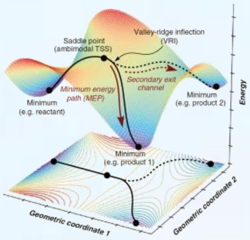
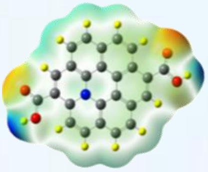
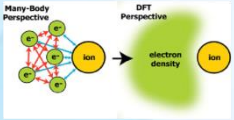
Chapter 2

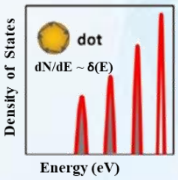
Brief of Density Functional Theory

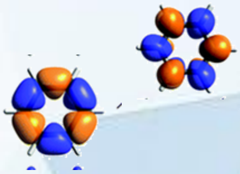






$$H\Psi = E\Psi$$





2.1 Many Body Problem

As it is known, materials created from electrons and nuclei interact according to the Coulomb's law. Classical mechanics is unsuccessful in depicting the functions of electrons whereas it can be precisely given by quantum mechanics. Therefore, a quantum mechanical many-body problem is computed to comprehend (i.e. to solve Schrödinger's equation for interacting electrons and nuclei) the structural, electronic, optical and vibrational properties [1-3]. The designing of materials for specific properties depends upon various computational and theoretical approaches. One of the significant methods established on first principles calculations is density functional theory (DFT). The first principles calculations do not incorporate any variables (electronic charge, atomic numbers, mass of electrons and atoms are the only data for evaluation). The time independent Schrödinger equation is solved in DFT to examine three dimensional (3D), two dimensional (2D), one dimensional (1D) and zero dimensional (0D) materials. The core of DFT was composed by two well-known theories given by Hohenberg and Kohn [4] and Kohn and Sham [5] which evaluates ground state properties of many electron systems. The significant merit of DFT includes the deduction of 3N degrees of freedom with N particle system to three using particles density. Despite that, DFT does not provide an accurate result of Schrödinger equation, therefore, various approximations are adapted for exchange correlation (XC) functional that fulfills Pauli's principle and explain Coulomb potential surpassing electrostatic interactions of electrons. The aforementioned approximations comprise local density approximation (LDA) and generalized gradient approximation (GGA) which significantly increases the efficacy of calculations in contrast to conventional wave function based techniques [6-7]. The time independent Schrödinger equation [8] is stated by:

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

Where $\boldsymbol{E}$ and $\boldsymbol{\psi}$ being the total energy and wavefunction of system respectively. $\boldsymbol{H}$ is known as the Hamiltonian of a particular system provided by the total of electron's kinetic energy (K.E.) and potential energy (P.E.) and can be written as:

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

Considering the easiest scenario of hydrogen atom which comprises one electron and proton, the accurate solution of Schrödinger equation can be identified due to the fact that there are solely proton-electron interactions. This is also otherwise called as single electron problem. Through solving Schrödinger equation, the energy of -13.6 eV is found for hydrogen atom. On the other hand, the conventional materials include many nuclei and electrons resulting in complex interactions and therefore, Schrödinger equation becomes insignificant. Consequently to comprehend the characteristics of electrons in many electron system, one must identify the solution of many body Schrödinger equation for nuclei-electrons interactions. The many body problems consists of wavefunction based on the position of every electrons $(\overrightarrow{r_1}, \overrightarrow{r_2}, \overrightarrow{r_3}, \ldots, \overrightarrow{r_n})$ and nuclei $(\overrightarrow{R_1}, \overrightarrow{R_2}, \overrightarrow{R_3}, \ldots, \overrightarrow{R_n})$.

Accordingly, the many body Schrödinger equation is given by [9]:

$$\boldsymbol{H\psi = E\psi\,(\overrightarrow{r_1}, \overrightarrow{r_2}, \overrightarrow{r_3}, \ldots, \overrightarrow{r_n}\,;\, \overrightarrow{R_1}, \overrightarrow{R_2}, \overrightarrow{R_3}, \ldots, \overrightarrow{R_n})} \tag{2.3}$$

The Hamiltonian of interacting electron-nuclei in system in above equation (2.3) is written as:

$$\boldsymbol{H = T_E + T_I + V_{II} + V_{EE} + V_{IE}} \tag{2.4}$$

$$\begin{aligned}\boldsymbol{H} = {} & -\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \bar{r}_i{}^2} - \frac{\hbar^2}{2M}\sum_l \frac{\partial^2}{\partial \bar{R}_l{}^2} + \frac{1}{2}\sum_{\substack{l,l'\\ l\neq l'}} \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l Z_{l'}}{|\bar{R}_l - \bar{R}_{l'}|} \\ & + \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\bar{r}_i - \bar{r}_j|} - \sum_i \sum_l \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l}{|\bar{r}_i - \bar{R}_l|}\end{aligned} \tag{2.5}$$

Here, $\boldsymbol{T_E}$ and $\boldsymbol{T_I}$ represents the K.E. of electrons and ions respectively, whereas, $\boldsymbol{V_{II}}$, $\boldsymbol{V_{EE}}$, and $\boldsymbol{V_{IE}}$ represent P.E. of two nuclei, two electrons and nuclei-electron respectively. The $\boldsymbol{i}$ and $\boldsymbol{l}$ indices stand for electron and nuclei respectively. $\boldsymbol{m_e}$ and $\boldsymbol{M}$ correspond to the mass of electron and nuclei respectively, $\boldsymbol{Z_l}$ and $\boldsymbol{Z_{l'}}$ represent the charges on respective nuclei. $\boldsymbol{\bar{r}_i - \bar{r}_j}$, $\boldsymbol{\bar{R}_l - \bar{R}_l{}'}$ and $\boldsymbol{\bar{r}_i - \bar{R}_l}$ denote distances among electron-electron, nuclei-nuclei and electron-nuclei respectively. The solution of equation (2.5) provides the energy Eigenstate (ground state energy) of system and subsequently the ground state properties at equilibrium can be determined. The equation (2.5) requires constants like electronic charge, atomic numbers, mass of electrons and atoms and therefore called first principles calculation which does not need any adjustable parameters as input. Despite that, in reality, equation (2.5) is efficient for hydrogen atom only and inappropriate for large systems and for that suitable wavefunction and density based approximations are needed and proposed.

2.2 Traditional Wave Function Based Methods

2.2.1 Born-Oppenheimer Approximation

According to Born-Oppenheimer approximation, the Hamiltonian is split up in electronic and ionic parts. Since, electrons are 10^3-10^4 times lighter than ions, hence their motion will be faster in comparison with ions. The ions are kept stationary at their position and electrons tag after the motions of ions adiabatically. Corresponding to the approximation, the many body wave function is written as [10]

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

In equation (2.6), $\boldsymbol{\chi_i(\vec{R})}$ and $\boldsymbol{\Psi_E(\bar{r},\,\bar{R})}$ show ionic and electronic wave functions respectively. The discrete electronic and ionic sections are written as follows:

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

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

$\boldsymbol{\Psi_E(\bar{r},\,\bar{R})}$ shows many body electron wave function fulfilling the Schrödinger equation with stationary position of ions due to which the K.E. part will vanish with constant ion-ion repulsion potential. The only variable term will be $\boldsymbol{E_E}$ which is electron-ion attraction and counts on position of electrons. Therefore, the Born-Oppenheimer approximation is suitable for insulators and semiconductors due to the fact that motion of ions cannot stimulate electrons to higher energy states and they reside in ground state. Nevertheless, it is trivial for metals because of the zero bandgap and migration to higher energy state through motion of ions and hence the Born-Oppenheimer approximation breaks down.

2.2.2 Hartree and Hartree-Fock Approximations

Hartree Approximation

A year later, after the Born-Oppenheimer approximation, Hartree in 1928 presented the electronic version of wave function assuming it as single particle function [11]:

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

Here, $\boldsymbol{\Psi(\bar{r}_i,\sigma_i)}$ shows the wave function of *i*th electron with position coordinate $\boldsymbol{\bar{r}_i}$ with spin $\boldsymbol{\sigma_i}$. Using equation (2.7) and (2.9), the Schrödinger equation can be written as:

$$-\frac{\hbar^2}{2m_e}\nabla_i{}^2\Psi_i-\frac{1}{4\pi\varepsilon_0}\sum_l\frac{Ze^2}{|\bar{r}_i-\bar{R}_l|}\Psi_i+\frac{1}{4\pi\varepsilon_0}\sum_{j\neq i}\int\frac{e^2|\Psi_j|^2}{|\bar{r}_i-\bar{r}_j|}d^3r_j=\ \in_i\Psi_i \tag{2.10}$$

The first term in left hand side of equation (2.10) represents the K.E., second one shows ion-electron potential, V_{IE} which rely only on the position of electron and the last part depicts the Hartree potential, V_H. The equation (2.10) is named as Hartree equation. The Hartree equation is a result of variational principle which gives exact ground state energy to identify E and Ψ_i.

$$E=\langle\Psi_H|H|\Psi_H\rangle\ \geq\ E_0 \tag{2.11}$$

The Hartree approximation limits many body problem to one electron problem and hence also named as independent electron approximation. Though, in this approximation, the electron travels independently which results in the negligence of electrons correlation effect because of Coulomb interaction. Also, in Hartree approximation, as the electrons being fermions, the antisymmetric wave function nature of electrons is neglected, thereby conflicting Pauli's exclusion principle.

Hartree-Fock Approximation

Hartree-Fock approximation (in 1930) addressed antisymmetric wave function of electrons which overcomes the drawback of Hartree approximation and is given by following equation:

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

The antisymmetric requirement is fulfilled through the Slater's determinant [12]:

$$\Psi_{HF}(\overline{r_1},\sigma_1,\dots,\overline{r_N},\sigma_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\Psi_1(\overline{r_1},\sigma_1) & \Psi_1(\overline{r_2},\sigma_2)\dots & \Psi_1(\overline{r_N},\sigma_N)\\ \Psi_2(\overline{r_2},\sigma_2) & \Psi_2(\overline{r_2},\sigma_2)\dots & \Psi_2(\overline{r_N},\sigma_N)\\ \Psi_N(\overline{r_N},\sigma_N) & \Psi_N(\overline{r_N},\sigma_N)\dots & \Psi_N(\overline{r_N},\sigma_N)\end{vmatrix} \tag{2.13}$$

Here, N is the number of electrons and the determinant wave function can be given as:

$$\Psi_{HF}=\frac{1}{\sqrt{N!}}\sum_P(-1)^pP\,\Psi_1(x_1)\,\Psi_2(x_2)\dots\,\Psi_N(x_N) \tag{2.14}$$

Where, $x=(\bar{r},\sigma)$, P be the permutation operator and p represents the quantity of exchanges making up this permutation. Replacing the determinant form in variational principle (equation (2.11)) gives Hamiltonian, we get:

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

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

The above equation (2.15) differs from Hartree approximation because of the existence of last term namely exchange energy as it emerges due to the swapping of electronic coordinates along with only finite parallel spins. Through reducing the wavefunction by functional derivative of equation (2.15), the Hartree-Fock equation is attained [7]:

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

In above equation, $\boldsymbol{V_H}$ represents the Hartree potential. The Hartree-Fock approximation advances the Hartree approximation by emergence of exchange energy produced by taking the antisymmetric of wavefunction in consideration. Moreover, the Hartree-Fock approximation is mean field theory, as in, the many body problem is restricted to one electron problem in which the electron proceeds in field created by another electrons. However, it neglects the Coulomb correlation generated between parallel spins that induces exchange interaction. Additionally, Hartree-Fock approximation is rather computationally costly.

2.3 Density Based Methods

With the purpose to solve many body Schrödinger equation, the traditional wavefunction based approaches contain coordinates of all electrons with 3N variable function, N being the number of electrons. The wavefunction can be replaced with the consideration of electron density $\boldsymbol{n}(\vec{\boldsymbol{r}})$**,** making many body problem much easier. This is attributed to the fact that density involves three spatial coordinates solely, whereas wavefunction is based on three spatial coordinates of all electrons of system. A compact and precise of this illustration was given by Hohenberg and Kohn in 1964 and also entitles as well-known density functional theory (DFT). Considering the ease to solve many body Schrödinger equation, DFT has made a significant effect in understanding the electronic structure of atoms, molecules, clusters etc. Appreciating this accomplishment, Walter Kohn was awarded Nobel Prize in 1998 for his key role in the advancement of DFT. In the next section, Thomas-Fermi theory is discussed in which electron density is primarily used as basic variable. Following Thomas-Fermi theory, Hohenberg-Kohn theorems are described as it established the basis for DFT which is anything but the Kohn-Sham equation.

2.3.1 Thomas-Fermi Theory

The primary idea to define electronic systems like atoms, molecules or solids explicitly as a function of electron density was proposed by Thomas and Fermi in 1927 [13-14]. In this theory, electron density is considered as the elementary variable rather than single particle wave function or orbitals. This theory shows density of non-interacting electron inside homogeneous gas equivalent to local density at given point.

The total K.E. consisting N electrons is given by:

$$\boldsymbol{T_{TF} = C_k \int n(\bar{r})^{\frac{5}{3}} d^3r} \tag{2.17}$$

Here, $\boldsymbol{C_k = \frac{3}{10}\frac{\hbar^2}{m_e}(3\pi^2)^{\frac{2}{3}}}$. The total energy present in Thomas-Fermi theory is the addition of K.E., ion-electron potential and electron-electron Coulomb repulsion and can be written as:

$$\boldsymbol{E = T + V_{IE} + V_H}$$

$$\boldsymbol{E = T_{TF} + \int V_{IE}(\bar{r})\, n(\bar{r}) d^3r + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r'} \tag{2.18}$$

In above equation (2.18), one can see that the total energy $\boldsymbol{E}$, is explicitly given as functional of density only. The basic equation of Thomas-Fermi theory is attained through the reduction of $\boldsymbol{E}$ with constraint known by Lagrange multiplier $\boldsymbol{\mu}$ which is nothing but the chemical potential and written as:

$$\boldsymbol{\frac{5}{3} C_k n(\bar{r})^{\frac{2}{3}} + V_{IE}(\bar{r}) + \int \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' = \mu} \tag{2.19}$$

or

$$\boldsymbol{\mu = \frac{5}{3} C_k n(\bar{r})^{\frac{2}{3}} + V(\bar{r}),} \text{ where } \boldsymbol{V(\bar{r}) = V_{IE}(\bar{r}) + \int \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r'}$$

The above Thomas-Fermi equation (2.19) can be easily solved as it only relies upon $\boldsymbol{\vec{r}}$. Additionally, this theory has been expanded by Dirac and Weizsäcker to incorporate exchange interaction and correction to K.E. functional [15-16]. Nonetheless, this theory comprises the drawback of missing the most significant phenomena like shell structure of atoms. However, Thomas-Fermi theory contained the seeds for the advancement of DFT.

2.3.2 Hohenberg and Kohn Theorems

Hohenberg and Kohn in 1964 provided two significant theorems that set the groundwork of density functional theory (DFT) [4]. The theorems are as follows:

Theorem I: *The external potential* $\boldsymbol{V}(\bar{\boldsymbol{r}})$ *is a unique functional of electron density* $\boldsymbol{n}(\vec{\boldsymbol{r}})$. *As result, the total ground state energy E of any many electron system is also unique functional of* $\boldsymbol{n}(\vec{\boldsymbol{r}})$,$\boldsymbol{E} = \boldsymbol{E}[\boldsymbol{n}]$**.**

Proof: Starting with the assumption that there are two different external potentials $\boldsymbol{V}_{\boldsymbol{ext}}^{(\mathbf{1})}(\bar{\boldsymbol{r}})$ and $\boldsymbol{V}_{\boldsymbol{ext}}^{(\mathbf{2})}(\bar{\boldsymbol{r}})$ with similar density $\boldsymbol{n}(\vec{\boldsymbol{r}})$. These external potentials give two different Hamiltonians $\boldsymbol{H}^{(\mathbf{1})}$ and $\boldsymbol{H}^{(\mathbf{2})}$ with wave functions $\boldsymbol{\Psi}_{\boldsymbol{ext}}^{(\mathbf{1})}(\bar{\boldsymbol{r}})$ and $\boldsymbol{\Psi}_{\boldsymbol{ext}}^{(\mathbf{2})}(\bar{\boldsymbol{r}})$respectively.

According to Raleigh-Ritz variational principle, we can write

$$\boldsymbol{E}^{(\mathbf{1})} = \langle \boldsymbol{\Psi}^{(\mathbf{1})} | \boldsymbol{H}^{(\mathbf{1})} | \boldsymbol{\Psi}^{(\mathbf{1})} \rangle < \langle \boldsymbol{\Psi}^{(\mathbf{2})} | \boldsymbol{H}^{(\mathbf{1})} | \boldsymbol{\Psi}^{(\mathbf{2})} \rangle \tag{2.20}$$

From equation (2.20), we get

$$\langle \boldsymbol{\Psi}^{(\mathbf{2})} | \boldsymbol{H}^{(\mathbf{1})} | \boldsymbol{\Psi}^{(\mathbf{2})} \rangle = \langle \boldsymbol{\Psi}^{(\mathbf{2})} | \boldsymbol{H}^{(\mathbf{2})} | \boldsymbol{\Psi}^{(\mathbf{2})} \rangle + \int \left[\boldsymbol{V}_{\boldsymbol{ext}}^{(\mathbf{1})}(\bar{\boldsymbol{r}}) - \boldsymbol{V}_{\boldsymbol{ext}}^{(\mathbf{2})}(\bar{\boldsymbol{r}}) \right] \boldsymbol{n}(\bar{\boldsymbol{r}})\, \boldsymbol{d}^{\mathbf{3}}\boldsymbol{r} \tag{2.21}$$

Similarly for $\boldsymbol{H}^{(\mathbf{2})}$, we get

$$\langle \boldsymbol{\Psi}^{(\mathbf{1})} | \boldsymbol{H}^{(\mathbf{2})} | \boldsymbol{\Psi}^{(\mathbf{1})} \rangle = \langle \boldsymbol{\Psi}^{(\mathbf{1})} | \boldsymbol{H}^{(\mathbf{1})} | \boldsymbol{\Psi}^{(\mathbf{1})} \rangle + \int \left[\boldsymbol{V}_{\boldsymbol{ext}}^{(\mathbf{2})}(\bar{\boldsymbol{r}}) - \boldsymbol{V}_{\boldsymbol{ext}}^{(\mathbf{1})}(\bar{\boldsymbol{r}}) \right] \boldsymbol{n}_{\mathbf{0}}(\boldsymbol{r})\, \boldsymbol{n}(\bar{\boldsymbol{r}})\, \boldsymbol{d}^{\mathbf{3}}\boldsymbol{r} \tag{2.22}$$

Adding equations 2.21 and 2.22, we get

$$\boldsymbol{E}^{(\mathbf{1})} + \boldsymbol{E}^{(\mathbf{2})} < \boldsymbol{E}^{(\mathbf{2})} + \boldsymbol{E}^{(\mathbf{1})} \tag{2.23}$$

which is contradictory.

Theorem II: *The functional* $\boldsymbol{E}[\boldsymbol{n}]$ *for the total energy has a minimum equal to the ground-state energy at the ground-state density*.

Proof: The ground state energy $\boldsymbol{E}[\boldsymbol{n}]$ can be written as:

$$\begin{aligned} \boldsymbol{E}[\boldsymbol{n}] &= \boldsymbol{T}[\boldsymbol{n}] + \boldsymbol{E}_{\boldsymbol{int}}[\boldsymbol{n}] + \int \boldsymbol{V}_{\boldsymbol{ext}}(\bar{\boldsymbol{r}}) \boldsymbol{n}(\bar{\boldsymbol{r}})\, \boldsymbol{d}^{\mathbf{3}}\boldsymbol{r} + \boldsymbol{E}_{\boldsymbol{II}} \\ &\equiv \boldsymbol{F}[\boldsymbol{n}] + \int \boldsymbol{V}_{\boldsymbol{ext}}(\boldsymbol{r}) \boldsymbol{n}(\bar{\boldsymbol{r}})\, \boldsymbol{d}^{\mathbf{3}}\boldsymbol{r} + \boldsymbol{E}_{\boldsymbol{II}} \end{aligned} \tag{2.24}$$

Here, $\boldsymbol{E}_{\boldsymbol{II}}$ is the interaction energy of nuclei, $\boldsymbol{F}[\boldsymbol{n}]$ is comprises electron-electron interaction potential and K.E. and P.E. of electrons for interacting systems.

Now, let the ground-state energy is given by ground state density, then

$$E^{(1)} = E\left[n^{(1)}\right] = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle \tag{2.25}$$

Here, E can be written as the functional of $n(\bar{r})$ and functional $F[n]$ in equation (2.24) can be divided in three terms:

$$F[n] = T_s[n] + \frac{1}{2} \iint \frac{e^2}{4\pi\varepsilon_0} \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r}-\vec{r}'|} d^3r d^3r' + E_{XC}[n] \tag{2.26}$$

Here, the first term $T_s[n]$ represents K.E. of non-interacting electron gas with ground-state density $n(\bar{r})$. The second part presents the classical Coulomb energy and the last part $E_{XC}[n]$ is the exchange-correlation energy along with total K.E.

2.3.3 The Kohn-Sham Approach

$$\begin{tikzcd}
V_{ext}(\vec{r}) \arrow[d] & n_0(\vec{r}) \arrow[l, "HK"'] \arrow[r, leftrightarrow, "KS"] & n_0(\vec{r}) \arrow[r, "HK_0"] & V_{KS}(\vec{r}) \arrow[d] \\
\Psi_i(\{\vec{r}\}) \arrow[r] & \Psi_0(\{\vec{r}\}) \arrow[u] & \Psi_{i=1,N_e}(\{\vec{r}\}) \arrow[u] & \Psi_i(\{\vec{r}\}) \arrow[l]
\end{tikzcd}$$

Figure 2.1: Demonstration of Kohn-Sham ansatz. The HK$_0$ represents Hohenberg and Kohn theorem for non-interacting system. The link between many body and the independent particle system is provided by Kohn – Sham (KS).

The Kohn-Sham ansatz changes the many body interacting present in external potential to non-interacting auxiliary system. The hypothesis is made such that they consist of similar ground-state electron density and properties. For this milestone work, Walter Kohn in 1998, was awarded Nobel Prize in chemistry. Fig. 2.1 shows the Kohn-Sham approach (left side) along with its comparison to non-interacting method of Hohenberg-Kohn theory (right side).

The Kohn-Sham theory disassociates K.E. from equation (2.26), which gives:

$$E[n(\bar{r})] = \int V(\bar{r}) n(\bar{r}) d^3r + T_s[n] + \frac{1}{2} \iint \frac{e^2}{4\pi\varepsilon_0} \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r' + E_{XC}[n] \tag{2.27}$$

Here, $\boldsymbol{T_s[n]}$ is now independent K.E. and $V_{ext}(\vec{\boldsymbol{r}})$ is replaced by $V(\vec{\boldsymbol{r}})$, which electrons-nuclei potential. Last term of equation $\boldsymbol{E_{XC}[n]}$ is the exchange and correlation energy explaining many body quantum mechanical effect. By minimizing equation (2.27), we get

$$\frac{\delta E[n]}{\delta n(\bar{r})} - \mu = 0 \tag{2.28}$$

$$\frac{\delta T_s[n]}{\delta n(\bar{r})} + V(\bar{r}) + V_H(\bar{r}) + V_{XC}(\bar{r}) - \mu = 0 \tag{2.29}$$

Here, $\boldsymbol{V_H(\bar{r})}$ represents the Hartree potential based on electron density and $\boldsymbol{V_{XC}(\bar{r}) = \frac{\delta E_{xc}[n]}{\delta n(\bar{r})}}$, is the exchange-correlation potential resulting in the solution of electron density and further to the total energy. However, there are two main concerns in equation (2.29), (i) $\boldsymbol{T_s[n]}$ is not known and (ii) exchange-correlation potential $\boldsymbol{V_{XC}(\bar{r})}$ is unknown. Therefore, approximation is to be introduced to solve the equation (2.29), for instance, Kohn-Sham considered density as square of orbitals of the system, then,

$$n(\bar{r}) = \sum_{i=1}^{N} \left| \Psi_i(\bar{r}) \right|^2 \tag{2.30}$$

Where, Kohn-Sham orbitals are presented by $\boldsymbol{\Psi_i(\bar{r})}$**.** Kohn-Sham K.E. can be given by following expression:

$$T_s[n] = -\frac{\hbar^2}{2m_e} \sum_i^N \left\langle \Psi_i(\bar{r}) \middle| \nabla^2 \middle| \Psi_i(\bar{r}) \right\rangle = -\frac{\hbar^2}{2m_e} \nabla^2 \tag{2.31}$$

Here, $\boldsymbol{T_s[n]}$ is reliable for density oscillation of shell structure and contains large part of the total K.E. of system. Here, $\boldsymbol{E_{xc}[n]}$ is the addition of electron exchange and correlation energy i.e. $\boldsymbol{E_{xc}[n] = E_x[n] + E_c[n]}$, where Slater's determinant $E_x[n]$ is generally given by Slater's determinant (equation 2.13). By solving equation (2.27), we get:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff}(\bar{r}) \right] \Psi_i(\bar{r}) = \epsilon_i \, \Psi_i(\vec{r}) \tag{2.32}$$

This equation is well-known as Kohn-Sham equation and similar to Schrödinger equation. The $\boldsymbol{V_{eff}(\bar{r})}$ in above equation (2.32) is called effective potential and is evaluated through the sum of exchange potential $\boldsymbol{(V_{ext}(\bar{r}))}$**,** Hartree potential $\boldsymbol{V_H(\bar{r})}$ and exchange-correlation potential $\boldsymbol{(V_{XC}(\bar{r}))}$. The Kohn-Sham theory is the powerful tool to evaluate ground state properties of materials with reduced computation cost. Nevertheless, exchange-correlation potential $\boldsymbol{V_{XC}(\bar{r})}$ is still unknown and for that various approximations emerged like local density approximation (LDA) and generalized gradient approximation (GGA).

2.4 Exchange and Correlation Functional and Basis Set

Density functional theory explains many body problem by means of Kohn-Sham equation with approximations by developing exchange and correlation potential. Various approximations like LDA, GGA, meta-GGA are utilized for this potential [5]. The exchange interaction is given by:

$$\boldsymbol{E_x[n] = \langle \Psi[n] | V_{EE} | \Psi[n] \rangle - U[n]} \tag{2.33}$$

It is the repulsion between electrons evaluated through Kohn-Sham function and provides Hartree and exchange interaction. The Slater determinant is used to determine the Kohn-Sham wave function and Fock integrals of Kohn-Sham orbitals contributes in exchange energy [17]. There are intricate differences between Hartree-Fock exchange and Kohn-Sham DFT exchange and considered from two different origins.

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

The correlation energy can be defined by the following expression

$$\boldsymbol{E_c[n] = F[n] - T_S[n] - U[n] - E_X[n]} \tag{2.34}$$

So far, correct formalism of exchange correlation is yet remote. Better approximations like LDA and GGA are successful in investigating the properties of various systems.

Local Density Approximation (LDA)

In LDA, the density is expected to be a homogenous electron gas, however, it does not consider the dissimilarity of electron density. The Hohenberg-Kohn delivered exchange-correlation energy functional and potential as follows if density varies gradually with position:

$$\boldsymbol{E_{xc}^{LDA}[n(\bar{r})] = \int dr\ n(\bar{r})\ \epsilon_{xc}^{LDA}[n(\bar{r})]} \tag{2.35}$$

$$\boldsymbol{V_{xc}[n(r)] = \left(E_{xc}[n] + n\frac{\delta E_{xc}[n]}{\delta n}\right)_{n=n(r)}} \tag{2.36}$$

Here, the integral goes over all spaces and *$E_{xc}[n]$* is the energy per electron of exchange-correlation in a uniform electron with density $\boldsymbol{n}$. The LDA is considered a better approximation in case of systems with electrons located in infinite area of space. However, LDA fails in case of strongly correlated systems like transition metals. This drawback is accomplished in generalized gradient approximation (GGA) dealing with the inhomogeneities of electron density.

Generalized Gradient Approximation (GGA)

In GGA, density along with its gradient is studied for calculating the exchange and correlation term. It is sometimes known as gradient-corrected functional and can be written as:

$$\boldsymbol{E_{xc}^{GGA}[n(\bar{r})] = \int dr\, n(\bar{r})\, \epsilon_{xc}^{GGA}(n(\bar{r}), \nabla n(\bar{r}), \dots)} \tag{2.37}$$

Exchange and correlation are shown as semi empirical functional and degree of non-locality relies upon electron density. By assuming gradient in charge density, GGA approximation can be written as:

$$\boldsymbol{E_{xc}[n] = \int \varepsilon_{xc}(n)\,|_{n=n(r)} n(r) F_{xc}[n(r), \nabla n(r)] dr} \tag{2.38}$$

The GGA approximation usually gives better results regarding structural and magnetic properties of materials than LDA and in the vicinity of experimental values. However, it is also unsuccessful sometimes.

The introduction of hybrid functional provides more precision in predicting the ground-state energy as LDA and GGA tends to underestimate and overestimate the minimum energy respectively. This is achieved through the mixture of Hartree-Fock exchange along with DFT exchange-correlation. For instance, B3LYP (Becke three parameter Lee Yang Parr) is a hybrid functional which comprises non-local correlation functional from LYP and local correlation from Vosko, Wilk and Nusair (VWN). Three in B3LYP denotes three parameter functional and have the form given by Becke in 1993 [18]:

$$\boldsymbol{E_{xc} = E_{xc}^{LSDA} + a_0(E_x^{exact} - E_x^{LSDA}) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{PW91}} \tag{2.39}$$

In equation (2.39), $\boldsymbol{E_x^{exact}}$ is the exact exchange energy. $\Delta \boldsymbol{E_x^{B88}}$ and $\Delta \boldsymbol{E_c^{PW91}}$ is Becke's 1988 gradient correcting for exchange to local spin density approximation (LSDA) [19] and Perdew and Wang's 1991 gradient correction for correlation respectively [20]. The $\boldsymbol{a_0}$, $\boldsymbol{a_x}$ and $\boldsymbol{a_c}$ are semiempirical coefficients with values 0.21, 0.72 and 0.81 respectively, evaluated by suitable fit to experimental data of molecules [18].

Basis Sets

The basis set is the set of functions employed to build molecular orbitals (MO). So as to represent MOs, an entire group of basis functions ought to be formed which needs infinite number of basis functions, however practically, finite number of basis functions were utilized [21]. MOs are generally understandable as linear combinations of pre-defined set of one-electron functions called “basis functions”. A single particle MO is defined as:

$$\boldsymbol{\phi_i = \sum_{\mu=1}^{N} C_{\mu i}\, X_{\mu}} \tag{2.40}$$

Here, $\boldsymbol{C_{\mu i}}$ are the expansion coefficients of MOs. The basis functions $\boldsymbol{X_i \ldots X_N}$, are generally normalized. The basis functions are categorized in two main types: plane waves and Gaussian type orbitals. The *ab initio* programming package like Gaussian software package [22] uses Gaussian type orbitals to configure basis sets and is considered in the following work. Gaussian-type orbitals (GTO) or Gaussian functions consists exponential dependence ($e^{-\alpha r^2}$) and written as:

$$\boldsymbol{G(\alpha, \vec{r}) = c x^l y^m z^n e^{-\alpha r^2}} \tag{2.41}$$

Here, $\boldsymbol{\vec{r}}$ is constituted of x, y and z. $\boldsymbol{\alpha}$ is constant characterizing size. Linear combinations of one-electron functions are adopted to produce the definite basis functions and these are called the contracted Gaussians which can be written as:

$$\boldsymbol{X_{\mu} = \sum_{p} \sigma_{\mu p} G_p} \tag{2.42}$$

The $\boldsymbol{\sigma_{\mu p}}$ are constants for particular basis set and aforementioned functions are also normalized. The MOs for basis set can be given by:

$$\boldsymbol{\phi_i = \sum_{\mu=1}^{N} C_{\mu i}\, X_{\mu} = \sum_{\mu=1}^{N} C_{\mu i}\left(\sum_{p} \sigma_{\mu p} G_p\right)} \tag{2.43}$$

Basis sets are considered as the foundation on ab initio calculations and therefore essential to understand it’s basic as it widely establishes the quality of results [23]. For the accuracy of results, various basis sets are optimized and tested. The nominal basis set consists of Slater-Type Orbital (STO) per AO with further approximation of linear combination of N Gaussian functions. Most often, the value of N is three resulting in STO-3G basis set. Furthermore, basis set can be upgraded by expanding amount of basis functions for every atom. This includes polarization (*d* and *p* or * and **) and diffusion (+ and ++) functions. The addition of polarization functions allows the inclusion of orbitals with angular momentum with adjustability in diverse bonding states. For instance, polarized basis set 6-31G* includes *d* polarization functions on every atoms excluding hydrogen and 6-31G** basis set incorporates *p* functions to hydrogen atom too. Additionally, 6-31+G** basis set provides diffuse functions (+ and ++) to atoms excluding hydrogen, which plays significant role in systems with free valence electron pair, anions and excited states [24].

2.5 Response Theory

Density or wavefunction presents a significant part in the calculation of molecular properties. Considering time-independent densities have been taken account to a limited extent, it only articulates the static properties. However, the condition alters as the time-dependent electric field is introduced due to the fact that wavefunction turns out to be dependent on time. Various absorption and emission spectroscopy methods are evolved to evaluate the optical characteristics of molecules. The properties are altered when a particular material undergoes absorption in time-dependent field. For instance, it experiences an electronic excitation along with relaxation. Response theory provides the expectation value of arbitrary Hermitian operator $\hat{A}$ operating over time-dependent wavefunction ($|\tilde{0}\rangle$) in terms of powers of applied field and can be given by:

$$\langle\tilde{\mathbf{0}}|\hat{\boldsymbol{A}}|\tilde{\mathbf{0}}\rangle = \langle\tilde{\mathbf{0}}|\hat{\boldsymbol{A}}|\tilde{\mathbf{0}}\rangle^{(\mathbf{0})} + \langle\tilde{\mathbf{0}}|\hat{\boldsymbol{A}}|\tilde{\mathbf{0}}\rangle^{(\mathbf{1})} + \langle\tilde{\mathbf{0}}|\hat{\boldsymbol{A}}|\tilde{\mathbf{0}}\rangle^{(\mathbf{2})} + \cdots \tag{2.44}$$

Various approximations are needed to unfold time-dependent Schrödinger equation along with the determination of expectation values with time:

$$\hat{\boldsymbol{H}}(\boldsymbol{t})|\tilde{\mathbf{0}}\rangle = \boldsymbol{i}\,\frac{\boldsymbol{d}}{\boldsymbol{dt}}\,|\tilde{\mathbf{0}}\rangle \tag{2.45}$$

Where, $\hat{\boldsymbol{H}}(\boldsymbol{t}) = \hat{\boldsymbol{H}}_{\mathbf{0}} + \hat{\boldsymbol{V}}(\boldsymbol{t})$ (2.46)

In equation (2.46), the Hamiltonian is represented as the total of Hamiltonian of unperturbed system ($\hat{\boldsymbol{H}}_{\mathbf{0}}$) and time-dependent perturbation $\hat{\boldsymbol{V}}(\boldsymbol{t})$. However, besides time, frequency perturbation can be given as:

$$\hat{\boldsymbol{V}}(\boldsymbol{t}) = \int_{-\infty}^{+\infty} \boldsymbol{d\omega}\hat{\boldsymbol{V}}^{\boldsymbol{\omega}}\,\boldsymbol{exp}(-\boldsymbol{i\omega} + \boldsymbol{\epsilon})\boldsymbol{t} \tag{2.47}$$

Here, $\boldsymbol{\epsilon}$ denotes positive infinitesimal stating $V^{-\infty}$ is zero. Hence, due to the presence of perturbing field, wave function converts to time-dependent ($|\tilde{0}\rangle$) and further perhaps extended in power series perturbation at finite time 't' which can be written as:

$$\boldsymbol{|\tilde{0}\rangle = |0\rangle + \int_{-\infty}^{+\infty} d\omega_1 \, |0^{(\omega_1)}\rangle \, exp[(-i\omega_1 + \epsilon)t]}$$

$$\boldsymbol{+ \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \, |0^{(\omega_1 \omega_2)}\rangle \, exp[(-i(\omega_1 + \omega_2 + 2\epsilon)\, t] + \cdots} \tag{2.48}$$

The first term in above equation represents unperturbed system's wave function, second one is the change in wave function which shows linearity in perturbation, third denotes the quadratic perturbation etc.

Now, adding time-dependent wave function presented in equation (2.48) to (2.44) resulting in the emergence of time in expectation value of time-independent operator $\hat{A}(\epsilon \to 0)$

$$\boldsymbol{\langle \tilde{0}|\hat{A}|\tilde{0}\rangle = \langle \tilde{0}|\hat{A}|\tilde{0}\rangle + \int_{-\infty}^{+\infty} d\omega_1 \, \langle\langle \hat{A}; \hat{V}^{(\omega_1)} \rangle\rangle_{\omega_1} \times exp(-i\omega_1 t) +}$$

$$\boldsymbol{\frac{1}{2} \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \times \langle\langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle\rangle_{\omega_1\omega_2} \times exp(-i\omega_1 - i\omega_2)t + O\,(V^3)} \tag{2.49}$$

Here, $\boldsymbol{\langle\langle \hat{A}; \hat{V}^{(\omega_1)} \rangle\rangle_{\omega_1}}$ and $\boldsymbol{\langle\langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle\rangle_{\omega_1\omega_2}}$ are the Fourier coefficients denoting linear response function and quadratic response function respectively. Equation (2.49) is given as the set of Eigen functions of Hamiltonian for ($\boldsymbol{\hat{H}_0}$):

$$\boldsymbol{\langle\langle \hat{A}; \hat{V}^{(\omega_1)} \rangle\rangle_{\omega_1} = \sum_{k>0} \left(\frac{\langle 0|\hat{A}|k\rangle\langle k|\hat{V}^{\omega_1}|0\rangle}{\omega_1 - \omega_k} - \frac{\langle 0|\hat{V}^{\omega_1}|k\rangle\langle k|\hat{A}|0\rangle}{\omega_1 + \omega_k} \right)} \tag{2.50}$$

The poles $\boldsymbol{\omega_1} = \pm\boldsymbol{\omega_k}$ shows the excitation energy between $\boldsymbol{|0\rangle}$ **and** $\boldsymbol{|\, k\, \rangle}$ states. The associated transition moments are the result of leftovers of above equation.

$$\boldsymbol{\lim_{\omega_1 \to \omega_k} (\omega_1 - \omega_k) \, \langle\langle \hat{A}; \hat{V}^{(\omega_1)} \rangle\rangle_{\omega_1} = \langle 0|\hat{A}|k\rangle\langle k|\hat{V}^{\omega_1}|0\rangle} \tag{2.51}$$

Similarly, the higher order quadratic response function can be given by:

$$\boldsymbol{\langle\langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle\rangle_{\omega_1\omega_2} = P_{12} \sum_{k,l>0} \Bigg[\frac{\langle 0|A|k\rangle\langle k|V^{\omega_1} - {V_0}^{\omega_1}|l\rangle\langle l|V^{\omega_2}|0\rangle}{(\omega_1 + \omega_2 - \omega_k)\,(\omega_2 - \omega_l)} - \frac{\langle 0|V^{\omega k}|k\rangle\langle k|A - A_0|l\rangle\langle l|V^{\omega_2}|0\rangle}{(\omega_1 + \omega_k)\,(\omega_2 - \omega_l)} +}$$

$$\boldsymbol{\frac{\langle 0|V^{\omega_1}|k\rangle\langle k|V^{\omega_2} - {V_0}^{\omega_2}|l\rangle\langle l|V^{\omega_2}|0\rangle}{(\omega_1 + \omega_k)\,(\omega_2 + \omega_k + \omega_l)} \Bigg]} \tag{2.52}$$

On setting $\boldsymbol{\hat{A} = \hat{\mu}}$ and $\boldsymbol{V^{\omega_1} = \hat{H}_{S0}\ (\omega_1 = 0)}$, the single and double leftovers of above equation (2.52) gives spin-orbit induced transition moments and transition moment between excited states respectively. Therefore, for acquiring optical properties like absorption and emission wavelengths along with their oscillator strengths, the response functions etc. perform as an anchor.

2.6 Time-Dependent Density Functional Theory (TD-DFT)

The DFT has been reduced to incorporated time-dependent potentials and is called time-dependent density functional theory (TD-DFT). The TD-DFT is considered to be time-dependent quantum mechanics in respect of time-dependent electron density $n(\vec{r},t)$. Runge and Gross developed the TD-DFT in 1984 providing the Runge–Gross theorem which is relative to the Hohenberg–Kohn theorem for the time-dependent electron density. Contrary to DFT, TD-DFT comprises no minimum energy principle. Rather, it is based upon stationary action principle. Equivalent to DFT, it can provide an imaginary system of non-interacting electrons with similar density $n(\vec{r},t)$ as of real system which hops in time-dependent effective potential $v_{eff}(\vec{r},t)$. This results in equation equivalent to time-dependent Schrödinger equation and named as time-dependent Kohn-Sham equation:

$$i\hbar \frac{\partial}{\partial t}\Psi_i(\vec{r},t) = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{eff}(\vec{r},t)\right]\Psi_i(\vec{r},t) \tag{2.53}$$

Here, $v_{eff}(\vec{r},t) = v_{ext}(\vec{r},t) + v_{xc}(\vec{r},t) + e^2\int \frac{1}{4\pi\varepsilon_0}\frac{n(\vec{r}',t)}{|\vec{r}-\vec{r}'|}d^3r'$, where $v_{xc}(\vec{r},t)$ represents the time-dependent exchange-correlation potential and is unknown and therefore has to be approximated. The $n(\vec{r},t)$ is given through:

$$n(\vec{r},t) = \sum_i |\Psi_i(\vec{r},t)|^2$$

The easiest approximation for $v_{xc}(\vec{r},t)$ is the adiabatic local density approximation (ALDA) in which uniform gas with the instantaneous density is utilized.

$$v_{xc}^{ALDA}(\vec{r},t) = v_{xc}^{unif}\ (n((\vec{r},t))$$

The above expression evaluates the energies of excited states along with photo-absorption cross-section of molecules and clusters.

2.7 Applications of Quantum Chemical Methods

2.7.1 Geometry Optimization

Geometry Optimization of a molecule can be defined as the methodology to identify minimum energy configuration. It is generally given in relation to bond length, bond angle and dihedral (torsion) angle. In order to evaluate the initial guess of geometry, energy and wave functions are determined. The geometry is conditioned as far as the stationary point on potential surface is found which then modulates repeatedly until two conditions (i) minimum energy is obtained, (ii) forces enclosed in molecules tends to zero. However, this can be difficult in non-rigid molecules which comprise numerous energy minima, thereby required extra efforts in attaining global minima.

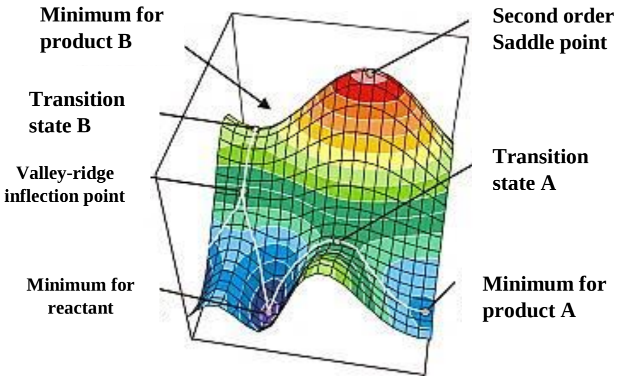


Figure 2.2: The PES curve presenting minima, transition states, saddle points along with reaction paths. Reproduced with permission from Keil, Comput. Math. Appl. 65, 1674 (2013). Copyright 2013 Elsevier.

Subsequently, in these cases, geometry optimization is useful in locating least on potential energy surface (PES) resulting in the prediction of symmetric structure of molecules. A PES demonstrates the discrepancy of energy as a result of configuration of molecule in a specific state. Figure 2.2 presents simple representation of PES depicting energy (vertical axis) as a function of any two geometric variables (horizontal axes). The equilibrium structure in the Fig. 2.2 corresponds to the minima position in the PES valleys. The difference in energy between product and reactant valley minima depicts the energetics of reaction. Further, reaction path joins reactants and products valleys [26]. Additionally, the highest peak on lowest energy reaction pathway is the transition structure (TS) and is also known as first-order saddle point. In order to demonstrate whether the geometry optimization has attained minima or TS, it is essential to carry out frequency calculations. The character of imaginary frequency depends upon the Eigenvector from Hessian force constant matrix and also shows probable reaction coordinates. Hence, a minimum structure will not contain any imaginary frequencies.

2.7.2 Frequency Calculation

The geometry optimization of molecular structure helps in the prediction of IR and Raman spectra. The frequency calculation provides the position and intensity of vibration of bands and is independent of experimental work. The calculated frequencies rely upon the harmonic model, however, in practical they are anharmonic. Consequently this describes the discrepancies between experimental and calculated frequencies.

The total energy of a molecule involving N atoms neighboring to its equilibrium structure can be given by:

$$\boldsymbol{E = T_k + V_p = \frac{1}{2}\sum_{i=1}^{3N} q_i^2 + V_{eq} + \sum_{i=1}^{3N}\sum_{j=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_{eq} q_i q_j} \tag{2.54}$$

Where, q_i represents the mass-weighted Cartesian displacements and written as:

$$\boldsymbol{q_i = M_i^{1/2}\,(X_i - X_{ieq})} \tag{2.55}$$

Where, X_i is the location of nuclei with respect to their equilibrium positions X_{ieq} and M_i are their masses. V_{eq} in equation (2.54) represents the P.E. at the equilibrium nuclear conformation, and the extension of a power series is concise at second order [27]. Therefore, the classical-mechanical equation can be written as:

$$\boldsymbol{Q_i = \sum_{i=1}^{3N} f_{ij} q_i} \tag{2.56}$$

Here, f_{ij} represent the quadratic force constants calculated through:

$$\boldsymbol{f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_{eq}} \tag{2.57}$$

And can be calculated through numerical second differentiation

$$\boldsymbol{\frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\Delta(\Delta V)}{\Delta q_i \Delta q_j}} \tag{2.58}$$

Or directly through analytical second differentiation as follows:

$$\boldsymbol{\frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\Delta(\partial V/\partial q_j)}{\partial q_i}} \tag{2.59}$$

In the present thesis the Raman intensities investigation along with their vibrational modes are done with respect to potential energy distribution. The Raman intensities were calculated in Gaussian 09 package [22] through obtained Raman activities (S_i) along with the relationship derived from intensity theory of Raman scattering [28-29]:

$$\boldsymbol{I_i = \left[\frac{f(v_0 - v_i)^4 S_i}{v_i\{1 - \exp(-hcv_i/kT\}}\right]} \tag{2.60}$$

In above equation (2.60), v_0 denotes the exciting wavenumbers in cm^{-1}, v_i be the vibrational wavenumber of ith normal mode. The h, c and k are universal constants, while, f is a appropriate chosen common normalization factor for all peak intensities.

2.7.3 Electric Moments

The dipole moment (μ) and polarizability (α) were calculated using Gaussian 09 package [22] based upon finite field (FF) method. It can be given by Buckingham's definitions [30] in Cartesian form:

$$\boldsymbol{\mu} = \left(\boldsymbol{\mu}_x^2 + \boldsymbol{\mu}_y^2 + \boldsymbol{\mu}_z^2\right)^{1/2} \tag{2.61}$$

$$< \boldsymbol{\alpha} > = 1/3 \left(\boldsymbol{\alpha}_{xx} + \boldsymbol{\alpha}_{yy} + \boldsymbol{\alpha}_{zz}\right) \tag{2.62}$$

2.7.4 UV Spectra

The UV-vis spectra present significant characteristics that are of restricted use for distinguishing of sample rather it is essential in quantitative estimations. The specimen concentration in certain solution is evaluated through measuring absorbance at particular wavelength and employing Beer-Lambert Law which states that "When light passes through / reflected from the sample, the amount of light absorbed is the difference between the incident (I_o) and the transmitted (I) radiation. The light absorbed is expressed as absorbance or transmittance." The transmittance (T) is given by:

$$\boldsymbol{T} = \boldsymbol{I}/\boldsymbol{I_0} \tag{2.63}$$

$$\%\boldsymbol{T} = (\boldsymbol{I}/\boldsymbol{I_0})/100 \tag{2.64}$$

The absorbance (A) is given by:

$$\boldsymbol{A} = -\log \boldsymbol{T} = \boldsymbol{\eta c r} \tag{2.65}$$

Where, η is the molar absorptivity, c be the molar concentration and r is the length of sample cell in cm. The above absorbance relationship shows the directly proportional nature between absorbance and number of molecules absorbing light. In UV-vis region, the incident photon energy represents electronic excitations from occupied orbitals to unoccupied orbitals. The energy difference between ground state and first excited state is given by the longest wavelength absorbed. For instance, π → π* transition is attained when photon energy is associated with the energy variation among bonding (π) and antibonding (π*) orbitals.

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