A Brief Review of Density Functional Theory and Solvation Model

Anoop Kumar Kushwaha

School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Khordha, Odisha-752050, India

Corresponding Author: ak20@iitbbs.ac.in

In recent years, the applications of first-principles density functional theory (DFT) is diversified and expanded in a wide range due to the development of robust algorithms and more powerful computer systems. In general, DFT is used in condensed matter physics, chemistry, material science and biology to predict and interpret the behaviour of complex-system at atomic-scale. Specifically, DFT is widely applied to study the effect of dopants on phase transformation, magnetic and electronic behaviour, spin and charge transport properties, etc. in material science/condensed matter physics; geometrical and electronic structure, dynamics, spectral hyperfine-interaction, excited-state, etc. in chemistry; interactive behaviour, bond formation and breaking, stabilization, etc. in the biological system. Furthermore, the solvation models are used to include a solvent for the accuracy and realistic approach. To study the physical/chemical and biological system with DFT embedded tools such as Gaussian, Vienna Ab initio software package (VASP), Quantum espresso etc., require a basic theoretical understanding of DFT. Therefore, I have summarised DFT including basis set and solvation models for easy understanding in a short time.

1 Introduction

Efficient computer programming of the theoretical model provides a great insight into molecular/cluster systems with different perspectives. These computer-aided simulation techniques have effectively influenced both the basic understanding of atomic/molecular systems and their application in various fields of interest[1–5]. Despite the advent of more powerful computer systems such as HPC (high-performance computing), the computational capability for solving scientific problems is still facing stiff challenges, especially in the context of the atomic-level study of large molecular systems. For a few decades, first principles (Ab initio) methods, based on quantum mechanics, have emerged as a powerful tool to probe the properties of matter at an atomic scale[4,5]. The first principles-based density functional theory (DFT) has gained significant popularity because of its capability in providing the ground state properties with good accuracy[6,7]. Recently, the DFT method has been found to be effective in bringing significant acceleration in the development and optimization of new energy storage materials[8–15]. For example, in the case of rechargeable batteries, many intrinsic properties of electrode/electrolyte materials, i.e., working potential window, structural stability, metal-ion diffusivity, band structure, and electronic hopping barriers can now be computed accurately with the first-principles computation methods[16–22]. Apart from the energy storage, DFT is widely used to study charge transport[23,24], material interface[25–27], biological system[28–30], etc. Therefore, this report is focused on the theoretical methodologies, e.g. Hartree-Fock (HF) theory and DFT, which were earlier developed for finding the solution of many-body Schrodinger equation. Since the solvent effect are generally included in the molecular system, therefore, the solvation models have been also discussed in the report.

Electronic structure calculations began in the early, 1930s with the proposal of an approximate solution for the movement of electrons by Dirac, Wigner and Seitz[31–33]. The approximation suggested that each and individual electron of molecule/solid must be considered to be in motion in the self-consistent field (SCF). In the late 1930s, a few methods, for example, Hartree-Fock-Slater method, effective potential method, orthogonalized and augmented plane wave method was proposed and used for the electronic structure calculation till 1960s[34–40]. The electronic structure calculations rapidly increased in the latter part of 1960s after the formulation of DFT based on the Hohenburg-Kohn theorem and Kohn-Sham approach[41–44]. In the DFT, the electron density is considered as fundamental quantity for describing the interaction between electrons, which provides the ground state properties[43]. In the Kohn-Sham DFT, the interacting electrons in a static external potential are switched towards the non-interacting electron with the implementation of an effective potential[44]. External potential and the Coulombic interactions between the electrons are included in the effective potential, the details of which have been discussed later in this chapter. The first-principles based DFT calculations were not generally used until 1980s, due to the lack of adequate powerful computation facilities. With the development of the advanced computer system, e.g., high-performance computing (HPC) clusters, DFT based electronic structure calculations are getting more popular. At present, DFT is a leading method in solid-state physics and quantum chemistry along with several biological systems of interest[45–48].

2 Many electron systems

Calculation of the electronic structure of many-electron systems (atom, molecule/cluster or extended solid system) begin with the fundamental equation of quantum mechanics, i.e., Schrödinger equation[49]. The time-independent Schrödinger equation for many-body system is given as below;

$$\hat{\mathrm{H}}\Psi = \mathrm{E}\Psi \qquad (1)$$

where $\widehat{H}$ is Hamiltonian operator, E represents the total energy of the system in the atomic unit and Ψ is the many-body/electron wave function. Consider a molecular system with N electron with position $\{\boldsymbol{r_i}\}$ and M nuclei with position $\{\boldsymbol{R_A}\}$ as shown in the Figure 1. The corresponding Hamiltonian for such system can be written as;

$$\hat{\mathrm{H}} = \frac{1}{2}\sum_{\mathrm{i}=1}^{\mathrm{N}} \nabla_{\mathrm{i}}^2 - \frac{1}{2\mathrm{M}}\sum_{\mathrm{A}=1}^{\mathrm{M}} \nabla_{\mathrm{A}}^2 - \sum_{\mathrm{i}=1}^{\mathrm{N}} \sum_{\mathrm{A}=1}^{\mathrm{M}} \frac{\mathrm{Z_A}}{\mathrm{r_{iA}}} + \sum_{\substack{\mathrm{A,B} \\ \mathrm{A}\neq\mathrm{B}}}^{\mathrm{M}} \frac{\mathrm{Z_A\,Z_B}}{\mathrm{R_{AB}}} + \sum_{\substack{\mathrm{i,j} \\ \mathrm{i}\neq\mathrm{j}}}^{\mathrm{N}} \frac{1}{\mathrm{r_{ij}}} \qquad (2)$$

where $\mathrm{Z_A}$ and $\mathrm{Z_B}$ correspond to the mass of nuclei A and B, respectively. In Equation 2, the first and second terms represent the kinetic energies of electrons ($\mathrm{T}_{\boldsymbol{e}}$) and kinetic energies of nuclei ($\mathrm{T_n}$), respectively. Third term corresponds to the electron-nuclei coulombic interaction ($\mathrm{V_{en}}$) and fourth term represents the nuclei-nuclei coulombic repulsion ($\mathrm{V_{nn}}$). The last term of the above equation corresponds to electron-electron coulomb repulsion ($\mathrm{V_{ee}}$). Therefore, Equation 2 can be written as;

$$\widehat{H} = T_e + T_n + V_{en} + V_{nn} + V_{ee} \qquad (3)$$

The basic task is related to finding the solution of many-body Schrödinger equation which can only be solved by considering certain approximations required for simplifying the Hamiltonian. Since the masses of protons and neutrons are much greater than that of electrons, therefore, with the use of Born-Oppenheimer approximation[50] we can simplify molecular Hamiltonian as given in Equation 3.

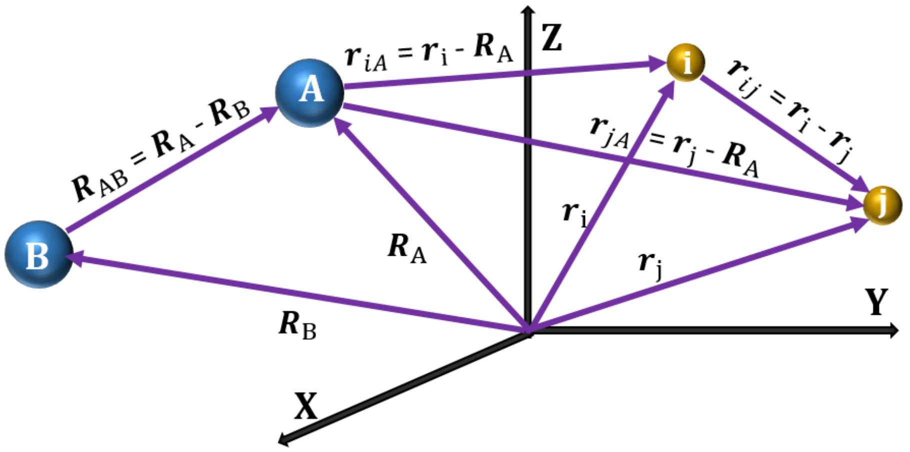

Figure 1: A molecular co-ordinate system; i,j are electrons and A,B are nuclei.

3 Born-Oppenheimer approximation

Finding the solution of Schrödinger equation for simple molecular species such as H_2^+ is quite easy; however, dealing with the molecular systems is very complicated. Born-Oppenheimer approximation plays an important role in the case of electronic structure calculation of the molecular/cluster systems due to simplification of the molecular Schrödinger equation[50]. The mass of a proton is 1836 times higher than an electron, due to which the nuclei will have a much smaller velocity compared to the electron. On the time scale of the nuclear motion, we can consider that the electrons will relax to the ground state which can find out by using equation 2. This approximation makes it possible to separate the motion of the atomic nuclei and the motion of the electrons within the molecule. The Born-Oppenheimer approximation is primarily based on the following assumptions;

a. The electronic wave function depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
b. The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the fast-moving electrons.

Applying this approximation, the molecular wave function (Ψ) can be separated into the electronic wave function (ψ) and the nuclear wave function (Φ) i.e.

$$\Psi(\{r_i\},\{r_\alpha\}) = \psi(\{r_i\},\{r_\alpha\})\ \ \Phi(\{r_\alpha\}) \qquad (4)$$

The Born-Oppenheimer approximation treats the nuclei as classical and stationary particles, and the electrons are said to be on the Born-Oppenheimer surface. Under this approximation, the nuclear kinetic energy is neglected and repulsion between the nuclei is considered as constant for fixed nuclei. The molecular Hamiltonian (given in Equation 3) is then reduced to the electronic Hamiltonian ($\hat{\mathrm{H}}_{\boldsymbol{elec}}$) which contains only electronic part given as;

$$\hat{\mathrm{H}}_{\boldsymbol{elec}} = \frac{1}{2}\sum_{\mathrm{i}=1}^{\mathrm{N}} \nabla_{\mathrm{i}}^{2} + \sum_{\substack{\mathrm{i,j} \\ \mathrm{i} \neq \mathrm{j}}}^{\mathrm{N}} \frac{1}{\mathrm{r_{ij}}} - \sum_{\mathrm{i}=1}^{\mathrm{N}} \sum_{\mathrm{A}=1}^{\mathrm{M}} \frac{\mathrm{Z_A}}{\mathrm{r_{iA}}} \tag{5}$$

Since the electron feels the external potential due to the static nuclei in the system, therefore we can write the electron-nuclei coulombic interaction term (last term of Equation 5) as external potential ($\mathrm{V_{ext}}$). i.e.

$$\widehat{\mathrm{H}} = \mathrm{T_e} + \mathrm{V_{ee}} + \mathrm{V_{ext}} \tag{6}$$

$\mathrm{V_{ext}}$ which act as an external potential for the electronic system is described as:

$$\mathrm{V_{ext}} = \sum_{i=1}^{N} v_{ext}(r_i)\,; \qquad v_{ext}(\boldsymbol{r}) = \sum_{k}^{nuclei} \int \frac{Z}{|r-r_k|} d\boldsymbol{r} \tag{7}$$

Finding the solution of the Schrodinger equation with the aforementioned Hamiltonian (given in Equation 6) is still too complex due to having 3N variables by the many-electron wave-function[51]. Therefore, for solving many-electron problems, it is required to use special approaches, e.g., Thomas-Fermi theory[52,53] and Hartree-Fock method[54,55] which has been discussed in the following section.

4 Hartree - Fock Theory

This method provides the approximate solution for the many-body Schrödinger equation in the ground state. This method was initially introduced by D. R. Hartree at the end of 1920s and further developed by V. Fock in 1930, just after the discovery of the Schrödinger equation[54,56]. HF method serves as the backbone of the molecular orbital theory which suggests that the motion of each electron can be described with the single-particle function and this particle function does not depend explicitly on instantaneous motions of other electron[57]. The electron-electron interaction is approximated through the Hartree approximation where N-electron wave-function (Ψ) is considered as the product of single-particle orbitals ($\psi_i(\boldsymbol{r}_i\sigma_i)$).

$$\Psi_1(\boldsymbol{r}_1\sigma_1, \boldsymbol{r}_2\sigma_2, \cdots\cdots, \boldsymbol{r}_N\sigma_N) = \frac{1}{\sqrt{N!}}\, \psi_1(\boldsymbol{r}_1\sigma_1)\, \psi_1(\boldsymbol{r}_1\sigma_1) \cdots\cdots \psi_N(\boldsymbol{r}_N\sigma_N) \tag{8}$$

where $\psi_i(\boldsymbol{r}_i\sigma_i)$ is consists of spatial function and electron spin function

The Hartree approximation does not account for the exchange interaction under the interchange of particle coordinates. This problem was rectified by Fock with subsequent development of Hartree-Fock approximation[58]. This approximation assumes that electron exchange interaction can be written by the wave-function (Ψ_{HF}) which is defined as an antisymmetrised product of orbitals. Ψ_{HF} is determined as a linear combination of $\psi_i(\boldsymbol{r}_i\sigma_i)$, which includes all permutations of the electron coordinates with the corresponding weights ±1. In 1951, Slater found that Ψ_{HF} can be efficiently represented with N×N determinant which is defined as the Slater determinant[34];

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\boldsymbol{r}_1\sigma_1) & \psi_1(\boldsymbol{r}_2\sigma_2) & \cdots & \cdots & \cdots & \psi_1(\boldsymbol{r}_N\sigma_N) \\ \psi_2(\boldsymbol{r}_1\sigma_1) & \psi_2(\boldsymbol{r}_2\sigma_2) & \cdots & \cdots & \cdots & \psi_2(\boldsymbol{r}_N\sigma_N) \\ \vdots & \vdots & & & & \vdots \\ \vdots & \vdots & & & & \vdots \\ \vdots & \vdots & & & & \vdots \\ \psi_N(\boldsymbol{r}_1\sigma_1) & \psi_2(\boldsymbol{r}_2\sigma_2) & \cdots & \cdots & \cdots & \psi_N(\boldsymbol{r}_N\sigma_N) \end{vmatrix} \tag{9}$$

The full Hartee-Fock equation with Hartree-Fock wave function is given as

$$\mathrm{E}[\Psi_{HF}] = \left(-\frac{1}{2}\nabla^2 + v_{ext}\right)\psi_i(\boldsymbol{x}) + \sum_j \int dx' \frac{|\psi_i(\boldsymbol{x}')|^2}{|r-r'|} -$$

$$- \sum_j \delta\sigma_i\sigma_j \int dx' \frac{\psi_j^*(x')\,\psi_i(x')}{|r-r'|}\psi_j(\boldsymbol{x}') \tag{10}$$

Here, the wavefunction $\psi(\boldsymbol{r}\,\sigma)$ is represented as $\psi(\boldsymbol{x})$ for the simplification of the above equation. The Hartree-Fock equation consists of four terms; the first term represents the kinetic energy of electrons while the second term includes the electron-ion potential contribution. The third term, which is known as Hartree potential, is an electrostatic potential, appears due to the charge distribution of N-electrons. The last term, known as the exchange term, arises due to the inclusion of the Pauli principle and determinant form of the wavefunction.

The HF approximations correspond to the single electron concept of the electronic structure, i.e., the distribution of N-electron can be simply defined as the sum of one-electron distribution. The HF method was developed with the assumption of a single determinant form of wave-function and negligible correlation between the electrons. Due to neglected electrons correlation, the HF method produces higher energies, large band gaps and very small band width. Therefore, HF method is found to be suitable for the small organic molecule which has small number of localized electron[59]. However, the HF method fails to describe the high electron density transition materials as it ignores the collective coulomb screening[60]. Therefore, due to the aforementioned shortcoming of HF theory, the density functional theory was developed where electron density is considered as a central parameter.

5 Thomas-Fermi Theory

The Thomas-Fermi method, developed by Thomas and Fermi, is one of the oldest methods for finding the solution of the many-electron problem[52,53]. In this method, the electron density ρ(r) is considered as a central variable rather than wavefunction. Thus, the total energy of the system, composed of three terms as given below, can be defined as a functional $E_{TF}[\rho(r)]$.

$$E_{TF}[\rho(r)] = A_k \int \rho(r)^{\frac{5}{3}} dr + \int \rho(r) v_{ext}(r) dr + \frac{1}{2} \int \int \frac{\rho(r)\rho(r)'}{|r-r'|} drdr' \qquad (11)$$

The first term of the above equation represents the kinetic energy of a non-interacting electron system which has a similar characteristic as homogeneous electron gas. Furthermore, A_k is the coefficient which is defined as $A_k = \frac{3}{10}(3\pi^2)^{2/3}$. The next term corresponds to the classical electrostatic interaction energy term between the nuclei and the electrons. The static coulombic potential term $v_{ext}(r)$ arises due to nuclei. The last term of the above equation represents the electron-electron interaction energy, known as Hartree energy. The Thomas-Fermi method provides a rough description of electrostatic potential and charge density. However, this model could not explain the binding mechanism of atoms, which leads the failure in the case of the molecule and solid system[61]. Apart from many serious defects, this theory provides a way for the development of DFT, which is discussed below.

6 Density functional theory

Density functional theory is a powerful method to predict the electronic properties of molecule/clusters and materials due to accuracy and high computational efficiency. In this method, the electron density is treated as a central variable instead of many-electron wavefunction. The implementation of electron density leads to a significant reduction in the level of difficulty as well as the computational cast. In other words, 3N variables (in the case of many-electron wavefunction) are reduced to only three variables (three Cartesian directions) with the use of density, which shows that variables do not depend on the number of electrons.

Earlier, DFT (proposed by Thomas-Fermi), where kinetic energy is considered as functional of electron density, incorporated with only electron-electron interactions via mean-field potential. Similar to Hartree-Fock method, old DFT neglected both exchange and correlation energy. Later, the expression for exchange energy term was formulated by Dirac as a function of electron density, although the significant improvement was not found with the implementation of this method. In 1964, Hohenberg-Kohn-Sham formulated the DFT, based on their proposed theorems (Hohenberg-Kohn theorems), which became the foundation of modern DFT[62,63].

6.1 Hohenberg-Kohn (H-K) theorems:

These theorems relate the system which consists of the electrons moving under the influence of an external potential $v_{ext}(\boldsymbol{r})$. The Hamiltonian obtained from Born-Oppenheimer approximation (Equation 6) can be written as

$$\hat{\mathrm{H}} = \hat{\mathrm{F}} + \hat{\mathrm{V}}_{\mathrm{ext}} \qquad \textit{where,} \qquad \hat{\mathrm{F}} = \hat{\mathrm{T}}_{\mathrm{e}} + \hat{\mathrm{V}}_{\mathrm{ee}} \tag{12}$$

The electron operator, $\hat{\mathrm{F}}$ is same for all N-electron systems, therefore, $\hat{\mathrm{H}}$ is only dependent on the number of electrons (N) and the external potential $v_{ext}(\boldsymbol{r})$. In addition, the number of electrons can be determined by the integration of the density over all space.

$$N = \int \mathrm{dr}\,\rho(\mathrm{r}) \tag{13}$$

The energy of the system is defined as

$$\mathrm{E_v}[\rho(\mathrm{r})] = \mathrm{F}[\rho(\mathrm{r})] + \int \mathrm{dr}\,\mathrm{V}(\mathrm{r})\rho(\mathrm{r}) \tag{14}$$

where, F is the electronic Hamiltonian for given Equation 12.

There are two fundamental theorems proposed by Hohenberg and Walter Kohn, stated below:

6.1.1 First theorem

The external potential is a unique functional of the electron density only. Thus the Hamiltonian, and hence all ground state properties, are determined solely by the electron density[63].

Proof: This theorem can be proved by *reductio ad absurdum* method. Consider the external potential $\hat{\mathrm{V}}_{\mathrm{ext}}$ is related to the ground state wavefunction ($|\Psi_{\mathrm{o}}>$) and density $\rho(\mathrm{r})$. Now assume that the second external potential $\widehat{V'}_{ext}$ corresponds to a different ground state wavefunction ($|\Psi_o >$) although with the same density $\rho(r)$. The ground state energies of the two systems are given as:

$$E_0 = < \Psi_o|\,\widehat{H}\,|\Psi_o > \tag{15}$$

$$E'_0 = < \Psi'_o|\,\widehat{H'}|\Psi'_o > \tag{16}$$

Since $|\Psi'_o >$ is not an eigenfunction of Hamiltonian $\widehat{H}$, therefore let us consider $|\Psi'_o >$ as a trail wavefunction of $\widehat{H}$. Hence,

$$E_0 < \ < \Psi'_o|\,\widehat{H}\,|\Psi'_o > \tag{17}$$

$$E'_0 < \ < \Psi'_o|\,\widehat{H'}\,|\Psi'_o > \tag{18}$$

By adding and subtracting $< \Psi'_o|\widehat{H}'|\Psi'_o >$ in the right side of the equation, we can write

$$\begin{aligned} < \Psi'_o\big|\widehat{H}\,\big|\Psi'_o > \ &= < \Psi'_o\big|\,\widehat{H'}\,\big|\Psi'_o > + < \Psi'_o|(\widehat{H} - \widehat{H'})|\Psi'_o > \\ &= \ E'_0 + \int dr\,\rho(r)[V_{ext}(r) - V'_{ext}(r)] \end{aligned} \tag{19}$$

Similarly, by considering $|\Psi_o >$ as a trial wavefunction for Hamiltonian $\widehat{H'}$, we can get

$$\begin{aligned} < \Psi_o\big|\widehat{H'}\,\big|\Psi_o > \ &= < \Psi_o\big|\,\widehat{H}\,\big|\Psi_o > + < \Psi_o|(\widehat{H'} - \widehat{H})|\Psi_o > \\ &= \ E_0 + \int dr\,\rho(r)[V_{ext}(r) - V'_{ext}(r)] \end{aligned} \tag{20}$$

Re-writing the inequalities from Equations 2.27 and 2.28 and making use of the Equations 2.29 and 20.

$$E'_0 \ < \ E_0 + \int dr\,\rho(r)[V_{ext}(r) - V'_{ext}(r)]$$

$$E_0 \ < \ E'_0 + \int dr\,\rho(r)[V'_{ext}(r) - V_{ext}(r)]$$

By adding the above two equations, we found that

$$E_0 + \ E'_0 < \ E_0 + E'_0$$

Above condition is clearly a contradiction. Therefore, the external potential $V_{ext}(r)$ is uniquely determined by the ground state density $\rho(r)$.

6.1.2 Second theorem:

The ground state energy can be obtained variationally: the density that minimises the total energy is the exact ground state density[63].

The proof of this theorem is straightforward with the use of variational principle. This theorem dictates that every trial function, except the ground state function, will give energy higher than the ground state energy;

$$< \hat{H} > = \frac{<\psi|\hat{H}|\psi>}{<\psi|\psi>} \geq E_0$$

where, E_0 is the smallest eigenvalue of the $\hat{H}$. The calculated energy ($E_v[\rho(r)]$) with electron density ($\rho(r)$), is larger than ground state energy (E_0). i.e.,

$$E_v[\rho(r)] \geq E_0$$

Using the ground state wavefunction $|\Psi_o>$ as a trial state for external potential $V(\mathbf{r})$, we can write the total energy as given below

$$\begin{aligned} < \Psi|\hat{H}|\Psi > &= < \Psi|\hat{F}|\Psi > + < \Psi|\hat{V}|\Psi > \\ &= F[\rho(r)] + \int dr\, V(r)\rho(r) \qquad (21) \\ &= E_v[\rho(r)] \geq E_0 \end{aligned}$$

With minimization of the functional $E_v[\rho(r)]$, the energy will approach the ground state energy (E_0), however can never be equal to E_0.

The Hohenberg-Kohn theorems were found to be extremely powerful, although they do not provide a direction for the computation of ground-state density of a system. Approximately one year later, Kohn and Sham published a seminal DFT paper with simple method (known as Kohn-Sham approach) for carrying-out DFT calculations. The details of Kohn-Sham approach is given in the following section.

6.2 Kohn-Sham Approach

Kohn-Sham formulation allows to transform a system of interacting electrons in a static external potential to a system of non-interacting electrons in an effective potential called Kohn-Sham potential $v_{KS}(\boldsymbol{r})^{62}$. Major benefit of using the Kohn-Sham scheme is that the Kohn-Sham equations are the set of single-particle equations which are easier to solve in comparison to previously coupled Schrodinger equations.

Using second Hohenberg-Kohn density functional theorems, the variational method for N electron system can be written as

$$\delta[\, F[\rho(r)] + \int dr\, V_{ext}(\mathbf{r})\, \rho(\mathbf{r}) - \mu(\int d\mathbf{r}\, \rho(\mathbf{r}) - N)] = 0 \qquad (22)$$

where, μ is the Lagrange multiplier. Corresponding Euler Equation for the above equation is given as below;

$$\mu = \frac{\delta\, F[\rho(\mathbf{r})]}{\delta\rho(\boldsymbol{r})} + V_{ext}(\boldsymbol{r}) \qquad (23)$$

The functional $F[\rho(r)]$ can be segregated into the three terms;

$$F[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})] \qquad (24)$$

First, two constitute the majority of energy and are known exactly, while the third is a small unknown quantity. Here, $T_s[\rho(r)]$ is the kinetic energy of a non-interacting electron gas of density $\rho(r)$. The second term, i.e., $E_H[\rho(r)]$ is the classical electrostatic energy (in Hartree unit) of the electrons is defined as

$$E_H[\rho(\mathbf{r})] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}\prime)}{|\, r - r\prime\, |}\, d\mathbf{r}\, d\mathbf{r}' \qquad (25)$$

The third term, i.e., $E_{XC}[\rho(r)]$ represents the exchange-correlation energy which contains the difference of exact kinetic energy and kinetic energy of non-interacting electron system. Furthermore, the third term includes the non-classical contribution of the electron-electron interaction energy of which the exchange energy is a part.

Differentiating Equation 2.34 with respect to density and using Euler equation as given in Equation 2.33, we get the final form;

$$\mu = \frac{\delta\, T_s[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} + V_{KS}(\mathbf{r}) \qquad (26)$$

Where Kohn-Sham potential $\mathrm{V_{KS}}(\mathbf{r})$ is given by

$$\mathrm{V_{KS}}(\mathbf{r}) = \mathrm{V_{ext}}(\mathbf{r}) + \mathrm{V_H}(\mathrm{r}) + \mathrm{V_{XC}}(\mathbf{r}) \qquad (27)$$

The Hartree potential ($\mathrm{V_H}(\mathrm{r})$) describes the Coulomb interaction between electron and electron density. As the electron is a part of total electron density, hence it further includes self-interaction contribution. The exchange-correlation potential ($\mathrm{V_{XC}}(\mathbf{r})$) is related to the exchange-correlation functional. Both the potential, i.e., Hartree potential and exchange-correlation potential are defined by the following equations;

$$\mathrm{V_H}(\mathrm{r}) = \frac{\delta\, \mathrm{E_H}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\,\mathbf{r}-\mathbf{r}'\,|} d\mathbf{r}' \qquad (28)$$

$$\mathrm{V_{XC}}(\mathbf{r}) = \frac{\delta\, \mathrm{E_{XC}}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \qquad (29)$$

The Kohn-Sham potential ($\mathrm{V_{KS}}(\mathbf{r})$) depends on the density through the exchange-correlation potential, therefore, must be solved self-consistently as discussed in the next section. To find the ground state density, $\rho_0(\mathbf{r})$, which corresponds to the energy minimum of the electronic system, we can use N single-electron Schrodinger equation with Kohn-Sham potential as given below;

$$[-\tfrac{1}{2}\nabla^2 + V_{KS}(\boldsymbol{r})]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r}) \qquad (30)$$

Where ε_i are Lagrange multipliers corresponding to orthonormality of the N single-particle states, $\psi_\mathbf{i}(\mathbf{r})$. The density is constructed as;

$$\rho(\boldsymbol{r}) = 2\sum_{n=1}^{N/2}|\psi_i(\boldsymbol{r})|^2 \qquad (31)$$

Here factor two in the equation has been introduced due to the spin degeneracy from the assumption that the orbitals are singly-occupied.

The non-interacting kinetic energy $\mathrm{T_s}[\rho(\mathbf{r})]$ is therefore given by the equation;

$$\mathrm{T_s}[\rho(\mathbf{r})] = -\tfrac{1}{2}\sum_{\mathrm{i}=1}^{\mathrm{N}} \psi_\mathrm{i}^*(\mathbf{r})\,\nabla^2\psi_\mathbf{i}\, d\mathbf{r} \qquad (32)$$

By switching over to the Kohn-Sham scheme, we have effectively changed our problem from a system of many interacting particles with 3N coordinates in an external potential to a system of non-interacting particles in an effective potential with only 3 coordinates. The contribution of the unknown energy in the total energy of the non-interaction electron system is reduced as much as possible by Kohn and Sham with the implementation of the concept of exchange-correlation energy[64]. The treatment of the exchange-correlation term is discussed below.

6.3. Exchange and Correlation Term

The Kohn-Sham equation (given in Equation 30) is exact and has not used any approximation for the solution of the many-body Schrödinger equation. With the mapping of the fully interacting system to the auxiliary non-interacting system, we can find the same ground-state density. Since Kohn-Sham kinetic energy is not a true kinetic energy, therefore, we have to define the exchange-correlation energy ($\mathrm{E_{XC}}[\rho(\mathbf{r})]$) implicitly as given below;

$$\mathrm{E_{XC}}[\rho(\mathbf{r})] = T[\rho(\boldsymbol{r})] - \mathrm{T_s}[\rho(\mathbf{r})] + \mathrm{E_{ee}}[\rho(\mathbf{r})] - \mathrm{E_H}[\rho(\mathbf{r})] \qquad (35)$$

where, $T[\rho(\boldsymbol{r})]$ and $\mathrm{E_{ee}}[\rho(\mathbf{r})]$ are the exact kinetic energy and electron-electron interaction energy, respectively. Since the $\mathrm{E_{XC}}[\rho(\mathbf{r})]$ term is not fully known, therefore, an approximate functional depending upon the electron density has been used to describe $\mathrm{E_{XC}}[\rho(\mathbf{r})]$. Till now, several approximated exchange-correlation functionals have been proposed. These functionals can be categorised according to Jacob’s ladder scheme (Figure 2) which was proposed by Perdew[65,66].

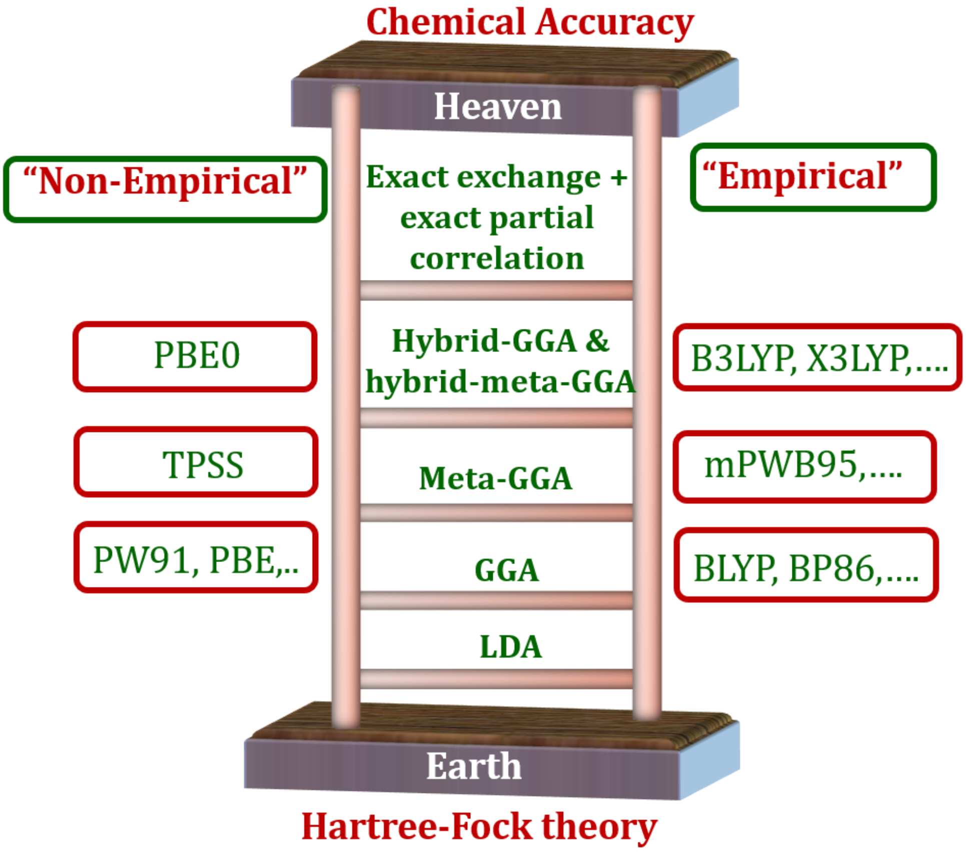

Figure 2: Schematic diagram of "Jacob's ladder" for exchange-correlation functional.

In Jacob's ladder scheme, each rung of the ladder contains a group of a different functional set, which have been categorised on basis of their complexity. This ladder provides a direction from the Hartree approximation on "earth" to the exact exchange-correlation functional in "heaven". Furthermore, the exchange correlational functional can be categorized into empirical and non-empirical, as mentioned in Figure 2. A number of possible approximations, e.g., local density functional (LDA, generalised gradient approximation (GGA) etc. and a few of the exchange-correlation functional which are generally used in the DFT calculations, are discussed in the following section.

6.3.1 Local Density Approximation (LDA)

This approximation is the simplest approximation for finding the exchange-correlation energy[67,68]. This approximation assumes that the exchange-correlation energy at a point $\mathbf{r}$ is equal to the exchange-correlation energy of a uniform electron gas that has the same density at the point $\mathbf{r}$. In general, for a spin unpolarised system, the LDA for exchange-correlation energy is written as;

$$E_{XC}^{LDA}[\rho(\mathbf{r})] = \int d\mathbf{r}\, \varepsilon_{xc}[\rho(\mathbf{r})]\, \rho(\mathbf{r}) \qquad (36)$$

where, $\varepsilon_{\mathbf{xc}}[\rho(\mathbf{r})]$ is the exchange-correlation energy per particle of the uniform electron gas having density $[\rho(\mathbf{r})]$. Since$\boldsymbol{E_{XC}^{LDA}}$ depends only on the value of electron density at each point in the space (not depends on derivative of density or Kohn-Sham orbitals), therefore, this method is called the Local Density Approximation[69,70]. The term $\varepsilon_{xc}[\rho(\mathbf{r})]$ can be split into the two term: exchange and correlation energy which is given below;

$$\varepsilon_{xc}[\rho(\mathbf{r})] = \varepsilon_x[\rho(\mathbf{r})] + \varepsilon_c[\rho(\mathbf{r})] \qquad (37)$$

The exchange energy ($\varepsilon_x[\rho(\mathbf{r})]$) term has been analytically calculated by Dirac for the homogeneous system[68], as given below;

$$\varepsilon_x[\rho(r)] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int \rho(\boldsymbol{r})^{4/3}\, d\mathbf{r} = \frac{0.458}{r_s} \qquad (38)$$

Where $r_s (= (\frac{3}{4\pi\rho(r)})^{1/3}$ is known as Wigner-Seitz parameter.

The accurate value of correlation energy has been determined analytically from the Quantum Monte Carlo (QMC) calculations, value of which is given as;

$$\varepsilon_c[\rho(r)] = \frac{0.44}{r_s+7.8} \qquad (39)$$

Incorporating Equations 38 and 39, Equation 37 can be re-written as;

$$\varepsilon_{xc}[\rho(\mathbf{r})] = -\frac{0.458}{r_s} - \frac{0.44}{r_s+7.8} \qquad (40)$$

Furthermore, exchange-correlation potential corresponding to the exchange-correlation energy for LDA is given by,

$$V_{XC}^{LDA}[\rho(r)] = \frac{\delta(E_{XC}^{LDA}[\rho(r)])}{\delta(\rho(r))} = \varepsilon_{xc}[\rho(\boldsymbol{r})] + \rho(\boldsymbol{r})\frac{\partial(\varepsilon_{xc}[\rho(r)])}{\partial(\rho(r))} \qquad (41)$$

This potential can be inserted in Equation 27 for the calculation of Kohn-Sham potential. The LDA method has been found to provide an accurate result for the systems, where charge density varies slowly. However, in strongly correlated systems, where independent particle picture breakdown, the LDA method show very inaccurate results[71]. For example, LDA prediction shows that transition metal oxides XO (X=Fe, Mn, Ni) can be either metal or semiconductor, while in the real picture, they are only Mott insulators. Furthermore, LDA does not account for the van der Waal bonding, which provides a poor description of hydrogen bonding. The mentioned as well as other limitations of LDA method, motivated to develop the other approximation such as generalised gradient approximation.

6.3.2 Generalised Gradient Approximation (GGA)

The LDA method which depends on homogeneous charge distribution does not regularly predict accurate chemical bonding properties, therefore, it is required to modify the LDA energy density. In the GGA scheme, electron density and each coordinate of the system are considered with the gradient of the density, therefore known as Generalised-Gradient approximations[72,73]. The inclusion of higher derivatives of electron density and density gradient provides better results in comparison to the LDA method. The general form of the GGA exchange-correlation functional is given below;

$$\mathrm{E}_{\mathrm{XC}}^{\mathrm{GGA}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\, \varepsilon_{\mathrm{XC}}^{\mathrm{LDA}}[\rho(\mathbf{r})]\, F_{XC}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]\, d\mathbf{r} \qquad (42)$$

Where $\mathrm{F}_{\mathrm{XC}}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]$ is defined as the enhancement factor, which directly depends on electron density and density gradient. The enhancement factor is written in terms of the Seitz radius (r_s) and a dimensionless reduced density gradient (sometimes called smoothing factor) $\mathrm{s}(\mathbf{r})$ which is given as;

$$\mathrm{s}(\mathrm{r}) = \frac{|\nabla\rho(\mathbf{r})|}{2\mathrm{k}_{\mathrm{F}}(\mathbf{r})\, \rho(\mathbf{r})} \qquad (43)$$

where, $\mathrm{k}_{\mathrm{F}}(\mathbf{r})$ is the Fermi-wavevector and is defined as;

$$\mathrm{k}_{\mathrm{F}}(\mathbf{r}) = [3\pi^2 \rho(\boldsymbol{r})]^{1/3} \qquad (44)$$

As GGA is the analytical functional method, therefore, with plotting $\mathrm{F}_{\mathrm{XC}}(r_s, s)$ with respect to s for various value of r_{s}, we can get an effective way of examining and comparing different GGAs. GGA has shown great importance for various chemical systems, especially covalent bond energies and distance, although it has a shortcoming in describing van der Waals bonding. There are a few GGA functional, e.g., PW91, PBE which are generally used in the DFT calculation or embedded in hybrid functional (discussed in next section) and have been discussed below.

6.3.2.1 Perdew-Wang GGA functional (PW91)

Consider a GGA functional PW91 which was developed by the Perdew and Wang in 1991, is generally used in solid-state DFT calculations[74,75]. This functional does not contain any experimental data-dependent parameter, rather the parameters are determined by exact quantum mechanical calculation. The exchange enhancement factor for the PW91 functional is given as;

$$\mathrm{F_X^{PW91}}(s) = \frac{1+0.19645s\ sinh^{-1}(7.7956s)+(0.2743-0.15084e^{-100s^2})s^2}{1+0.19645s\ sinh^{-1}(7.7956s)+0.004s^4} \qquad (45)$$

Above equation shows that the exchange enhancement factor slowly varies with smoothing factor (s) and does not depend on the Seitz radius (r_s).

The calculation of GGA correlation energy for the PW91 functional is quite complicated due to various interactions between spin components. The spin-compensated PW91 correlation energy can be defined as;

$$\mathrm{E_C^{PW91}}[\rho_\alpha, \rho_\beta] = \int \rho(\mathrm{r})[\varepsilon_\mathrm{C}(\mathrm{r_s}, \zeta) + \mathrm{H}(\mathrm{t}, \mathrm{r_s}, \zeta)]\mathrm{d}\mathbf{r} \qquad (46)$$

where, ζ is the degree of spin-polarization and $\varepsilon_\mathrm{C}(\mathrm{r_s}, \zeta)$ is defined as Perdew-Wang parametrisation of homogeneous electron gas correlation energy. Furthermore, the parameter t is another dimensionless gradient term as given below;

$$\mathrm{t} = \frac{|\nabla\rho(\mathbf{r})|}{2\mathrm{g}\ k_s\ \rho(\mathbf{r})} \qquad (47)$$

Where k_s and g factor are defined as;

$$\mathrm{k_s} = \left[\frac{4k_F}{\pi}\right]^{1/2} \qquad (48)$$

$$\mathrm{g} = \left[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}\right]/2 \qquad (49)$$

6.3.2.2 Perdew-Burke-Ernzerho GGA functional (PBE)

The PBE GGA functional was developed by Perdew, Burke and Ernzerho for the simplification of the PW91 GGA functional[73,76]. The modified exchange enhancement factor is given as;

$$\mathrm{F}_{\mathrm{X}}^{\mathrm{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1+\frac{\mu s^2}{\kappa}} \quad (50)$$

where, the analytical predicted value of the parameters are: μ=0.21951 and $\boldsymbol{\kappa}$=0.804.

6.3.3 Meta-GGA Functional

The First and second rungs of the Jacob's ladder, i.e., LDA and GGA method, are typically employed in the solid-state calculations while third and fourth rungs, e.g., Meta-GGA and hybrid functional are generally used in the quantum chemistry simulations for the prediction of molecular properties[77]. The meta-GGA method is a semi-local approximation which is developed through the extension of GGA with consideration of the second derivative of the density[78]. As it comprises similar physical information and higher stability, generally orbital kinetic energy density is used at the place of the second derivative of density. The mathematical expression of meta-GGA is given as;

$$\mathrm{E}_{\mathrm{XC}}^{\mathrm{meta-GGA}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\, \varepsilon_{\mathrm{XC}}^{\mathrm{meta-GGA}}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r})]\, \mathrm{d}\mathbf{r} \quad (51)$$

$$= \int \rho(\mathbf{r})\, \varepsilon_{\mathrm{XC}}^{\mathrm{meta-GGA}}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau(\mathbf{r})]\, \mathrm{d}\mathbf{r} \quad (52)$$

where $\tau(\mathbf{r})$ is the orbital kinetic energy density defined as;

$$\tau(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N} |\nabla\psi_{\boldsymbol{i}}(\boldsymbol{r})|^2 \quad (53)$$

The meta-GGAs such as the TPSS functional is found to have improved performance over LDAs and GGAs, especially, in the calculation of gas-phase molecular properties.

6.3.4 Hybrid Functional

The functional of the fourth rung of Jacob's ladder is called hybrid functional because of the incorporation of exact exchange terms from the Hartree-Fock formalism and correlation terms from other areas such as experiments or theoretical calculations. One of the most powerful and highly accurate hybrids functional is B3LYP. The mathematical expression for the B3LYP functional is given below, which consists of Becke-three-parameters exchange functional[79,80]and Lee-Yang-Parr correlation functional[74,81].

$$E_{xc}^{B3LYP} = (1-a)E_x^{LDA} + aE_x^{HF} + b\Delta E_x^{Becke} + E_c^{LDA} + c\Delta E_c^{LYP} \quad (54)$$

where, the parameters a, b and c are semi-empirical coefficients having numerical values 0.20, 0.72 and 0.81, respectively. These coefficients were optimised to match extensive molecular data sets as mentioned above. The first term, ((E_x^{LDA}), of Equation 2.64 is the full LDA exchange term while the second term, (E_x^{HF}) is the exact Hartree-Fock exchange functional which is expressed below;

$$E_x^{HF}[\{\psi_i\}] = \frac{1}{2}\int d\boldsymbol{r}\int d\boldsymbol{r}'\ \frac{\sum_{i,j}\psi_i^*(\boldsymbol{r})\psi_j^*(\boldsymbol{r}\prime)\psi_i(\boldsymbol{r}\prime)\psi_j(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}\prime|} \qquad (55)$$

The third term of the Equation 2.64, i.e., $E_x^{Becke}$is known as Becke’s B88 exchange functional which have the mathematical expression,

$$E_x^{Becke}[\rho(\boldsymbol{r})] = -\beta\int d\boldsymbol{r}\ \rho(\boldsymbol{r})^{4/3}\frac{\alpha^2}{1+6\beta sinh^{-1}\alpha} \qquad (56)$$

where, the value of the parameter (β) is 0.0042 Hartree, which is found by molecular data sets. The other parameter, (α) can be expressed as;

$$\alpha = \frac{|\nabla\rho(\boldsymbol{r})|}{\rho(\boldsymbol{r})^{4/3}} \qquad (57)$$

Beyond the fourth rung of Jacob’s ladder, there exist many other exchange-correlation functionals, which have higher complexity. However, climbing towards higher on Jacob’s ladder with the addition of complexity does not bring necessarily improvement in total energies.

6.4 Self-consistent method

As the Kohn-Sham potential, $v_{KS}(\boldsymbol{r})$ depends on the density, $\rho(\boldsymbol{r})$ through the Hartree potential and exchange-correlation potential (as mentioned in Equations 27, 28 and 29), therefore, the density can be found through solving the Kohn-Sham equation self-consistently. First, an initial guess for density $(\rho_0(\boldsymbol{r}))$ is used for creating the effective Kohn-Sham potential, $v_{KS}(\boldsymbol{r})$**,** then solving the Kohn-Sham Schrodinger equation. This provides a new set of wave functions, $\{\psi_i(\boldsymbol{r})\}$. From these wave functions, a new density is found based on Equation 2.41. This new density then become the next guess for the Kohn-Sham Schrodinger equation, which gives a new set of the wave function and another new density, $(\rho_1(\boldsymbol{r}))$. If the energy difference between the energy that this new density, $(\rho_1(\boldsymbol{r}))$, produces with the energy of the previous density, $(\rho_0(\boldsymbol{r}))$, is smaller than a set value, then the calculation is considered "converged".

However, if the difference is greater than this tolerance, then the new density is put back through the cycle until the energy difference is below the specified value. This tolerance is called the convergence criteria for energy. By making this number smaller and smaller, the resulting calculations become more and more accurate at the cost of increased calculation time. This process is known as a self-consistent calculation because the ground state density is found with the self-consistent calculation of density. The flow chart for the self-consistent method is given below;

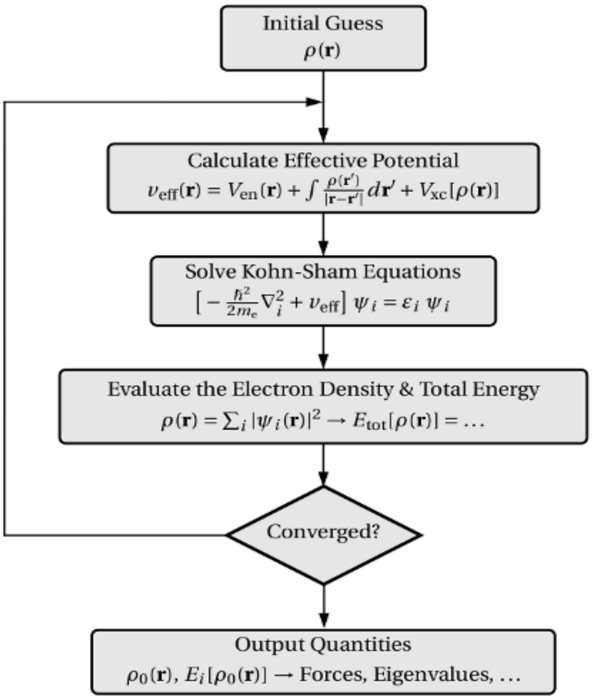

Figure 3: Flow chart for SCF calculations

7 Basis sets

In general, a basis set is the linear combination of numerical functions (called basis functions) which are used for the representation of the electron wave function[82]. In DFT, the Kohn-Sham orbitals are represented with an appropriate basis set for the practical application in computers. Any basis functions, e.g., Gaussian, exponential, polynomial, plane-wave, spline, Slater type orbitals, numeric atomic orbitals, etc. may be used to construct the basis set depending on the certain criteria as mentioned below[83];

1. The basis function must allow to find highly accurate wave function/density with low computational cost as possible.

2. The behaviour of the basis function must ideally capture some of the physics problems. For example, for the bound atomic or molecular system, the function should go to zero when the distance between the nucleus and electron becomes large.

Due to low computational cost and high efficiency, few functions like Slater type orbitals and Gaussian type orbitals (discussed below) are commonly used in the calculations of chemical properties.

7.1 Slater-type orbitals (STOs) functions

The Slater-type orbitals (introduced by John C. Slater in 1930) are the natural basis functions in quantum molecular calculations[84], though these functions show restricted application due to difficulty in mathematical integration. The mathematical expression of STOs functions in polar coordinates are;

$$\psi_{\zeta,n,l,m}(r,\theta,\phi) = NY_{l,m}(\theta,\phi)r^{n-1}e^{-\zeta r} \qquad (58)$$

Where N is the normalization constant and $Y_{l,m}$ are spherical harmonic functions. The n, l and m represent the quantum numbers, principle: angular momentum and magnetic respectively. The exponent parameter, $\boldsymbol{\zeta}$, controls the width of STOs. The exponential term dependent on the distance between nucleus and electron (r) shows the exact behaviour of the orbitals for the hydrogen atom. Furthermore, the exponential dependent term ensures the fairly rapid convergence with an increasing number of functions. Since STOs do not have any radial nodes, therefore linear combinations of STOs have been introduced, which shows the nodes in radial parts. The STOs are generally used in atomic and diatomic systems which require high accuracy.

7.2 Gaussian-type orbitals (GTOs) functions

The Gaussian-type orbitals (proposed by Boys in 1950) is the most generally used basis function in quantum chemical program package[85]. The primary reason for superior performance in computation over STOs is related to the “Gaussian Product Theorem” which guarantees that the product of two GTOs centred on two different atoms is a finite sum of Gaussians centred on a point along the axis connecting them. In this manner, the four-centre integrals are reduced to finite sums of two-centre integrals, and in the next step, reduced to finite sums of one-centre integrals which demands the lower computational cast. The mathematical expression for the GTOs in both, i.e., polar and Cartesian coordinates is given as;

$$\psi_{,n,l,m,\zeta}(r,\theta,\phi) = NY_{l,m}(\theta,\phi)r^{2(n-1)-1}e^{-\zeta r^2} \tag{59}$$

$$\psi_{l_x,l_y,l_z,\zeta}(x,y,z) = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2} \tag{60}$$

where, l_x, l_y and l_z are the parameters that provide the important information about the orbital. The sum of the parameters, i.e., $l_x + l_y + l_z = L$ is analogous to angular momentum for the atom. The varying value of L corresponds to the different shapes of orbitals, for example, s-type (L=0), p-type (L=1), d-type (L=2) and f-type (L=3). The Gaussian function mentioned in Equation (60) is called the primitive Gaussian function. The group of the several primitive Gaussian functions provide the new one-Gaussian function which is known as “contracted Gaussian function”, given as below;

$$\psi^{CGTO}_{l_x,l_y,l_z,\zeta}(x,y,z) = N\sum_{\alpha=1}^{M} c_\alpha x^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2} \tag{61}$$

where M is the number of GTOs used in the linear combination. N is the normalization constant and the coefficients (c_α), which are then called a linear combination of atomic orbitals (LCAO), are chosen for the shape of the basis function. There are two different ways of contracting a set of Primitive-GTOs (PGTOs) to a set of Contracted-GTOs (CGTOs), namely, segmented and general contractions. In segmented contractions, each primitive of a given atom and angular momentum is, very strictly used only in one contracted function, while in general contractions all primitives of a given atom and angular momentum are used in all the contracted functions.

By contracting with any of the mentioned methods, several Gaussians into one, the computational cost can be reduced, yet maintaining the STO’s accuracy, therefore, the technique has been very popular in quantum chemical calculations.

7.2.1 Minimal basis sets

One question always arises that how many basis functions should be used to describe the atomic system. The basis set selection process requires a lot of expertise. In practice, we should start with only contracted functions that are enough to describe the atomic system, which is known as a minimum basis set. The minimum basis functions which are needed to describe the individual atom is called the Minimal Basis set (MBS). For example, hydrogen only needs a single s-function while first row elements of the periodic table require two s-function and a set of p-functions (2px, 2py and 2pz) to describe its occupied atomic orbitals. The MBS for carbon atom is a set of 1s function, one 2s function and one set of 2p functions. The function, STO-nG is found as the most common minimal basis set, where n is an integer, e.g. STO-3G, STO-4G etc. The value “n” is used to represent the available primitive Gaussian functions that are contained within a single basis function. In the minimal basis set, the same number of primitive Gaussian functions comprise the core and valence orbitals, therefore, typically giving rough results that are not sufficient for predicting the chemical properties.

7.2.2 Split valence basis sets

As we know the outer shell electrons, i.e. valance electrons, usually participate in the chemical bond formation, therefore it is necessary to distinguish the core and valence electron considering the basis functions allocation. More the sets of the basis function (larger zeta) allocated for the valance electrons in comparison to the core electrons, the higher will be the accuracy of the results. Basis sets are categorised, e.g. valence double, triple, quadruple-zeta, on basis of the available number of basis functions for defining the valance atomic orbital. When the basis set has two/three sets of basis functions to represent each orbital, they are called double/triple-zeta (DZ)/TZ) basis set. For example, two s-functions (1s and 1s’) are used as DZ basis set for the hydrogen atom. The first row of the element in the periodic table needs four sets of s-functions (1s, is’, 2s, 2s’) and two sets of p-functions (2p, 2p’) for DZ basis sets. It is noted that the primed and un-primed orbitals differ in size. The commonly used basis sets 6-31G and 6-311G are examples of double and triple zeta valence basis sets, respectively, where two/three sets of contracted functions are used for each valence orbital.

The mentioned basis sets are enough for the free isolated atom which has spherical symmetry in nature. However, the atom in a molecule or some other chemical environment exhibit distortion in the electron density. Therefore, for the inclusion of these effects in the basis set, it is required to use augmented basis sets with some additional functions, which are described in detail below.

- **Polarized functions:** In the case of the molecules, the one atomic orbitals are shifted towards one side or other side (means polarized) due to mixing of other orbitals, which distorts the orbital shape. In other words, the s orbital can polarize in one direction if it’s mixed with a p orbital and the p orbitals can polarize if mixed with d orbitals. These polarization effect can be implemented in the basis set with consideration of additional functions of higher angular momentum. For example, in the case of ethylene, *p* functions sufficiently describe the π-bonds, but the *d* functions allow the electron density to bend away from the π-bond towards the hydrogen. The common polarised basis sets are 6-31G(d) and 6-311G(d,p).

- **Diffused functions:** In the case of negative ions, where the electron is held far away from the nucleus, the atomic orbital is distorted from its original shape. For the correct description of such kind of system, it is required to the addition of Gaussian functions with a small exponent, known as diffused functions. These functions represent the “tail” of the atomic orbitals or the regions which are far from nuclei. The diffused basis functions are necessary for the negative ions, very electronegative atoms, excited states and weak bonds (e.g. hydrogen bonds). Furthermore, the diffused basis functions are mandatory to use for the calculation of some of the properties which depend on the tail of the wavefunction (e.g. dipole moment and polarizabilities). The basis set, 6-311+G(d,p) is an example of diffused basis set, which is generally used in the evaluation of chemical properties of interest.

8 Solvent model

In the physical and biological systems, most of the reactions take place in the fluid/liquid medium rather than the gas phase. In the coming chapters, we have studied the lithium cluster in the electrolytic media in the perspective of the Li-ion battery system. Therefore, it is necessary to discuss the mathematical model/theory which is used to simulate the atomic/molecular component in the fluid media. These media can be incorporated in the quantum chemical calculation with the proper implementation of the solvent model. In general, the solvent models are the computational technique/method that has been developed to account for the behaviour of the solvated condensed phase. The solvent models allow to simulate the chemical reaction and biological process in the solvated phases with improved understanding and prediction. There are various solvation models which are generally classified into two classes, explicit and implicit models, on basis of the physical appearance of the solvent molecule[86,87]. Both the models are discussed in the following section.

8.1 Explicit solvent model

The explicit solvent model treats the solvent by considering the molecules explicitly. With this solvent model, the most realistic picture of solute-solvent interaction can be obtained among all solvent models. This model has wide application in molecular dynamics, molecular mechanics, and Monte Carlo simulation. In the field of quantum chemical calculations, this model can be further applied with the use of the molecular cluster as the solvation shell. In general, molecular mechanics (force field) are utilized for the computation of physical and chemical properties including motion of the large molecular system. In the force fields method, the molecules are treated as the mechanically connected system of atoms, which generally consist of empirical and parametrized functions, leading to highly efficient simulation. The force field generally consists of various interaction terms, which describe the respective possible strain in the molecular system[83]. The total strain energy of the molecular system is given as follows;

$$E_{MM} = V_{str} + V_{bend} + V_{tor} + V_{cross} + V_{vdW} + V_{ES} \qquad (62)$$

where V represents the potential energy term coming from the bond stretching (V_{str}), bending (V_{bend}), torsional energy (V_{tor}), van der Waals energy (V_{vdW}), electrostatic energy (V_{ES}), and cross terms (V_{cross}). With the separation of the van der Waals interaction and electrostatic interaction terms in the above equation, the constant parameters of the remaining interaction in the force field could be generated in such a way that the parameters become more transferrable over the whole molecule in comparison to the spectroscopic force field.

This solvent model provides descriptive information about the solvent, though the extremely computational expensiveness restricts their application. Therefore, the limitation of the computation cost motivated to develop the other solvent models based on a continuous distribution of solvent, e.g., an implicit solvent model which is discussed in detail in the following sections.

8.2 Implicit/Continuum solvent model

In the Implicit solvent model, it is assumed that continuum solvent media can be replaced by the homogeneous polarizable medium. This model considers thermally averaged and usually isotropic solvents, therefore, only a small number of parameters are required to represent the solvent with reasonable accuracy. The main parameter is the dielectric constant (ε) which is responsible for defining the degree of the polarizability of various solvents. In comparison to the explicit solvent model, this model doesn’t consider the coordinate of an individual molecule, therefore, found to be computationally not too expensive. There are many implicit solvent models are developed, e.g. Polarised Continuum Model (PCM), universal solvent model (SMD) etc., of which PCM has been used to study the chemical properties of molecule/cluster in the solvent[88–90].

Polarised Continuum Model

In this case, the solute which is embedded into a cavity is treated as a polarizable charge distribution and solvent (surrounded by the solute) is represented with a dielectric continuum medium that is polarized by the solute. The induced charge on the solvent affects the charge distribution of solutes as well as their geometry. The solvent reaction field found because of induced solvent charge can be acquired with the self-consistent method by solving the non-homogeneous Poisson equation, which is coupled to the quantum mechanical electron density of the solute molecule.

$$-\nabla \times [\varepsilon(\boldsymbol{r})\, \nabla V(\boldsymbol{r})] = 4\pi \rho_M(\boldsymbol{r}) \qquad (63)$$

Where, $\rho_M(\boldsymbol{r})$ represents the solute charge distribution while $\varepsilon(\boldsymbol{r})$ symbolizes the position-dependent permittivity. If the charge distribution, $\rho_M(\boldsymbol{r})$ is contained in the molecular cavity "C" which is built with an isotropic and homogeneous solvent, then $\varepsilon(\boldsymbol{r})$ can be represented as;

$$\varepsilon(\boldsymbol{r}) \quad = \quad \begin{cases} 1 & \boldsymbol{r} \in C \\ \varepsilon & \boldsymbol{r} \notin C \end{cases}, \qquad (64)$$

Using the boundary condition (as given in Equations 2.74), Equation 2.73 is solved in terms of V, which is the sum of the solute potential and apparent charge distribution, σ(**s**) (arises on the boundary between the solute and the solvent) and is given as;

$$V(\boldsymbol{r}) = V_M(\boldsymbol{r}) + V_\sigma(\boldsymbol{r}) \qquad (65)$$

$$V_\sigma(\boldsymbol{r}) = \int_\Gamma \frac{\sigma(s)}{|r-s|}\, d^2 s \qquad (66)$$

This equation is generally solved by the discretization of integral into the finite number of the element. The whole problem can be solved, once we find the numerical value of the term $\sigma(\boldsymbol{s})$. Following equation represents the electrostatic component of the solvation free energy, and depends on the $\sigma(\boldsymbol{s})$ as given below;

$$G_{es} = \int_\Gamma \sigma(\boldsymbol{s}) \left[\int_V \frac{\sigma(s)}{|\boldsymbol{r}-\boldsymbol{s}|}\, d^3 r\right] d^2 s \qquad (67)$$

In the PCM framework, the different alternatives depend on the apparent surface charge, ($\sigma(\boldsymbol{s})$). For example, D-PCM is defined with different value of apparent surface charge, given as;

$$\sigma(\boldsymbol{s}) = \frac{\varepsilon-1}{4\pi\varepsilon}\frac{\partial}{\partial n}(V_M(\boldsymbol{r}) + V_\sigma(\boldsymbol{r}))_s \qquad (68)$$

Now, the molecular free energy in the solutions can be calculated through PCM model as;

$$G_{sol} = G_{ES} + G_{DR} + G_{CAV} \qquad (69)$$

Where the electrostatic (ES) component is calculated with the help of Equation 2.77 with different apparent surface charges. The components, dispersion-repulsion (DR) and cavitation energy (CAV) are computed using the creation of cavity which is defined with the interlocking van der Waals spheres centred at atomic positions. The point charges which represent the reaction field, are located on the surface of a molecular cavity (known as the Apparent Surface Charge model). Hartree-Fock (UAHF) model is used to build the cavity, which is in-built in the particular version of PCM model[91,92]. The implementation of the PCM/UAHF model in computational code "Gaussian 03/09" can be invoked using the SCRF keyword in combination with PCM specific modifiers.

The polarizable continuum model is a well-known and verified solvent model, which is often used to predict the electrolyte structure/stability and to understand the chemical properties in a practical environment. There are several reports where the solvent model has been used for the prediction and investigation of the electrolytic solvent[93–95]. For example, electrochemical windows of sulfone based electrolytes were studied by shao et al. with the PCM model for their application as high voltage electrolytes and later verified by Erik et al. through experimental technique[96,97]. Furthermore, stable fluorinated sulfone electrolytes have been synthesised and further studied with the PCM model, which shows excellent agreement between both the theoretical and experimental results[98]. In the last few decades, several articles have appeared in reputed journals, where both solvation model and experimental results are combined and support each other[99–102]. With the above discussions, we conclude that the solvation model is very trustable and provides a direction for the development and understanding of the electrolyte.

Zhang et al. have studied the solvation free energy of several organic solvents with both implicit and explicit solvent models.[103] The implicit solvent model was found to be in good agreement with the experimental results, however, it didn't fit well with the explicit solvent model. The detailed investigation reveals that the dielectric constant of a solvent is found as a powerful predictor for polar contribution to the free energy in the implicit model. However, due to the consideration of the Onsager reaction field in case of the implicit model, the numerical value differs in comparison to the explicit model[103]. Further, with the implicit solvent model, the neutral and ionic solute with different dielectric constant and various radii scaling factors were investigated by Klamt et.al[104]. Their study found a good agreement between the calculated and the experimental solvation free energy of the order of 0.5-1.0 kcal/mol (0.02 – 0.04 eV).

9. Summary

In this report, I have discussed the theoretical background of density functional theory and the solvation model. We extensively describe Born-Oppenheimer approximation, Hartree-Fock and Thomas-Fermi theory, Hohenberg-Kohn theorems, Kohn-sham approach, Exchange-correlation approximation and self-consistent method. Furthermore, we have discussed Basis-set and solvation model, especially the polarisable continuum model. I hope that this brief note will be very helpful to understand DFT and solvation model in a limited and short time.

References

(1) Gould, H.; Tobochnik, J.; Christian, W. *An Introduction to Computer Simulation Methods*; Addison-Wesley New York, 1988; Vol. 1.

(2) Zalka, C. Simulating Quantum Systems on a Quantum Computer. In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*; The Royal Society, 1998; Vol. 454, pp 313–322.

(3) Feynman, R. P. Simulating Physics with Computers. *Int. J. Theor. Phys.* **1982**, *21* (6–7), 467–488.

(4) Lanyon, B. P.; Whitfield, J. D.; Gillett, G. G.; Goggin, M. E.; Almeida, M. P.; Kassal, I.; Biamonte, J. D.; Mohseni, M.; Powell, B. J.; Barbieri, M. Towards Quantum Chemistry on a Quantum Computer. *Nat. Chem.* **2010**, *2* (2), 106.

(5) Kassal, I.; Whitfield, J. D.; Perdomo-Ortiz, A.; Yung, M.-H.; Aspuru-Guzik, A. Simulating Chemistry Using Quantum Computers. *Annu. Rev. Phys. Chem.* **2011**, *62*, 185–207.

(6) Grimme, S. Accurate Description of van Der Waals Complexes by Density Functional Theory Including Empirical Corrections. *J. Comput. Chem.* **2004**, *25* (12), 1463–1473.

(7) Van Mourik, T.; Gdanitz, R. J. A Critical Note on Density Functional Theory Studies on Rare-Gas Dimers. *J. Chem. Phys.* **2002**, *116* (22), 9620–9623.

(8) Hafner, J.; Wolverton, C.; Ceder, G. Toward Computational Materials Design: The Impact of Density Functional Theory on Materials Research. *MRS Bull.* **2006**, *31* (9), 659–668.

(9) Giustino, F. *Materials Modelling Using Density Functional Theory: Properties and Predictions*; Oxford University Press, 2014.

(10) Hautier, G.; Jain, A.; Ong, S. P. From the Computer to the Laboratory: Materials Discovery and Design Using First-Principles Calculations. *J. Mater. Sci.* **2012**, *47* (21), 7317–7340.

(11) Jain, A.; Shin, Y.; Persson, K. A. Computational Predictions of Energy Materials Using Density Functional Theory. *Nat. Rev. Mater.* **2016**, *1* (1), 15004.

(12) Kushwaha, A. K. Theoretical and Computational Investigations of Li-Ion Battery Materials and Electrolytes. In *Electrochemical Energy Conversion and Storage Systems for Future Sustainability*; Apple Academic Press, 2020; pp 217–249.

(13) Kushwaha, A. K.; Sahoo, M. R.; Nayak, S. Probing Potential Li-Ion Battery Electrolyte through First Principles Simulation of Atomic Clusters. In *AIP Conference Proceedings*; AIP Publishing, 2018; Vol. 1951, p 20014.

(14) Kushwaha, A. K.; Nayak, S. K. Wobbled Electronic Properties of Lithium Clusters: Deterministic Approach through First Principles. *Phys. E Low-dimensional Syst. Nanostructures* **2017**, *97*, 368–374.

(15) Kushwaha, A. K.; Sahoo, M. R.; Nanda, J.; Nayak, S. K. Engineering Redox Potential of Lithium Clusters for Electrode Material in Lithium-Ion Batteries. *J. Clust. Sci.* **2017**, *28* (5), 2779–2793.

(16) Ceder, G.; Hautier, G.; Jain, A.; Ong, S. P. Recharging Lithium Battery Research with First-Principles Methods. *Mrs Bull.* **2011**, *36* (3), 185–191.

(17) Zhang, T.; Li, D.; Tao, Z.; Chen, J. Understanding Electrode Materials of Rechargeable

Lithium Batteries via DFT Calculations. *Prog. Nat. Sci. Mater. Int.* **2013**, *23* (3), 256–272.

(18) Ladha, D. G. A Review on Density Functional Theory–based Study on Two-Dimensional Materials Used in Batteries. *Mater. Today Chem.* **2019**, *11*, 94–111.

(19) Kang, K.; Meng, Y. S.; Bréger, J.; Grey, C. P.; Ceder, G. Electrodes with High Power and High Capacity for Rechargeable Lithium Batteries. *Science (80-.).* **2006**, *311* (5763), 977–980.

(20) Kushwaha, A. K.; Jena, S. S.; Jena, P.; Nayak, S. K. Halogen-Free Electrolytes Based on Modified Boranes for Alkali-Ion Batteries. *J. Phys. Chem. C* **2022**.

(21) Kushwaha, A. K.; Jena, S. S.; Sahoo, M. R.; Nayak, S. K. Electrolytic Solvation Effects in Fluoroethylene Carbonateand Trifluoropropylene Carbonate: A Comparative Study Based on First-Principles Calculation. *J. Electron. Mater.* **2021**, *50* (4), 1807–1816.

(22) Kushwaha, A. K.; Sahoo, M. R.; Nayak, S. K. Understanding the Role of Fluorination on the Interaction of Electrolytic Carbonates with Li+ through an Electronic Structure Approach. *ChemistrySelect* **2019**, *4* (4), 1251–1258.

(23) Swain, D. K.; Mallik, G.; Srivastava, P.; Kushwaha, A. K.; Rajput, P.; Jha, S. N.; Lim, S.; Kim, S.; Rath, S. Single Mn Atom Doping in Chiral Sensitive Assembled Gold Clusters to Molecular Magnet. *ACS Nano* **2021**, *15* (4), 6289–6295.

(24) Sahoo, M. R.; Kushwaha, A. K.; Pati, R.; Ajayan, P. M.; Nayak, S. K. First-Principles Study of a Vertical Spin Switch in Atomic Scale Two-Dimensional Platform. *J. Magn. Magn. Mater.* **2019**, *484*, 462–471.

(25) Sahoo, M. R.; Sahu, S.; Kushwaha, A. K.; Nayak, S. Study of Electronic and Magnetic Properties of H-BN on Ni Surfaces: A DFT Approach. In *AIP Conference Proceedings*; AIP Publishing LLC, 2018; Vol. 1951, p 30003.

(26) Sahoo, M. R.; Sahu, S.; Kushwaha, A. K.; Nayak, S. K. Band Gap Modulation of Graphene by Metal Substrate: A First Principles Study. In *AIP Conference Proceedings*; AIP Publishing LLC, 2018; Vol. 1942, p 90047.

(27) Sahu, S.; Sahoo, M. R.; Kushwaha, A. K.; Rout, G. C.; Nayak, S. K. Charge Transfer and Hybridization Effect at the Graphene-Nickel Interface: A Tight Binding Model Study. *Carbon N. Y.* **2019**, *142*, 685–696.

(28) Rokob, T. A.; Srnec, M.; Rulíšek, L. Theoretical Calculations of Physico-Chemical and Spectroscopic Properties of Bioinorganic Systems: Current Limits and Perspectives. *Dalt. Trans.* **2012**, *41* (19), 5754.

(29) Fernández-Ramos, A.; Miller, J. a.; Klippenstein, S. J.; Truhlar, D. G. Modeling the Kinetics of Bimolecular Reactions. *Chem. Rev.* **2006**, *106* (11), 4518–4584.

(30) Nanda, A.; Nasker, S. S.; Kushwaha, A. K.; Ojha, D. K.; Dearden, A. K.; Nayak, S. K.; Nayak, S. Gold Nanoparticles Augment N-Terminal Cleavage and Splicing Reactions in Mycobacterium Tuberculosis SufB . *Frontiers in Bioengineering and Biotechnology* . 2021.

(31) Corminboeuf, C.; Tran, F.; Weber, J. The Role of Density Functional Theory in Chemistry: Some Historical Landmarks and Applications to Zeolites. *J. Mol. Struct. THEOCHEM* **2006**, *762* (1–3), 1–7.

(32) Wigner, E.; Seitz, F. On the Constitution of Metallic Sodium. *Phys. Rev.* **1933**, *43* (10), 804.

(33) Dirac, P. A. M. Note on Exchange Phenomena in the Thomas Atom. In *Mathematical Proceedings of the Cambridge Philosophical Society*; Cambridge University Press, 1930; Vol. 26, pp 376–385.

(34) Slater, J. C. A Simplification of the Hartree-Fock Method. *Phys. Rev.* **1951**, *81* (3), 385.

(35) Baerends, E. J.; Ellis, D. E.; Ros, P. Self-Consistent Molecular Hartree—Fock—Slater Calculations I. The Computational Procedure. *Chem. Phys.* **1973**, *2* (1), 41–51.

(36) Becke, A. D.; Johnson, E. R. A Simple Effective Potential for Exchange. AIP 2006.

(37) Callaway, J. Orthogonalized Plane Wave Method. *Phys. Rev.* **1955**, *97* (4), 933.

(38) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953.

(39) Antončík, E. Approximate Formulation of the Orthogonalized Plane-Wave Method. *J. Phys. Chem. Solids* **1959**, *10* (4), 314–320.

(40) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59* (3), 1758.

(41) Gross, E. K. U.; Dreizler, R. M. *Density Functional Theory*; Springer Science & Business Media, 2013; Vol. 337.

(42) Ziegler, T. Approximate Density Functional Theory as a Practical Tool in Molecular Energetics and Dynamics. *Chem. Rev.* **1991**, *91* (5), 651–667.

(43) Yang, W.; Ayers, P. W. Density-Functional Theory. In *Computational Medicinal Chemistry for Drug Discovery*; CRC Press, 2003; pp 103–132.

(44) Bickelhaupt, F. M.; Baerends, E. J. Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry. *Rev. Comput. Chem.* **2000**, 1–86.

(45) van Mourik, T.; Bühl, M.; Gaigeot, M.-P. Density Functional Theory across Chemistry, Physics and Biology. The Royal Society 2014.

(46) Cole, D. J.; Hine, N. D. M. Applications of Large-Scale Density Functional Theory in Biology. *J. Phys. Condens. Matter* **2016**, *28* (39), 393001.

(47) Friesner, R. A.; Beachy, M. D. Quantum Mechanical Calculations on Biological Systems. *Curr. Opin. Struct. Biol.* **1998**, *8* (2), 257–262.

(48) Labanowski, J. K.; Andzelm, J. W. *Density Functional Methods in Chemistry*; Springer Science & Business Media, 2012.

(49) Schrödinger, E. Quantisierung Als Eigenwertproblem. *Ann. Phys.* **1926**, *385* (13), 437–490.

(50) Born, M.; Oppenheimer, R. Zur Quantentheorie Der Molekeln. *Ann. Phys.* **1927**, *389* (20), 457–484.

(51) Woolley, R. G.; Sutcliffe, B. T. Molecular Structure and the born—Oppenheimer Approximation. *Chem. Phys. Lett.* **1977**, *45* (2), 393–398.

(52) Thomas, H. L. On the Capture of Electrons by Moving Electrified Particles. *Proc. R. Soc. Lond. A* **1927**, *114* (768), 561–576.

(53) Fermi, E. Eine Statistische Methode Zur Bestimmung Einiger Eigenschaften Des Atoms Und Ihre Anwendung Auf Die Theorie Des Periodischen Systems Der Elemente. *Zeitschrift für Phys.* **1928**, *48* (1–2), 73–79.

(54) Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. In *Mathematical Proceedings of the Cambridge Philosophical Society*; Cambridge University Press, 1928; Vol. 24, pp 89–110.

(55) Ring, P.; Schuck, P. *The Nuclear Many-Body Problem*; Springer Science & Business

Media, 2004.

(56) Fock, V. Näherungsmethode Zur Lösung Des Quantenmechanischen Mehrkörperproblems. *Zeitschrift für Phys.* **1930**, *61* (1–2), 126–148.

(57) Sherrill, C. D. An Introduction to Hartree-Fock Molecular Orbital Theory. *Georg. inst. Technol.* **2000**.

(58) Wigner, E. On the Interaction of Electrons in Metals. *Phys. Rev.* **1934**, *46* (11), 1002.

(59) Echenique, P.; Alonso, J. L. A Mathematical and Computational Review of Hartree–Fock SCF Methods in Quantum Chemistry. *Mol. Phys.* **2007**, *105* (23–24), 3057–3098.

(60) Pietronero, L.; Zirilli, F. Limitations and Validity of the Hartree-Fock Method. *Nuovo Cim. B* **1974**, *24* (1), 57–62.

(61) Lieb, E. H.; Simon, B. Thomas-Fermi Theory Revisited. *Phys. Rev. Lett.* **1973**, *31* (11), 681.

(62) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140* (4A), A1133.

(63) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136* (3B), B864.

(64) Gunnarsson, O.; Jonson, M.; Lundqvist, B. I. Exchange and Correlation in Inhomogeneous Electron Systems. *Solid State Commun.* **1977**, *24* (11), 765–768.

(65) Perdew, J. P.; Ruzsinszky, A.; Tao, J.; Staroverov, V. N.; Scuseria, G. E.; Csonka, G. I. Prescription for the Design and Selection of Density Functional Approximations: More Constraint Satisfaction with Fewer Fits. *J. Chem. Phys.* **2005**, *123* (6), 62201.

(66) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2006**, *2* (2), 364–382.

(67) Becke, A. D. Completely Numerical Calculations on Diatomic Molecules in the Local-Density Approximation. *Phys. Rev. A* **1986**, *33* (4), 2786.

(68) Dirac, P. A. M. Quantum Mechanics of Many-Electron Systems. *Proc. R. Soc. Lond. A* **1929**, *123* (792), 714–733.

(69) Perdew, J. P.; Zunger, A. Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems. *Phys. Rev. B* **1981**, *23* (10), 5048.

(70) Ceperley, D. M.; Alder, B. J. Ground State of the Electron Gas by a Stochastic Method. *Phys. Rev. Lett.* **1980**, *45* (7), 566.

(71) Seidl, M.; Perdew, J. P.; Kurth, S. Density Functionals for the Strong-Interaction Limit. *Phys. Rev. A* **2000**, *62* (1), 12502.

(72) Perdew, J. P.; Yue, W. Accurate and Simple Density Functional for the Electronic Exchange Energy: Generalized Gradient Approximation. *Phys. Rev. B* **1986**, *33* (12), 8800.

(73) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865.

(74) Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy. *Phys. Rev. B* **1992**, *45* (23), 13244.

(75) Perdew, J. P.; Wang, Y. Pair-Distribution Function and Its Coupling-Constant Average for the Spin-Polarized Electron Gas. *Phys. Rev. B* **1992**, *46* (20), 12947.

(76) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1992**, *46* (11), 6671.

(77) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta–generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91* (14), 146401.

(78) Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. Accurate Density Functional with Correct Formal Properties: A Step beyond the Generalized Gradient Approximation. *Phys. Rev. Lett.* **1999**, *82* (12), 2544.

(79) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652.

(80) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38* (6), 3098.

(81) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37* (2), 785.

(82) Leach, A. R.; Leach, A. R. *Molecular Modelling: Principles and Applications*; Pearson education, 2001.

(83) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; John Wiley & Sons, 2013.

(84) Slater, J. C. Atomic Shielding Constants. *Phys. Rev.* **1930**, *36* (1), 57.

(85) Boys, S. F. Electronic Wave Functions-I. A General Method of Calculation for the Stationary States of Any Molecular System. *Proc. R. Soc. Lond. A* **1950**, *200* (1063), 542–554.

(86) Skyner, R. E.; McDonagh, J. L.; Groom, C. R.; Van Mourik, T.; Mitchell, J. B. O. A Review of Methods for the Calculation of Solution Free Energies and the Modelling of Systems in Solution. *Phys. Chem. Chem. Phys.* **2015**, *17* (9), 6174–6191.

(87) Shivakumar, D.; Deng, Y.; Roux, B. Computations of Absolute Solvation Free Energies of Small Molecules Using Explicit and Implicit Solvent Model. *J. Chem. Theory Comput.* **2009**, *5* (4), 919–930.

(88) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. Ab Initio Study of Solvated Molecules: A New Implementation of the Polarizable Continuum Model. *Chem. Phys. Lett.* **1996**, *255* (4–6), 327–335.

(89) Cances, E.; Mennucci, B.; Tomasi, J. A New Integral Equation Formalism for the Polarizable Continuum Model: Theoretical Background and Applications to Isotropic and Anisotropic Dielectrics. *J. Chem. Phys.* **1997**, *107* (8), 3032–3041.

(90) Marenich, A. V; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113* (18), 6378–6396.

(91) Scalmani, G.; Frisch, M. J. Continuous Surface Charge Polarizable Continuum Models of Solvation. I. General Formalism. *J. Chem. Phys.* **2010**, *132* (11), 114110.

(92) Barone, V.; Cossi, M.; Tomasi, J. A New Definition of Cavities for the Computation of

Solvation Free Energies by the Polarizable Continuum Model. *J. Chem. Phys.* **1997**, *107* (8), 3210.

(93) Ding, W.; Lei, X.; Ouyang, C. Coordination of Lithium Ion with Ethylene Carbonate Electrolyte Solvent: A Computational Study. *Int. J. Quantum Chem.* **2016**, *116* (2), 97–102.

(94) Sun, Y.-Y.; Li, J.-F.; Zhou, F.-Q.; Li, J.-L.; Yin, B. Probing the Potential of Halogen-Free Superhalogen Anions as Effective Electrolytes of Li-Ion Batteries: A Theoretical Prospect from Combined Ab Initio and DFT Studies. *Phys. Chem. Chem. Phys.* **2016**, *18* (41), 28576–28584.

(95) Sikorska, C. Magnesium-based Clusters as Building Blocks of Electrolytes in Lithium-ion Batteries. *ChemPhysChem* **2019**, *20* (17), 2236–2246.

(96) Shao, N.; Sun, X.-G.; Dai, S.; Jiang, D. Electrochemical Windows of Sulfone-Based Electrolytes for High-Voltage Li-Ion Batteries. *J. Phys. Chem. B* **2011**, *115* (42), 12120–12125.

(97) Björklund, E.; Göttlinger, M.; Edström, K.; Younesi, R.; Brandell, D. Sulfolane-Based Ethylene Carbonate-Free Electrolytes for LiNi0. 6Mn0. 2Co0. 2O2− Li4Ti5O12 Batteries. *Batter. Supercaps* **2020**, *3* (2), 201–207.

(98) Su, C.-C.; He, M.; Redfern, P. C.; Curtiss, L. A.; Shkrob, I. A.; Zhang, Z. Oxidatively Stable Fluorinated Sulfone Electrolytes for High Voltage High Energy Lithium-Ion Batteries. *Energy Environ. Sci.* **2017**, *10* (4), 900–904.

(99) Cresce, A. V; Russell, S. M.; Borodin, O.; Allen, J. A.; Schroeder, M. A.; Dai, M.; Peng, J.; Gobet, M. P.; Greenbaum, S. G.; Rogers, R. E. Solvation Behavior of Carbonate-Based Electrolytes in Sodium Ion Batteries. *Phys. Chem. Chem. Phys.* **2017**, *19* (1), 574–586.

(100) Ghiasi, M.; Oskouie, A. A.; Saeidian, H. Dynamic Stereochemistry of Topiramate (Anticonvulsant Drug) in Solution: Theoretical Approaches and Experimental Validation. *Carbohydr. Res.* **2012**, *348*, 47–54.

(101) Haregewoin, A. M.; Leggesse, E. G.; Jiang, J.-C.; Wang, F.-M.; Hwang, B.-J.; Lin, S. D. A Combined Experimental and Theoretical Study of Surface Film Formation: Effect of Oxygen on the Reduction Mechanism of Propylene Carbonate. *J. Power Sources*

2013, *244*, 318–327.

(102) Jiang, B.; Ponnuchamy, V.; Shen, Y.; Yang, X.; Yuan, K.; Vetere, V.; Mossa, S.; Skarmoutsos, I.; Zhang, Y.; Zheng, J. The Anion Effect on Li+ Ion Coordination Structure in Ethylene Carbonate Solutions. *J. Phys. Chem. Lett.* **2016**, *7* (18), 3554–3559.

(103) Zhang, J.; Zhang, H.; Wu, T.; Wang, Q.; van der Spoel, D. Comparison of Implicit and Explicit Solvent Models for the Calculation of Solvation Free Energy in Organic Solvents. *J. Chem. Theory Comput.* **2017**, *13* (3), 1034–1043.

(104) Klamt, A.; Moya, C.; Palomar, J. A Comprehensive Comparison of the IEFPCM and SS (V) PE Continuum Solvation Methods with the COSMO Approach. *J. Chem. Theory Comput.* **2015**, *11* (9), 4220–4225.