2.1 Basic Origin

Among different computational and theoretical techniques, one of the prestigious methods widely used for predicting ground state properties of materials with large number of electrons is density functional theory (DFT). Utilizing DFT, one can solve time-independent Schrödinger like Kohn-Sham equation for studying the properties of bulk, nano materials as well as complex systems of biomolecules with nano materials. This theory is the developed version of Thomas and Fermi model proposed in early twentieth century, and further treated by Hartree, Fock, Dirac and Slater. The foundation of DFT was formulated by the two famous theories, one proposed by Hohenberg and Kohn [1] and later by Kohn and Sham [2] which provides an inexpensive tool for calculating the ground state properties of many electron systems. DFT is widely utilized for evaluating the electronic band structure, adsorption and surface defect energy, electric dipole and quadruple moments, infrared and Raman spectra, etc.

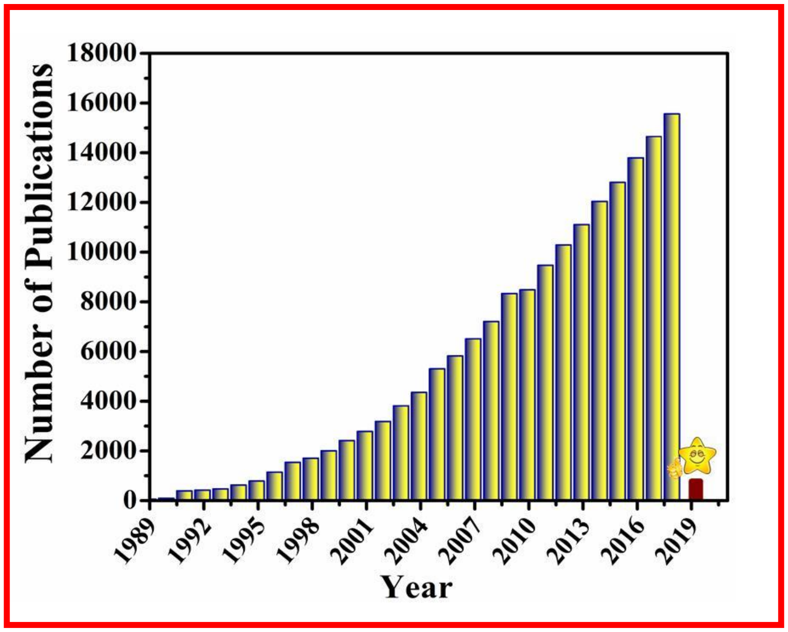

Figure 2.1: *Growth of research papers based on DFT calculation (From web of science data www.webofknowledge.com).*

The Figure 2.1 shows the growth of research articles till 2019 reporting DFT based calculations. The major advantage of DFT over other approaches is the reduction in the 3N degrees of freedom to 3 by incorporating overall electron density instead of number density for constructing the wave-function. However, it is a known fact that the DFT does not give an exact solution of the Schrödinger equation, instead several approximations are used for the exchange and correlation functional that determine the Coulomb interaction beyond electrostatic interaction. Such approximation includes local density approximation (LDA) and generalized gradient approximation (GGA), which enhances the calculation efficiency than traditional wave function based methods [3, 4].

2.1.1 Many Body Problem

At atomic level, the properties of crystalline solids are governed by quantum mechanics. Fundamental constituents of any material are the nuclei and electrons which suggest that all properties are related with the interactions taking place between electrons and ions. These electrons and ions do not obey classical mechanics, so to understand the interaction between nuclei and electrons we have to treat the system by quantum mechanical approach. The behavior of electrons and ions governed under quantum mechanical approach can be understood by solving the time independent Schrödinger equation given by [5]

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

Here, H is the Hamiltonian of the system, $\boldsymbol{\psi}$ is the wave function and $\mathbf{E}$ is the energy eigen value of the system known as total energy of the system. 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. However, in conventional solids, there are large number of electrons and ions, and thus it results into complex interactions between the electron and ions. So, the Hamiltonian of the system also acquires complex form and is given by

$$\boldsymbol{H = T_E + T_I + V_{II} + V_{EE} + V_{IE}} \tag{2.2}$$

$$\begin{aligned}\boldsymbol{H} = &-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \bar{r}_i^{\,2}} - \frac{\hbar^2}{2M}\sum_l \frac{\partial^2}{\partial \bar{R}_l^{\,2}} + \frac{1}{2}\sum_{\substack{l,l'\\ l\neq l'}} \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l Z_{l'}}{|\bar{R}_l - \bar{R}_{l'}|} \\ &+ \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\bar{r}_i - \bar{r}_j|} - \sum_i\sum_l \frac{e^2}{4\pi\varepsilon_0}\frac{Z_l}{|\bar{r}_i - \bar{R}_l|}\end{aligned} \tag{2.3}$$

Here, T_E and T_I are the kinetic energy of electrons and ions, while V_{II}, V_{EE}, and V_{IE} are potential energy of two nuclei, two electrons and nuclei-electron system respectively. The indices *i* and *l* runs for electron and nuclei, m_e and M stands for the mass of electron and nuclei, Z_l and Z_l' defines the charges on different nuclei, $\bar{\boldsymbol{r}}_i - \bar{\boldsymbol{r}}_j$, $\bar{\boldsymbol{R}}_l - \bar{\boldsymbol{R}}_l{}'$ and $\bar{\boldsymbol{r}}_i - \bar{\boldsymbol{R}}_l$ represents distances between electron-electron, nuclei-nuclei and electron-nuclei respectively.

The solution of equation 2.1 gives the energy eigen state known as total energy of the system and from the total energy, we can calculate the ground state properties of materials at equilibrium condition. One has to note that the Hamiltonian presented in equation 2.3 requires only atomic mass, charge of electron, atomic number and mass of nuclei. The solution of equation 2.1 does not require any adjustable parameters hence is known as first-principle calculation.

In practice, for smaller system such as hydrogen we can solve the equation 2.1, whereas it is difficult to solve for large systems in which several approximations were proposed to solve many body Schrödinger equation.

2.2 Wave Function Based Method to Solve Many Body Problem

2.2.1 Born-Oppenheimer Approximation

Ions are 10^3-10^4 times heavier than electrons, so we can assume the movement of ions to be stationary with respect to electrons. According to Born-Oppenheimer (BO) approximation, wave function can be separated in two parts: (a) electronic part and (b) ionic part. Following the BO approximation, many body wave function can be expressed as [6]

$$\boldsymbol{\psi} = \boldsymbol{\chi_i}(\bar{R})\, \boldsymbol{\Psi_E}(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) \tag{2.4}$$

Here $\chi_i(\bar{R})$ represents ionic, while $\Psi_E(\bar{r},\, \bar{R})$ stands for electronic wave function. Separated ionic and electronic part of wave function leads to following equations 2.5 and 2.6

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

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial \overline{\bar{r}_i}^2} + \boldsymbol{V_{IE}}(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) + \boldsymbol{V_{EE}}(\bar{\boldsymbol{r}})\right] \boldsymbol{\Psi_E}(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) = \boldsymbol{E_E\Psi_E}(\bar{\boldsymbol{r}},\, \bar{\boldsymbol{R}}) \tag{2.6}$$

As ions are considered stationary, the kinetic energy term for ions vanishes and ion-ion potential becomes constant in equation 2.5, whereas electron-ion interaction depends on position of electrons only.

2.2.2 Hartree Approximation

After the separation of electronic and ionic wave functions by BO approximation, Hartree considered only electronic part of wave function and assumed that electronic wave function can be represented in terms of single particle function [7] given by

$$\boldsymbol{\Psi_H = \Psi(\overline{r_1}, \sigma_1)\Psi(\overline{r_2}, \sigma_2) \dots \Psi(\overline{r_N}, \sigma_N)} \tag{2.7}$$

where, $\boldsymbol{\Psi(\overline{r_\iota}, \sigma_i)}$ determines the wave function of i^{th} electron, $\overline{r_\iota}$ is the postion coordinate of ith electron with spin $\boldsymbol{\sigma_i}$.

Using the Hamiltonian of equation 2.6 and wave function from equation 2.7, one can write the complete Schrödinger equation for electronic part as follow

$$-\frac{\hbar^2}{2m_e}\nabla_i{}^2\Psi_i - \frac{1}{4\pi\varepsilon_0}\sum_l \frac{Ze^2}{|\bar{r}_i - \bar{R}_l|}\Psi_i + \frac{1}{4\pi\varepsilon_0}\sum_{j\neq i}\int \frac{e^2|\Psi_j|^2}{|\bar{r}_i - \bar{r}_j|}d^3r_j = \ \in_i \Psi_i \tag{2.8}$$

In left hand side of the equation, first term is the kinetic energy, 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 2.8 is known as Hartree equation and solution of equation is given by variational principle which provides exact ground state energy through minimization of expectation value of energy E.

$$\boldsymbol{E = \frac{\langle \Psi_H | H | \Psi_H \rangle}{\langle \Psi_H | \Psi_H \rangle}} \tag{2.9}$$

Hartree reduces many body problem into one electron problem which is also known as independent electron approximation. However, independency of electron neglects correlations between electrons. Also, Hartee did not consider the asymmetric wave function for electrons;

as the electrons are classified as Fermions, and according to the Pauli's exclusion principle the asymmetric nature should be considered.

2.2.3 Hartree-Fock Approximation

To understand the asymmetric nature of wave function and the effect of correlation, Hartree and Fock considered the asymmetric wave function given by the equation below:

$$\boldsymbol{\Psi_{HF}\left(\overline{r_1},\sigma_1,\ldots,\bar{r}_\iota,\sigma_i,\ \ldots,\bar{r}_J,\sigma_j,\ldots\right) = -\Psi_{HF}\left(\overline{r_1},\sigma_1,\ldots,\bar{r}_\iota,\sigma_i,\ \ldots,\bar{r}_J,\sigma_j,\ldots\right)} \quad (2.10)$$

HF approximation is based on minimization of equation 2.9 by considering the above asymmetric wave function in the determinant form known as Slater's determinant [8]

$$\boldsymbol{\Psi_{HF}(\overline{r_1},\sigma_1,\ldots,\overline{r_N},\sigma_N) = \begin{vmatrix} \Psi_1(\overline{r_1},\sigma_1) & \Psi_1(\overline{r_2},\sigma_2)\ldots & \Psi_1(\overline{r_N},\sigma_N) \\ \Psi_2(\overline{r_2},\sigma_2) & \Psi_2(\overline{r_2},\sigma_2)\ldots & \Psi_2(\overline{r_N},\sigma_N) \\ \Psi_N(\overline{r_N},\sigma_N) & \Psi_N(\overline{r_N},\sigma_N)\ldots & \Psi_N(\overline{r_N},\sigma_N) \end{vmatrix}} \quad (2.11)$$

The determinant of the wave function can be written as

$$\boldsymbol{\Psi_{HF} = \frac{1}{N!}\sum_P (-1)^p P\ \Psi_1(x_1)\ \Psi_2(x_2)\ \ldots\ \Psi_N(x_N)} \quad (2.12)$$

Where, $x = (\bar{r}, \sigma)$, P is the permutation number and p is number of interchanges making up this permutation. Substituting the determinant form of equation in variational principle (equation 2.9) gives expectation value of Hamiltonian as

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

$$\boldsymbol{-\frac{1}{2}\sum_{i,j}\sum_{j\neq i}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{\Psi_i{}^*(\vec{r})\Psi_j{}^*(\vec{r}')\,\Psi_i(\vec{r}')\,\Psi_j(\vec{r})}{|\vec{r}-\vec{r}'|}d^3rd^3r'} \quad (2.13)$$

The first term of above equation consist of kinetic energy and interaction of external potential, the second term represents Hartree potential and the last term appeared due to the Pauli's exclusion principle also known as exchange energy. Minimization of equation 2.13 leads to canonical form of Hartree-Fock equation

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

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

Involvement of exchange energy by taking asymmetric nature of wave-function improves Hartree method. However, total energy $\in_i$ contains minimization over sum of N particle Slater's determinant (equation 2.11) and this type of determinant are quite large; hence this approximation becomes computationally very costly for large as well as small systems.

2.3 Density Based Method –Density Functional Theory

Our aim is to calculate ground state energy of the many electron system by solving many body Schrödinger equation given in equation 2.6. For N number of electron there are 3N variables which leads to complex solution of equation 2.6, while in density based method, the interaction energy and potentials depend only on the density of electrons.

2.3.1 Thomas-Fermi Theory

Calculation of ground state energy using density based theory originated from the Thomas-Fermi (TF) theory for a many electron systems [9, 10]. In 1927, TF proposed that the total energy of the system can be written as a functional of electron density. In this method, the basic variable is electron density instead of single particle wave function or orbitals. TF theory can approximate the kinetic energy and potential of N interacting electrons by following equation

$$\boldsymbol{T_{TF} = C_k \int n(\bar{r})^{\frac{5}{3}} d^3 r} \tag{2.15}$$

Where, $\boldsymbol{C_k = \frac{3}{10}\frac{\hbar^2}{m_e}(3\pi^2)^{\frac{2}{3}}}$ and $n(\bar{r})$ is the density of electrons. T_{TF} is the local approximation to the kinetic energy that can be obtained by adding all free electron energy states up to Fermi wave vector. The TF theory gives total energy in equation 2.16 as a functional by adding above kinetic energy, electrostatic energy and interaction of external potential as a functional of electron density

$$\boldsymbol{E = T_{TF} + \int V_{IE}(\bar{r})\, n(\bar{r}) d^3 r + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r}-\vec{r}'|} d^3 r d^3 r'} \tag{2.16}$$

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

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

$$\boldsymbol{\mu = \frac{5}{3} C_k n(\bar{r})^{\frac{2}{3}} + V(\bar{r})} \tag{2.17}$$

This is the basic equation of TF theory and it can be solved self consistently. Here, TF have not included the exchange energy in the above equation. Further, this method has been extended by Dirac to include the exchange interaction and to include the correlation to kinetic energy functional [11, 12]. The TF theory does not show any shell structure as well as it does not describe the behavior of electrons for atoms to complex systems.

2.3.2 Hohenberg and Kohn Theorems

In this section, we will describe the two basic theorems of DFT given by Hohenberg and Kohn. Hohenberg and Kohn developed these two inventive theorems [1]. They showed that all the ground state properties of systems with many electrons can be calculated as a functional of electron density. Functional represents function of function that gives a number i.e. path for function to a finite number. Since the density of the electron depends only on three variables which reduces the complexity of calculations.

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

The external potential corresponding to the density of electrons can be used to get unique Hamiltonian which is used to solve many electron Schrödinger equation. For the proof of above theorem, the best way is to assume two external potentials $V_{ext}^{(1)}(\mathbf{r})$ and $V_{ext}^{(2)}(\mathbf{r})$ which differ by a constant and give same density $n(\mathbf{r})$. These different potentials give two

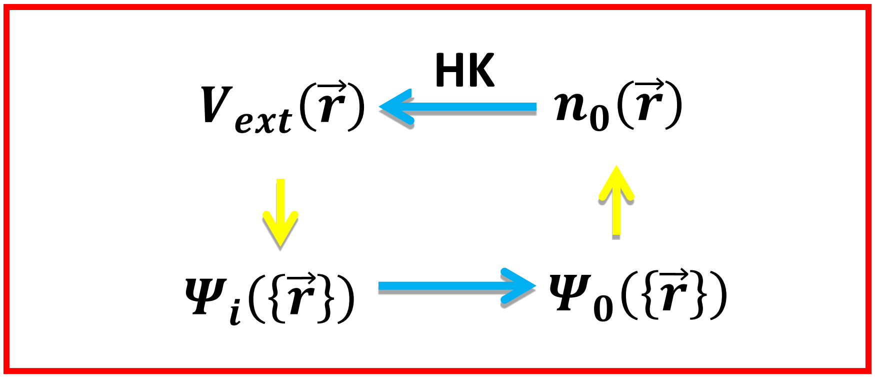

Figure 2.2: *Schematic representation of first Hohenberg and Kohn theorem. Here, the HK theorem completes the circle, while other smaller arrow shows the solution of Schrödinger equation. Image adapted from ref. [13].*

different Hamiltonians $H^{(1)}$ and $H^{(2)}$ and two distinct wave functions $\psi^{(1)}{}_{ext}(\boldsymbol{r})$ and $\psi^{(2)}{}_{ext}(\boldsymbol{r})$ respectively.

According to variational principle, $\psi^{(2)}{}_{ext}(\mathbf{r})$ cannot be the ground state of $H^{(1)}$, so we can write

$$\boldsymbol{E^{(1)} = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle} \tag{2.18}$$

For the sake of simplicity, we consider here the non-degenerate system (proof for degenerate system is given in ref. [14]. The last term of equation 2.18 can be written as

$$\boldsymbol{\langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | H^{(2)} | \Psi^{(2)} \rangle + \int dr \left[V^{(1)}_{ext}(r) - V^{(2)}_{ext}(r) \right] n_0(r)} \tag{2.19}$$

In the similar way we can write the equation for $H^{(2)}$ as below

$$\boldsymbol{\langle \Psi^{(1)} | H^{(2)} | \Psi^{(1)} \rangle = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle + \int dr \left[V^{(2)}_{ext}(r) - V^{(1)}_{ext}(r) \right] n_0(r)} \tag{2.20}$$

By adding above two equations 2.19 and 2.20 we get

$$\boldsymbol{E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)}} \tag{2.21}$$

This equation shows that the initial guess of two external potential giving same charge density becomes false and proves the theorem.

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

External potential is determined uniquely using density and that unique potential determines the electronic wave function and all the other observables can be determined uniquely. From this, every property can be expressed in term of density and total energy which can be written as

$$E[n] = T[n] + E_{int}[n] + \int V_{ext}(r)n(r) + E_{II} \equiv F[n] + \int V_{ext}(r)n(r) + E_{II} \qquad (2.22)$$

Here, F[n] encapsulated is the interaction potential of electrons and kinetic energy of electrons for all systems. The ground state energy determined by unique ground state density is

$$E^{(1)} = E\left[n^{(1)}\right] = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle \qquad (2.23)$$

Here, total energy can be written as functional of n(r). F[n] in equation 2.22 can be written as a functional of density n(r)

$$F[n] = T_s[n] + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')\,n(\vec{r})}{|\vec{r}-\vec{r}'|} d^3r d^3r' + E_{XC}[n] \qquad (2.24)$$

By knowing F[n], we can vary density until minimization of total energy for the system. Thus, the knowledge of total energy is sufficient to determine the ground state energy and density.

2.3.3 Kohn-Sham Equation-Density Functional Theory

Hohenberg and Kohn approach is just the reformulation of many body interacting

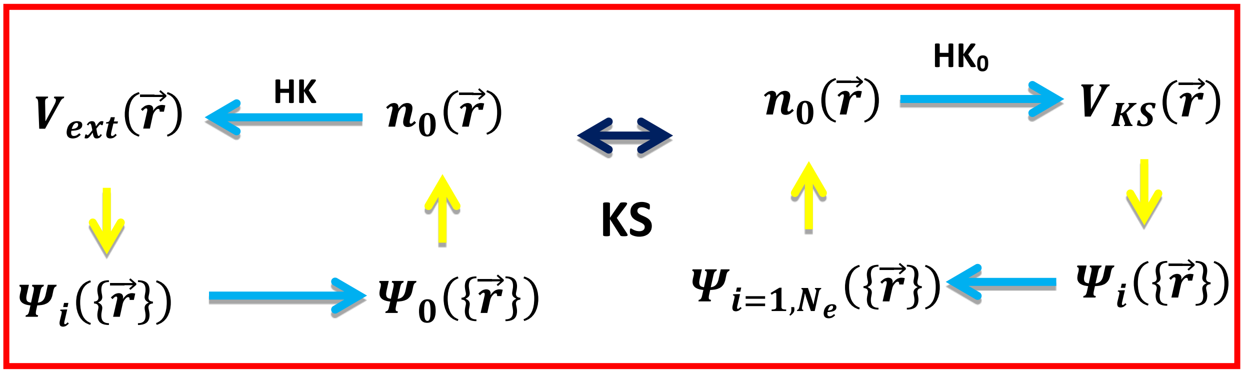

Figure 2.3: *Same as Figure 2.2 but for Kohn – Sham ansatz. HK$_0$ defines Hohenberg and Kohn theorem applied to non-interacting system. The connection between many body and the independent particle system is provided by Kohn – Sham.*

systems in terms of electron density. Also HK theory approximated kinetic energy of electrons and exchange-correlation energy same as TF theory. To overcome this problem, Kohn and Sham (KS) have handled kinetic energy much better way than earlier theories. KS replaced the potential of interacting system by an auxiliary non-interacting system with assumption of same ground state density and then same ground state properties [2].

For this groundbreaking work, Walter Kohn was awarded Noble prize in chemistry in 1998. The approach of KS is summarized in Fig. 2.3. The KS approach is just separate kinetic energy term from equation 2.24, which reformulate the many body equation as follows:

$$\boldsymbol{E[n(\bar{r})] = \int V(\bar{r})n(\bar{r})d^3r + T_s[n] + \frac{1}{2}\iint \frac{e^2}{4\pi\varepsilon_0}\frac{n(\vec{r}')\,n(\vec{r})}{|\vec{r}-\vec{r}'|}d^3r d^3r' + E_{XC}[n]} \quad (2.25)$$

Here, $\boldsymbol{T_s[n]}$ is now independent kinetic energy and $V_{ext}(\vec{\boldsymbol{r}})$ is replaced by $V(\vec{\boldsymbol{r}})$, which is the potential between electrons and nuclei. Last term of equation $\boldsymbol{E_{XC}[n]}$ is the exchange and correlation energy accounts for the many body quantum mechanical effect. Now by minimization of the energy by taking the functional derivatives of equation 2.25 gives

$$\boldsymbol{\frac{\delta E[n]}{\delta n(\bar{r})} - \mu = 0} \quad (2.26)$$

$$\boldsymbol{\frac{\delta T_s[n]}{\delta n(\bar{r})} + V(\bar{r}) + V_H(\bar{r}) + V_{XC}(\bar{r}) - \mu = 0} \quad (2.27)$$

Here, $\boldsymbol{V_H(\bar{r})}$ is the Hartree potential in terms of electron density and $\boldsymbol{V_{XC}(\bar{r}) = \frac{\delta E_{xc}[n]}{\delta n(\bar{r})}}$ solution of equation will give the electron density and further it leads to total energy of system. However, there are two unknown terms in equation 2.27, one is $\boldsymbol{T_s[n]}$ and other one is exchange correlation potential $\boldsymbol{V_{XC}(\bar{r})}$ arising from Pauli and Coulomb interaction. To overcome this problem, KS have considered density as square of orbitals of the system

$$\boldsymbol{n(\bar{r}) = \sum_{i=1}^{N} |\, \Psi_i(\bar{r})|^2} \tag{2.28}$$

Where, KS orbitals are determined by $\boldsymbol{\Psi_i(\bar{r})}$**.** KS Kinetic energy can be written as a single particle by following expression

$$\boldsymbol{T_s[n] = -\frac{\hbar^2}{2m_e} \sum_i^N \langle\, \Psi_i(\bar{r}) \big|\nabla^2\big|\, \Psi_i(\bar{r})\rangle = -\frac{\hbar^2}{2m_e}\nabla^2} \tag{2.29}$$

Here, $T_s[n]$ is responsible for density oscillation of shell structure and it has large part of the total kinetic energy of system. Here, $\boldsymbol{E_{xc}[n]}$ is the sum 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 2.11). By solving equation 2.25 we get

$$\boldsymbol{\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\bar{r})\right] \Psi_i(\bar{r}) = \epsilon_i\, \Psi_i(\vec{r})} \tag{2.30}$$

Here, $\boldsymbol{V_{eff}(\bar{r})}$ is known as effective potential and determined by sum of exchange potential ($V_{ext}(\bar{r})$), Hartee potential $V_H(\bar{r})$ and exchange-correlation potential ($V_{XC}(\bar{r})$). Equation 2.30 is Kohn-Sham equation and it is exactly same as the many body Schrödinger equation. Solution of KS equation gives exact ground state energy and it describes behavior of one electron moving in multiple electron system by effective potential. Solution of equation depends only on density of electrons and it has only 3 variables which reduces computational costs gradually. This makes KS theory become powerful tool in determination of ground state properties of materials. However, the form of exact exchange-correlation energy functional is still unknown and for that different approximation was taken into account such as local density approximation (LDA) and generalized gradient approximation (GGA).

2.4 Self-Consistency in Kohn-Sham Equation

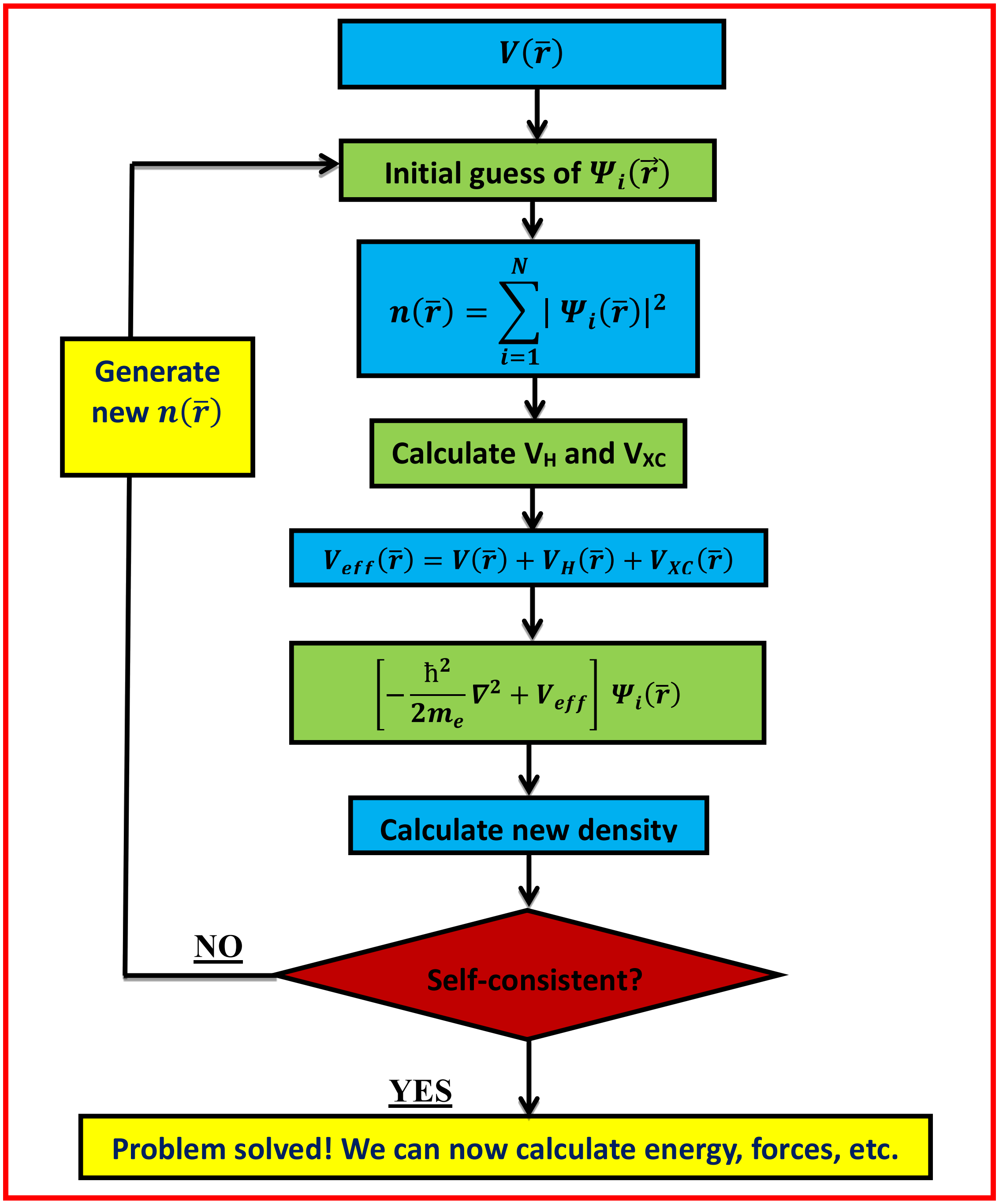

Figure 2.4: *Schematic flow chart to find the solution of KS equation. [From Quantum Espresso Tutorial].*

Above section describe in detail the KS theory and the derivation of KS equation. In practice, the solution of KS equation is obtained numerically by changing density of electrons and effective potential to achieve the self-consistency. Figure 2.4 presents the self-consistent process to solve KS equation in schematic manner. For the solution of KS equation, we must know the effective potential. Hartree potential and exchange correlation potential depends on electron density and this density yield correlation energy where initial guess of density is made. An approximation to initial guess for electron density is adding up densities of isolated atoms arranged in corresponding material.

The effective potential has been calculated and new density is obtained from unknown wave function $\boldsymbol{\Psi_i(\bar{r})}$**.** In self-consistency, first initial guess is made for electron density. This can be done by specifying nuclear coordinates which gives V(r) and for exchange. If new density is equal to old density then self-consistency is achieved otherwise new effective potential is obtained from new electron density. Once ground state density is obtained, total energy of system is calculated by the following equation [14]

$$\boldsymbol{E[n] = 2\sum_{v=1}^{N_e/2} \epsilon_v - \frac{e^2}{2}\int dr\, dr' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n] - \int dr\, n(r) V_{xc}(r) + E^{E_{wald}}} \tag{2.31}$$

$\boldsymbol{E^{E_{wald}}}$ is the nuclear-nuclear interaction energy and can be obtained by Ewald summation method.

2.5 Exchange and Correlation Functional

In practice, DFT solves many body problem using KS equation with approximation taken into account for exchange and correlation potential term. Different types of approximation such as LDA, GGA, meta-GGA etc. have been taken for this potential [2]. The exchange interaction term defined as

$$\boldsymbol{E_x[n] = \langle \Psi[n] | V_{EE} | \Psi[n] \rangle - U[n]} \tag{2.32}$$

is the repulsion between electrons and can be calculated from KS wave function, which further gives Hartree contribution and an exchange interaction. Slater determinant is used to evaluate the KS wave function and Fock orbitals gives exchange energy [15]. This exchange energy is totally different from the HF approximation. The differences between HF exchange and KS-DFT exchange are subtle. They can be thought of as having two different sources.

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

The correlation term can be determine by the following expression

$$\boldsymbol{E_c[n] = F[n] - T_S[n] - U[n] - E_X[n]} \tag{2.33}$$

Till date, exact formalism of exchange correlation is still not available. Better approximations such as LDA, GGA etc are taken account for this exchange and correlation term.

2.5.1 Local Density Approximation (LDA)

First approximation developed by Kohn and Sham is local density approximation (LDA) which is very successful in predicting electronic band structure of solids and molecules. It is assumed that the electron density varies very slowly in space, therefore electron gas in a small volume element (d^3r) is considered locally uniform. LDA which gives its resemblance with not so praised Slater approximation to HF is quite successful. Therefore, one could use the exchange-correlation energy of the homogeneous electron gas to evaluate E_{xc}. The exchange-correlation energy functional and potential can be written as:

$$\boldsymbol{E_{xc}^{LDA}[n(r)] = \int dr\ \ n(r)\ \epsilon_{xc}^{LDA}[n(r)]} \tag{2.34}$$

$$\boldsymbol{V_{xc}[n(r)] = \left(E_{xc}[n] + n\frac{\delta E_{xc}[n]}{\delta n}\right)_{n=n(r)}} \tag{2.35}$$

where, $E_{xc}[n]$ is the exchange-correlation energy per electron in an homogeneous electron with density **n**. Using quantum Monte Carlo simulations this functional for homogenous electron gas were obtained by Ceperly and Alder [16]. Further, Perdew and Zunger [17] and Ortiz and Ballone [18] have been parameterized above functional. For system in which electrons placed in infinite region of space, uniform positive external potential LDA is good approximation. Kinetic and exchange energies of such a system can be easily calculated by KS wave functions which are represented by Slater determinants of plane waves. However, there are some drawbacks in LDA mainly in strongly correlated systems such as LDA fails for transition metals s. In the field of quantum chemistry, LDA overestimates intermolecular bonds and molecular binding energy. To overcome this problem several efforts have been put to find better functional. For a system that contains an odd number of electrons, pure LDA performs badly, since it makes no difference between polarized and unpolarized densities.

2.5.2 Generalized Gradient Approximation (GGA)

In complex systems, electron density may vary with the volume element, so LDA can fail to determine ground state properties. To overcome this problem, gradient correction in density is required to improve the LDA [19]. In GGA, not only density is considered but also the gradient of density is considered for evaluating the exchange and correlation term

$$\boldsymbol{E_{xc}^{GGA}[n(r)] = \int dr\, n(r)\, \epsilon_{xc}^{GGA}(n(r), \nabla n(r), \dots)} \qquad (2.36)$$

Exchange and correlation is now semi empirical functional and degree of non-locality have a dependency of electron density. GGA favors density inhomogeneity more than LDA by the non-locality of the exchange with most common densities. This approximation assumes a gradient in the charge density. It can be written as

$$\boldsymbol{E_{xc}[n] = \int \varepsilon_{xc}(n)\,|_{n=n(r)} n(r) F_{xc}[n(r), \nabla n(r)] dr} \qquad (2.37)$$

For more simplification in calculation, E_{xc} and F_{xc} must be parameterized analytic functions. Perdew, Burke, and Ernzerhof have parameterized E_{xc} and F_{xc} from first principles calculation [20]. In predicting bond dissociation energy and the transition-state barrier, GGA is better than LDA (not always). To satisfy several further exact conditions, Perdew-Wang 1991 (PW91) [21] designed functional which is an analytic fit to this numerical GGA. Plane waves and pseudo potentials which form a very natural alliance are a hallmark of the method.

2.5.3 Pseudopotentials

In many cases it is convenient to perform DFT calculations by describing explicitly the valence electrons only. This simplification can be achieved by introducing so-called '*pseudopotential*'. When we consider the electronic charge densities associated with all core states or all valence states, we realize that the core electrons are tightly bound to nucleus, while the valence electrons tend to localize further away. The separation of core states from valence states suggests that we should be able to perform DFT calculations on poly-atomic systems by keeping the core electrons as they appear in the isolated atom [22]. If the core is to be held 'frozen', then there is not much point in describing the Kohn–Sham wave functions of core states. The next step is therefore to completely remove the core electrons from our description. This choice leads to saving of substantial computational cost. In practice, the distinction between core and valence is not a strict one, and depends on the level of accuracy that one is trying to achieve.

After deciding which electrons should be considered as the valence states, the procedure for eliminating the core electrons is not trivial and requires some care. For a start, near the nucleus, the valence electronic wave functions must undergo a change of sign in order to be orthogonal to the core states. If we simply ignore the core states, then the valence states would not exhibit the correct 'nodal structure' near the nucleus. A second issue is that, even if we were able to obtain the correct oscillating features in the wave functions, then it would be very difficult to describe them using a real-space grid or a plane wave basis.

In this case the description of the oscillations would be very poor, thereby undermining the accuracy and the numerical stability of the calculations. This issue can be fixed by using a fine real space grid or a higher kinetic energy cut-off in the case of a plane wave basis, but this would result into time-consuming calculations. The difficulties associated with the nodal structure of the valence wave functions can be overcome at once by replacing the oscillating part of the wave function by a smooth and nodeless curve. This wave function is typically referred to as the 'all-electron wave function'.

The introduction of pseudo-wave function which is smooth in the pseudization region eliminates the problems connected with the nodal structure of all-electron wave function. The remaining question now is how to obtain such a smooth pseudo wave function directly by solving the Kohn–Sham equations. The strategy underlying the pseudopotential method is to construct a modified nuclear potential which satisfies the following conditions: (i) outside pseudization region the modified potential coincides with the original Kohn–Sham potential (obtained from a calculation including all the electrons); (ii) inside pseudization region, potential is modified in such a way that the solution of the Kohn–Sham equation yields precisely the pseudo-wave function. There are mainly two kinds of pseudopotentials: Norm-Conserving and Ultrasoft type. There are few requirements for *ab-initio* pseudopotential given by Hamann, Schluter and Chiang [23]. The ultra-soft pseudopotentials fulfill the goal of accurate calculations by a transformation which expresses the problem in terms of a smooth and an auxiliary function around each ion core.

2.6 Density Functional Perturbation Theory

The lattice dynamical properties such as phonons, Raman intensities and infra-red absorption cross sections, electron-phonon interaction depend upon a system response to some form of perturbation. Density functional perturbation theory **(**DFPT) has ability to calculate such properties by knowledge of microscopic quantum mechanical mechanisms within the density functional framework. Predictions of material's vibrational properties are very important apart from their electronic structure. For perfect prediction of vibrational frequencies infrared, Raman spectroscopy, and inelastic scattering techniques are used. The resulting vibrational spectra are very important to describe the chemical structure and binding of atoms and molecules.

Gonze [24] and Baroni [25] have formalized DFPT systematically. The Baroni formalism is based upon self-consistent solution of a series of equations that may be solved using Green's function method while the perturbative expansion of the KS energy functional is given by Gonze formalism which leads to a variational problem. Second order force constants with respect to atomic displacements and electric fields can be calculated by DFPT. Any arbitrary wavelength can be calculated by response to a perturbation. The first derivative of the total energy with respect to the nuclear coordinates can be calculated using the Hellmann-Feynman theorem. The BO Hamiltonian depends on R via the electron-nucleus interaction

$$\boldsymbol{V_{ne}[\langle V_{ne}\rangle = \int dr\, n(r) v_{ext}(r) \Rightarrow \int dr\, n_R(r) v_R(r)]} \tag{2.38}$$

The classical interaction between nucleus is V_{nn}, whose energy for the nuclear configuration R is $E^{Ewald}{}_{R}$.

$$\boldsymbol{F_I = -\int n_R(r) \frac{\partial V_R(r)}{\partial R_I} dr - \frac{\partial E_R^{Ewald}}{\partial R_I}} \tag{2.39}$$

where $n_R(r)$ is the electron charge density for the nuclear configuration R:

$$\boldsymbol{n_R(r) = N_e \int dr_2 \ldots dr_{Ne} |\Psi_R(r, r_2, \ldots, r_{Ne})|^2} \tag{2.40}$$

To make the parametric R dependence explicit, notations are changed from $V_{ext}(r)$ to $V_R(r)$ and from $n(r)$ to $n_R(r)$. The Hessian of the BO energy surface is obtained by differentiating the Hellman-Feynman forces with respect to the nuclear coordinates:

$$\frac{\partial^2 E(R)}{\partial R_I \partial R_J} \equiv -\frac{\partial F_I}{\partial R_J} = \int dr\, \frac{\partial n_R(r)}{\partial R_J}\frac{\partial V_R(r)}{\partial R_I} + \int dr\, n_R(r)\, \frac{\partial^2 V_R(r)}{\partial R_I \partial R_J} + \frac{\partial^2 E_R^{Ewald}}{\partial R_I \partial R_J} \tag{2.41}$$

The calculation of the Hessian thus requires the calculation of the ground-state electron charge density, $n_R(r)$, as well as of its linear response to a distortion of the nuclear geometry, $\partial n_R(r)/\partial R_I$.

In DFT, the ground state electronic density and wave functions are found by solving self-consistently a set of one-electron equations [25].

$$\left(-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial r^2} + V_R^{SCF}(r)\right)\Psi_R^v = \epsilon_R^v \Psi_R^v \tag{2.42}$$

$$V_R^{SCF}(r) = V_R(r) + e^2 \int dr' \frac{n_R(r')}{|r-r'|} + V_{xc}[n_R](r) \tag{2.43}$$

$$n_R(r) = \sum\nolimits_v |\Psi_R^v(r)|^2 f_v \tag{2.44}$$

where f_v is the occupancy of the v^{th} state, V_{xc} is the exchange-correlation potential, $n_R(r)$ is the electronic-density, and $V_R(r)$ is the external potential acting on the electrons (actually a sum over an array of pseudo-potential).

In equation 2.41 electron-density response, $\frac{\partial n_R(r)}{\partial R_I}$ can be evaluated by linearizing above three equations ((2.42), (2.43), and (2.44)) with respect to wave-function, density, and potential variations, respectively. Linearization of Eq. (2.44) leads to:

$$\frac{\partial n_R(r)}{\partial R_I} = 4Re \sum\nolimits_{v=1}^{N_e/2} \psi_R^{v*}(r)\, \frac{\partial \psi_R^v(r)}{\partial R_I} \tag{2.45}$$

Since the external potential (both unperturbed and perturbed) is real, each KS eigen function and its complex conjugate are degenerate. As a consequence, the imaginary part of the sum appearing in equation 2.45 vanishes, so that the prescription to keep only the real part can be dropped.

The variation of KS orbitals $\frac{\partial \Psi_R^v(r)}{\partial R_I}$ is obtained by first order perturbation theory:

$$\left(H_R^{SCF} - \epsilon_R^v\right)\frac{\partial \Psi_R^v(r)}{\partial R_I} = -\left(\frac{\partial V}{\partial R_I} - \frac{\partial \epsilon_v}{\partial R_I}\right)\Psi_v \qquad (2.46)$$

where, $$H_R^{SCF} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial r^2} + V_R^{SCF}(r) \qquad (2.47)$$

with the unperturbed KS Hamiltonian,

$$\frac{\partial V_R^{SCF}(r)}{\partial R_I} = \frac{\partial V_R(r)}{\partial R_I} + e^2 \int dr' \frac{1}{|r-r'|}\frac{\partial n_R(r')}{\partial R_I} + \int dr' \frac{\delta V_{xc}(r')}{\delta n(r')}\frac{\partial n_R(r')}{\partial R_I} \qquad (2.48)$$

Equation 2.48 is first-order correction to the self-consistent potential, and

$$\frac{\partial \epsilon_R^v}{\partial R_I} = \langle \Psi_R^v | \frac{\partial V_R}{\partial R_I} | \Psi_R^v \rangle \qquad (2.49)$$

the above equation is first order variation of the KS eigenvalue. Equations 2.45 – 2.59 form a set of self-consistent equations for the perturbed system analogous to the KS equations in the unperturbed case. Equations 2.42, 2.43, and 2.44 with the KS eigenvalue equation, is being replaced by the equation of a linear system, equation 2.46. The linear system, equation 2.46 can be solved for each $\frac{\partial \Psi_R^v}{\partial R_I}$ with the electron density response calculated from equation 2.45 and the potential response $\frac{\partial V_R(r)}{\partial R_I}$ updated from equation 2.48 until self-consistency achieved. The computational cost for determining density response to a single perturbation is of the same order as that needed to calculate the unperturbed ground state density. Now by putting $\frac{\partial \psi_R^v(r)}{\partial R_J}$ and $\frac{\partial V_R}{\partial R_I}$ in equation 2.48, one gets the Hessian of the BO energy surface.

2.7 Dispersion Correction to Density Functional Theory

The capacity of Kohn – Sham DFT is to study the electronic structure of materials attributed to provide distinct properties of molecules and solids with reasonably accurate predictions. For exchange correlation term various approximations such as LDA, GGA and hybrid functional are taken into account. However, long-range electron interaction which results into van der Waals (vdW) forces, GGA as well as hybrid functionals failed. [26-28]. For vdW correction, total energy is given by

$$\boldsymbol{E_{DFT-D} = E_{KS-DFT} + E_{disp}} \tag{2.50}$$

where E_{DFT-D} is general KS self-consistency energy and the empirical vdW dispersion correction to the correlation functional E_{disp} is given by [29]

$$\boldsymbol{E_{disp} = -s_6 \sum_{i=1}^{(N_{at}-1)} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij})} \tag{2.51}$$

where N_{at} is the numbers of atoms in the system, C_6^{ij} defines the dispersion coefficient for atom pair *ij*, s_6 is global scaling factor that depends on the functional used and R_{ij} is an interatomic distance. To avoid near singularities for small R, damping function $f_{dmp}(R_{ij})$ is used and it is given by

$$\boldsymbol{f_{dmp}(R_{ij}) = \frac{1}{1+e^{-d\left(R_{ij}/R_{0ij}-1\right)}}} \tag{2.52}$$

where R_0 is the sum of atomic vdW radii. C_6^{ij} and R_{0ij} calculated by following relation

$$\boldsymbol{C_6^{ij} = \sqrt{C_6^i C_6^j} \qquad R_{0ij} = R_{0i} + R_{0j}} \tag{2.53}$$

For heavier elements, this approach can trace back to the combination rule employed for the composed C_6^{ij} that gives too much weight to the smaller coefficient [29]. Equation 2.53 shows geometric mean of the form which gives much better result by precise testing of systems including elements up to xenon and large hydrocarbons with many hydrogen atoms.

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