -----(2.35)}$$

here, $s = C \frac{|\nabla n(r)|}{n^{4/3}(r)}$. Typically, s ranging from 0 to 3 in solids. Several variations of GGA have been suggested, and the commonly favoured options include PW91 (Perdew and Wang, 1992; Perdew et al., 1992)[19] and PBE (Perdew et al., 1996).[20] In terms of the structural properties, GGA performs better than LDA and is also highly accurate in determining the magnetic properties of solids.

2.4 Electronic Approximation

Accurately solving the KS equations requires determining the electron-ion interaction term, V_{ext}. However, this becomes challenging when dealing with solids that have a large number of electrons and experience significant electron oscillations near the nuclei. Defining V_{ext} accurately is difficult due to the differing behaviour of electrons depending on their location within the solid, whether in the core or valence. Core electrons, unlike valence electrons, do not actively contribute to bond formation and have minimal impact on the material's physical properties. Consequently, a distinct approach utilizing DFT can be employed to effectively address the treatment of core electrons in solid-state systems. To solve the KS equations effectively, it is necessary to expand the auxiliary KS orbitals using established basis functions. There are several options available for choosing basis functions, and Gaussian functions are widely employed in traditional quantum chemistry tools. Gaussian functions are especially suitable for orbitals that are highly localized. The field of theoretical chemistry has developed basis sets over time that are well-adapted to a diverse range of materials. However, one drawback of Gaussian functions is that the quality of the basis sets relies on the preferences of the user, and their transferability and ability to produce consistent computational results can be problematic when dealing with diverse systems. Alternatively, Planes waves are turns out to be effective as compared to Gaussian basis functions as they are well-suited for systems that exhibits periodic boundary conditions.

2.4.1 Pseudopotential Formalism

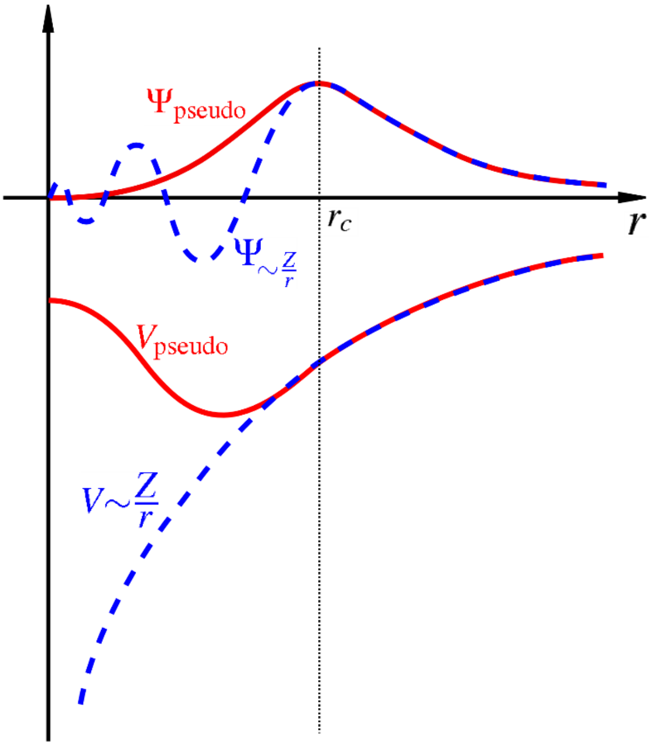

Figure 2.1: A schematic illustration of the concept of pseudopotential.

The use of Plane waves in calculation provides a simple approach which offers convenient way to evaluate forces and stress tensors like energy. Nonetheless, when dealing with system having localized core/valence orbitals within the core region of an atom, which needs to oscillate extensively to maintain the orthogonality with core orbitals. Consequently, the enormous Plane waves is necessary to accurately describe the significant variations in these orbitals. To overcome this challenge, pseudopotentials are implemented to represent the potential of the ionic core and the core electrons. This is elucidated in the Fig. 2.1 wherein; blue colour represents wave function for the coulomb potential of the nucleus while red colour indicates pseudo wave function. There are specific criteria that needs to be satisfied, which includes; (1) keeping the valence wave function unchanged outside the core region r_c, (2) achieving an exact match of the pseudo wave function within the core at the boundary, (3) maintaining continuity of the pseudo wave function and its first derivative at the boundary, and (4) ensuring that the pseudo wave function remains without any nodes within the core region. The pseudo wave functions are constructed to match the all-electron wave functions beyond a specified core radius r_c, ensuring their possible smoothness within this core radius. Over the years, different pseudopotentials such as norm-conserving, ultra-soft, projector-augmented wave methods and many more has been developed.[21–23]

2.4.2 Van der Waals Corrections

The standard DFT does not incorporate the van der Waals (vdW) interaction which is important to understand the adsorption behaviour of atoms and molecules on the surface and interfaces. Moreover, investigation of the materials with quantum confinement in particular direction such as 2D materials[24] must be treated with the inclusion of vdW interactions for the accurate calculation of several properties namely, electronic dispersion, adsorption energy etc., The solution for this is given by the Grimme which is known as D2 and D3 dispersion correction methods to include the long-range dispersion forces in the DFT.[25–27] The total energy with the inclusion of dispersion correction is written as;

$$E_{DFT+D} = E_{KS} + E_{dis} \text{ -----(2.36)}$$

where E_{KS} and E_{dis} represents the energies due to KS approach and Grimme's dispersion correction term, respectively. The empirical dispersion correction to the correlational functional E_{dis} is given by;

$$E_{dis} = -s_6 \sum_{i=1}^{(N_{at}-1)} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}\ (R_{ij}) \text{ -----(2.37)}$$

here, s_6 is global scaling factor and vary according to functionals used, N_{at} is number of total atoms, C_6^{ij} denotes the coefficient of dispersion for atomic pair ij, and R_{ij}^6 represents interatomic distance. The $f_{dmp}\ (R_{ij})$ indicates damping function which is given as;

$$f_{dmp}\left(R_{ij}\right) = \frac{1}{1+\ e^{-d(R_{ij}/R_{0ij}\ -1)}} \text{ -----(2.38)}$$

where, R_0 is sum of the atomic vdW radius. Also, C_6^{ij} and R_{0ij} are written as;

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \text{ -----(2.39)}$$

$$R_{0ij} = R_{0i} + R_{0j} \text{ -----(2.40)}$$

This method is also precisely calculated on larger elements.

2.5 Lattice Dynamics and Ab Initio Molecular Dynamics

2.5.1 Density Functional Perturbation Theory

The understanding of system's vibrational energies is essential for gaining insights into the arrangement of atoms, the bonding between them, and the overall dynamical stability of the system. This can be achieved experimentally using IR and Raman spectroscopy. However, the density functional perturbation theory provides a theoretical framework to address these phenomena, involving the investigation of the lattice dynamics of a material.[28–32] Applying linear response to the Kohn-Sham equation allows us to examine the alteration in the electron charge density solution caused by a slight perturbation in this approach. Therefore, external potential can be expanded in terms of a Taylor series. This can be represented as follow;

$$V_{\lambda,ext} = V_{ext} + \lambda\frac{\partial V_{ext(r)}}{\partial\lambda} + \frac{1}{2}\lambda^2\frac{\partial^2 V_{ext(r)}}{\partial\lambda^2} + \cdots \text{ -----(2.41)}$$

Likewise, electron density and energy functional are written as;

$$n_\lambda(r) = n(r) + \lambda\frac{\partial n(r)}{\partial\lambda} + \frac{1}{2}\lambda^2\frac{\partial^2 n(r)}{\partial\lambda^2} + \cdots \text{ -----(2.42)}$$

$$E_\lambda(r) = E(r) + \lambda\frac{\partial E(r)}{\partial\lambda} + \frac{1}{2}\lambda^2\frac{\partial^2 E(r)}{\partial\lambda^2} + \cdots \text{ -----(2.43)}$$

where, $\frac{\partial E(r)}{\partial\lambda} = \int n(r)\,\frac{\partial V_{ext(r)}}{\partial\lambda}\,dr$ which shows that the first-order derivative of energy is independent to the any derivative of $n(r)$ while the second-order derivative is explicitly depends on first-order derivative of $n(r)$. Hence, the dynamical matrix for phonon frequencies and Born effective charges is determined using the second-order derivative of energy.[28–32] In relation to the electron density, the energy functional is expressed as;

$$E\ [\psi] = \psi_{min}^{(1)}\ \sum_{i\epsilon_o cc} \langle \psi_i |\ T + V_{ext} | \psi_i \rangle + E_{H,xc}\ [n] \text{ -----(2.44)}$$

$$\frac{\partial^2 E(r)}{\partial \lambda^2} = \ \psi_{min}^{(1)}\ \sum_{i\epsilon_o cc} \left[\langle \psi_i^{(1)} \middle|\ H^{(0)} - \varepsilon_i^{(0)} \middle| \psi^{(1)} \rangle + \ \langle \psi_i^{(1)} \middle| V_{ext}^{(1)} \middle| \psi_i^{(0)} \rangle + \ \langle \psi_i^{(0)} \middle| V_{ext}^{(1)} \middle| \psi_i^{(1)} \rangle + \right.$$

$$\left. \langle \psi_i^{(0)} \middle| V_{ext}^{(2)} \middle| \psi_i^{(0)} \rangle \right] + \frac{1}{2} \left. \frac{\delta^2 E_{H,xc}}{\delta n(r) \delta n(r')} \right|_{n^{(0)}}\ n^{(1)}(r) n^{(1)}(r')\ d^3 r\ d^3 r' +$$

$$\int \left(\frac{d}{d\lambda} \left. \frac{\delta E_{H,xc}}{\delta n(r)} \right|_{n^{(0)}}\ n^{(1)}(r) d^3 r \right) \frac{1}{2} \left. \frac{\delta^2 E_{H,xc}}{d\lambda^2} \right|_{n^{(0)}} \text{ -----(2.45)}$$

here, variational principle is used to calculate the second-order energy term with respect to the first-order wave function provided that the first order wave-functions are orthogonal to the ground state wave-functions as represented in equation 2.46.

$$\langle \psi_i^{(0)} | \psi_j^{(j)} \rangle = 0 \text{ -----(2.46)}$$

Therefore, the obtained dynamical matrix is Hermitian. Consequently, the eigenvalues $\omega_j^2(q)$ and eigenvectors $\xi_j(q)$ are real and orthonormal, respectively. As the phonon band structure and density of states are related to each other, the details of phonon dispersions in the entire Brillouin zone are obtained.[31,33–37] Matrix diagonalization ($D_{\alpha\beta}$) spanning the entire Brillouin zone with the wavevector $\vec{q}$ in three dimensions, allows for the comprehensive determination of the phonon dispersion spectra. The summation over all the photon states will give the resultant phonon density of states which is defined as;

$$\mathrm{g}\ (\omega) = D' \int_{BZ} \sum_j \delta\ \left(\omega -\ \omega_j\ (q) \right) dq =\ D' \int_{BZ} \sum_{j,p} \delta\ \left(\omega -\ \omega_j\ (q) \right) dq_p \text{ -----(2.47)}$$

here D' is normalization constant such that $\int \mathrm{g}\ (\omega)\ d\omega = 1$ where $\mathrm{g}\ (\omega) d\omega$ represents fraction of phonon energies ranging from ω to $\omega + d\omega$.[31,33,38] In the discretized irreducible Brillouin zone, the mesh indices 'p' is characterized by the wave vector '$\vec{q}$', where the volume of p^{th} mesh in $\vec{q}$ space is given by the weighting factor dq_p.

2.5.2 Ab Initio Molecular Dynamics

The success of DFT can be largely credited to its scalability across different system sizes and its remarkable accuracy in replicating microscopic ground state properties throughout the years. Then, a question can be raised that is it possible to investigate the temperature effect on the system? As a solution, ab initio molecular dynamics (AIMD) method is implemented and successfully used to understand the effects of temperature and structural stability of materials. In classical molecular dynamics, the system is typically assumed as consisting of rigid and massive point-like nuclei. These nuclei are subject to forces derived from empirically devised effective potentials. By integrating Newton's equation of motion, one can obtain the microscopic trajectory of each atom in the system being studied. The AIMD is based on same consideration except that the calculation of forces is based on electron density obtained by DFT which makes this method more accurate. The computational cost is a serious concern for this method but it is highly effective for the systems with relatively lower number of atoms. In present thesis, we employed AIMD method to investigate the structural properties and stability of material at room temperature. Statistical mechanics involves determining the average of a physical variable by employing an ensemble average. However, the choice of ensemble in AIMD highly depends on desired properties under investigation. The two major ensembles used are microcanonical (N, V, E) and canonical (N, V, T) ensembles, respectively. In the microcanonical ensemble, the number of atoms and volume are fixed and the system evolves in time. The simulation generates spread-out configurations across the phase space, all of which reside on the constant energy hypersurface while in the canonical ensemble, the thermal averages are computed under a constant temperature, T. The numerical prescription to achieve this is to connect the system to the external heat bath. This heat bath has a significantly larger number of degrees of freedom compared to the system, ensuring that its temperature remains nearly constant. This approach was suggested by Andersen,[39] Nose,[40] and Hoover.[41] In simulation, they are referred to as Anderson thermostat or Nose-Hoover thermostat. We have used NVT ensemble in AIMD to calculate the thermal stability of the system at room temperature.

2.6 Computational Packages

This section will explore the computational packages utilized throughout the work conducted under this thesis which includes Quantum Espresso and Vienna Ab initio Simulation Package (VASP).

2.6.1 Quantum Espresso Package

In 2001, a group of renowned researchers, including Stefano Baroni, Paolo Giannozzi, Andrea Dal Corso, and others, began a collaborative project that would bring about a remarkable change. This initiative, known as Quantum Espresso,[42] captured the imagination of scientists and researchers around the world. Its open-source nature and endless possibilities turned it into a valuable resource in the fields of condensed matter physics and material chemistry. We have used Quantum Espresso for first-principles based structural optimization, to compute ground state energy of several 2D structures under the formalism of self-consistent field. All the calculations were performed with van der Waals dispersion correction as the present thesis have all 2D structures. To compute the electronic band structure, we have performed nonself-consistent field calculations to find the ground state eigen values for high symmetric crystal momentum. Furthermore, density of states, projected density of states and vibrational frequency calculation were performed using Quantum Espresso package.

2.6.2 Vienna Ab initio Simulation Package

VASP was developed in 1998 by Prof. George Kresse and his team.[43] It is package for performing ab initio quantum mechanical calculations using the PAW, and a plane wave basis set. Within the scope of this thesis, VASP is primarily utilized for calculation of AIMD using particular thermostat. VASP has basically four input files, which are:

INCAR: It is central input file which defines, how to do and what to do in the particular calculation.

POSCAR: A position card which includes geometrical parameters of structure.

POTCAR: A potential card which includes pseudopotential information for all the atoms present in the structure. To create the POTCAR file for the compound, the individual POTCAR of each atomic species are concatenated.

KPOINTS: This file specifies the necessary k-points (Bloch vectors) for sampling the Brillouin zone during computation. In the case of band-structure calculations, this file provides the high symmetry points along which bands will be plotted.

2.7 Summary

The present chapter delves into the detailed computational methodology utilized in this thesis. It begins by introducing the concept of many-electron systems and subsequently explores different approximate methods employed to solve the intricate many-electron Schrödinger equation, with particular emphasis on Density Functional Theory (DFT). Additionally, a comprehensive explanation of exchange-correlation functionals is included in the discussion. Finally, a succinct overview of the computational software used to calculate the diverse material properties examined in this thesis is provided.

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