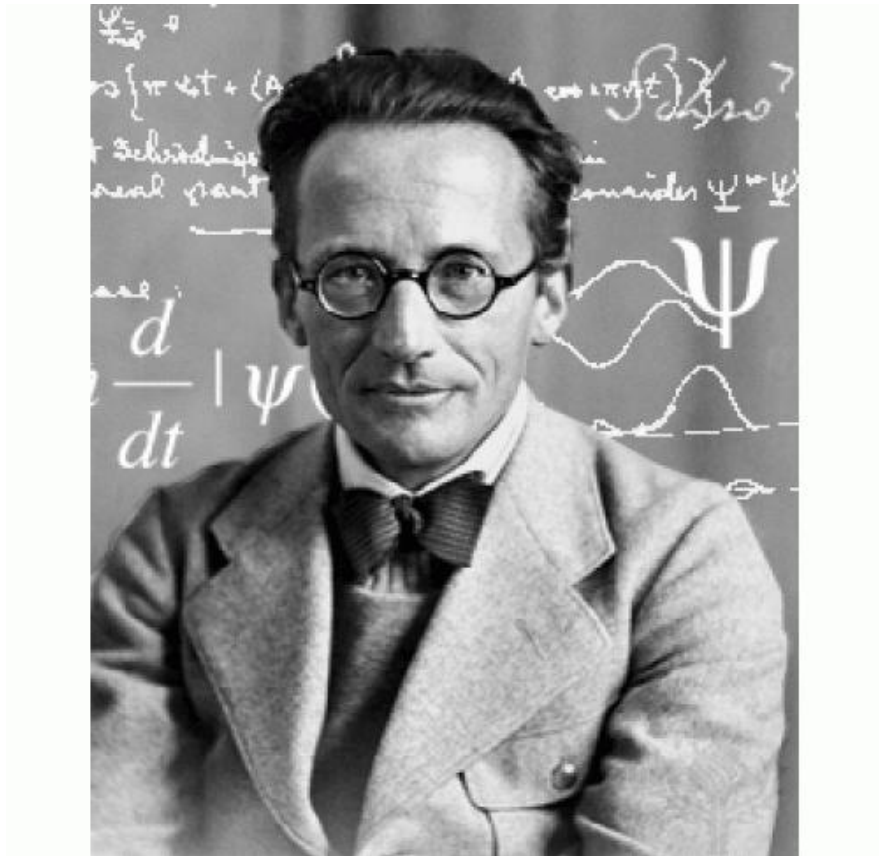

CHAPTER

2



“The mathematical framework of quantum theory has passed countless successful tests and is now universally accepted as a consistent and accurate description of all atomic phenomena”

-Erwin Schrodinger

BACKGROUND OF ELECTRONIC THEORY

2.1 INTRODUCTION

In the late seventeenth century, Sir Isaac Newton discovered classical mechanics based on the laws of motion of macroscopic objects. However, physicists in the early twentieth century observed that classical mechanics does not correctly describe the behavior of very small particles such as the electrons and nuclei of the atoms and molecules. This leads to the development of a new set of laws called Quantum Mechanics. The development of quantum mechanics is attributed mainly to the contributions made by Bohr, Schrödinger, Heisenberg, Born and Pauli. It is the science of motion of atomic and subatomic particles. It has great importance in all branches of chemistry because physico-chemical properties of atoms and molecules, their structures, spectral behaviors and reactions may be interpreted in terms of the motion of micro particles like electrons and protons. There are various methods based on quantum mechanics and their applications leads to the development of computational chemistry. Among different methods, Density Functional Theory (DFT) finds wide applications in various disciplines of science. The basis of this theory is the two Hohenberg–Kohn theorems which propose that the ground-state properties of an atom or molecule are determined by its electron density function, and that a trial electron density must give energy greater than or equal to the true energy. In recent years it is one of the most popular and successful methods for electronic structure calculations in many body systems. In this chapter, the computational methods utilized throughout the present work and their underlying theory will be outlined briefly.

2.2 OVERVIEW OF COMPUTATIONAL METHODS

The main focus of Computational chemistry is on the molecular characterization, structural determination, spectroscopic properties, energetics, and kinetics by way of numerical calculations. One of the first references of the term “computational chemistry” can be found in the 1970 book “Computers and Their Role in the Physical Sciences” by Sidney Fernbach and Abraham Haskell Taub [1] where

they state that “It seems, therefore, that 'Computational Chemistry' can finally be more and more of a reality.” With the development of quantum chemical methods, coupled with the rapid increase in computer power, the bridge between theory and experiment in solving problems of chemical relevance has become significant in modern chemistry.

A discussion on computational chemistry starts with an introduction to the time independent Schrödinger equation [2]

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

Where \hat{H} is the Hamiltonian operator, which is sum of kinetic and potential energy operators, thus, representing the total energy. Ψ is the wave function of the electron having coordinates x , y and z in three-dimensional space, and E is the total electronic energy of the system.

The Hamiltonian, \hat{H} is generally written as:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \sum_{i < j} \sum \frac{e_i e_j}{r_{ij}} \quad (2.2)$$

The first term in the right hand side of Eq. 2.2 represents the kinetic energy of the electrons and the nuclei, while the second term represents the potential energy. Unfortunately, analytic solutions of the Schrödinger equation exist only for the simplest systems which contain no more than two interacting particles. Real systems, that is, atoms, molecules and solids, contain many interacting electrons and nuclei and thus solving or approximating this equation for multi-electron system is the real goal in any quantum based computational method.

The difficulty of determining a solution can be reduced somewhat by employing a simple approximation known as the Born-Oppenheimer (BO) approximation [3]. According to this approximation, it is reasonable to suggest that the electrons can adjust rapidly to any change of the nuclear configuration because nuclei are much heavier than electrons. Under such a situation it can be assumed that the electronic distribution depends on the instantaneous positions of the nuclei and not on their velocities. This allows the separation of the Hamiltonian (Eqn. 2.2) into nuclear and electronic components so that energy calculation is made at fixed nuclear

configuration. The interactions between the electrons and the nuclei are treated as a static external potential (V_N). In the BO approximation, the electronic Schrödinger equation of Eqn. (2.1) can be written as

$$(\hat{H}_{el} + V_N) \Psi_{el}(r_i, R_i) = E_{el} \Psi_{el}(r_i, R_i) \quad (2.3)$$

Where the coordinates of the electrons, r_i depend only parametrically on the nuclear coordinates R_i . The BO approximation is an excellent approximation to the solution of molecular electronic Schrödinger equation. In addition, it provides practically the only way to define a molecular potential energy surface and molecular structure.

With this assumption all nuclear positions are supposed be fixed and only electronic motions are considered. Under this approximation, thus, the total energy of the molecule is the sum of the energies of the nuclei and electrons.

$$E_{total} = E_{nuclei} + E_{electron} \quad (2.4)$$

This makes the Hamiltonian to be separated into two parts- one for the nuclei and the other for electrons. Thus, the Schrödinger equation for electronic motion can be written as

$$\hat{H}_{el} \Psi_{el} = E_{el} \Psi_{el} \quad (2.5)$$

Where,

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_j \sum_{i>j} \frac{e^2}{r_{ij}} \quad (2.6)$$

The first term in Eqn. (2.6) is the kinetic energy operator for electrons, the second term is the potential energy sum due to attraction between the electrons and the nuclei, the third term is the potential energy of the repulsion between two electrons i and j .

2.3 POTENTIAL ENERGY SURFACE

The potential energy surface (PES) is the relationship between energy of a molecule and its geometry. It is a central concept of computational chemistry and based on BO approximations. The energy, E_{PES} is the sum of Schrödinger solved electronic

energy and the nuclear-nuclear repulsion term, V_{NN} .

$$E_{\text{PES}} = E_o + V_{\text{NN}} \quad (2.7)$$

By plotting the potential energy as a function of nuclear coordinates, various points of interest can be determined. A stationary point is the one in where $\delta E_{\text{PES}} / \delta q = 0$ for all q (q is the geometric parameter). The minimum stationary points are minima i.e.; $\delta^2 E_{\text{PES}} / \delta q^2 > 0$ for all q . The transition states or first order saddle points is a maximum along the reaction coordinate and a minimum along all the other directions i.e.; $\delta^2 E_{\text{PES}} / \delta q^2 > 0$ for all q , except reaction coordinate and $\delta^2 E_{\text{PES}} / \delta q^2 < 0$ along the reaction coordinate.

The stationary point with lowest energy along a PES is called a “global minimum” which corresponds to the most stable geometry of a molecule. The other possible minimum points are called “local minimum.” Figure 2.1 shows different point on a PES [4].

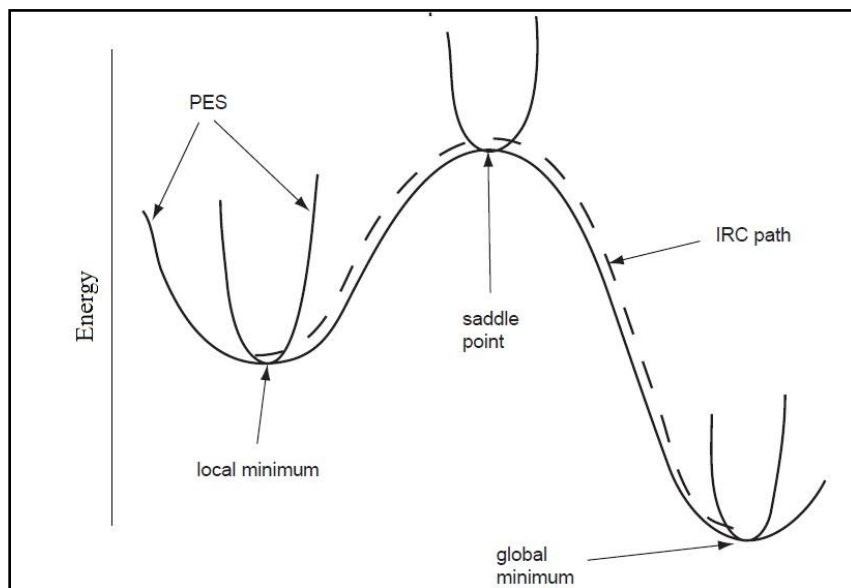


Figure 2.1 Points on potential energy surface

2.4 TOOLS OF COMPUTATIONAL CHEMISTRY

The main tools of computational chemistry can be broadly divided into five classes which are- molecular mechanics, ab initio methods, semiempirical methods, density functional calculations and molecular dynamics. The following subsections

briefly present some important computational chemistry tools.

2.4.1 Molecular Mechanics

Molecular mechanics (MM) [5,6] applies the laws of classical physics to predict the structures and properties of molecules. It considers a molecule as a collection of balls (atoms) connected via springs (chemical bonds). MM considers a conceptually mechanical model of a molecule to find the minimum energy structure. This method is often called force-field method. The object of molecular mechanics is to predict the energy associated with a given conformation of a molecule. The energy calculated by MM method consists of contributions made by various modes of spring motion described by different force fields. The total energy can be expressed as:

$$E_{\text{total}} = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{torsion}} + E_{\text{non-bonded}} \quad (2.8)$$

Where, E_{stretch} is the energy for stretching a bond between two atoms, E_{bend} is the energy required for bending a molecule, E_{torsion} is the torsional energy for rotation around a bond and $E_{\text{non-bonded}}$ is the non-bonded interaction energy. The equation together with the parameters required to describe the behavior of different kinds of atoms and bonds, is called a force-field. Molecular mechanics calculations are based on nuclear interactions and do not treat the electrons in the system. The main advantages of molecular mechanics are that it is fast, computationally less expensive, can be used for large biomolecules. However, it also possesses some disadvantages such as it can be applicable only for limited molecules, it ignores electrons and a parameterized force field performs well for only one class of compounds.

2.4.2 Ab initio methods

Ab initio method a major tool for investigating the structure, stability, reaction kinetics and mechanism of different molecular systems [7-12]. The basis of ab initio calculations are the laws of quantum mechanics that involve a small number of fundamental physical constants like the speed of light, the mass and charge of electron and proton, the Planck's constant, etc. These methods involve the solution of Schrödinger equation through a series of necessary mathematical approximations.

Abinitio methods include Hartree-Fock (HF) theory, Møller-Plesset Perturbation Theory (MPPT), Configuration Interaction (CI) & Couple-cluster(CC) method.

2.4.2.1 Hartree-Fock Theory

Hartree-Fock (HF) theory is the most common ab initio method. It is the basis of molecular orbital (MO) theory which proposes that each electronic motion can be described by a single particle function (orbital) that does not depend explicitly on the instantaneous motions of the other electrons. HF theory was developed to solve the electronic Schrödinger equation resulting from the time-independent Schrödinger equation after invoking the BO approximation. This approach was first proposed by Hartree and Fock [13,14] and is referred to as HF theory. Because the molecular orbitals are derived from their own effective potential, this method is also known as Self-Consistent Field (SCF) theory.

In HF-SCF theory [15], at first an approximate guess of the coefficient matrix C is made. This is achieved by either simply orthogonalising the atomic orbital basis by diagonalising the one-electron part of the Hamiltonian or utilizing semi-empirical methods like INDO or extended Huckel theory (EHT).

$$HC = SC\varepsilon \quad (2.9)$$

Secondly, the Fock matrix is constructed and diagonalised by solving the Roothaan-Hall equation. This is easy if a unitary transformation is performed in order to orthonormalise the original basis set so that the overlap matrix becomes the identity. The standard approach is to use the Löwdin orthogonalisation method [16] where the transformation is made using the $S^{-1/2}$ matrix.

$$S^{-1/2} F S^{-1/2} S^{1/2} C = S^{-1/2} S S^{-1/2} S^{1/2} C \varepsilon \quad (2.10)$$

which yield,
$$\tilde{F} \tilde{C} = \tilde{C} \varepsilon \quad (2.11)$$

Where, $\tilde{F} = S^{-1/2} F S^{-1/2}$, $\tilde{C} = S^{1/2} C$ and the eigenvalues ε are a more accurate estimate of the true orbital energies. In the simplest implementation of SCF optimization, orbitals in a given diagonalization step are used to construct a new Fock matrix. Thus, allowing a new set of orbitals to be generated. This process can be iterated until the coefficients

matrix is unchanged from one iteration to the next. The resulting orbitals are then said to be “Self-Consistent”. The total energy of the system at convergence is given by-

$$E = E_{orb} - \frac{1}{2} \sum_{i \neq j} \langle ij || ij \rangle \quad (2.12)$$

Where E_{orb} is the total orbital energy given as $E_{orb} = \sum_i \epsilon_i$.

Ab-initio methods are relatively slow and required very demanding computational power. Such drawbacks are simplified in semiempirical methods.

2.4.3 Semiempirical methods

Semi-empirical methods based on the parameters derived from experimental data to shorten the computations. These methods approximately solve the Schrödinger wave equations and depend on the availability of appropriate parameters for the chemical system of interest. Semi-empirical calculations are relatively inexpensive on the availability of good parameters and give fairly accurate energy and structure. Here, the Fock matrix is repeatedly diagonalized to refine the wave function and molecular energy. Three approximations schemes are generally used in semiempirical methods:

- (a) Elimination of core electrons from the calculations
- (b) Use of minimum number of basis sets &
- (c) Reduction of the number of two electron integrals

The various procedures of semiempirical methods include Pariser-Parr-Pople (PPP), Complete Neglect of Differential Overlap (CNDO), Intermediate Neglect of Differential Overlap (INDO) and Neglect of Diatomic Differential Overlap (NDDO). All these four use the Zero Differential Overlap (ZDO) approximation where the differential of overlap integral is set as zero.

Semiempirical methods are relatively takes less time than ab initio methods. However, their predictions are unreliable until comparison with experiment results or with some high level ab initio calculations.

2.4.4 Density Functional Theory

Density Functional theory (DFT) is mainly developed on the base of proof by Hohenberg and Kohn which states that the ground state electronic energy can be determined completely by the electron density (ρ). We can also say that density functional theory is based on the electron probability density function or electron density function. Mathematically, Hohenberg and Kohn proved that there exists a one to one correspondence between the electron density of a system and the energy. DFT is widely used in quantum chemical calculations because its computational requirement is comparable to HF techniques but accuracy is comparable to more exact techniques such as MP2. The computational cost in DFT is almost same as that of HF methods but less expensive than ab initio methods involving electrons correlation.

Unlike other methods, DFT not describes the wave function which depends on $3N$ spatial coordinates in a N -electron system. Instead of that it describes the system by its electron density which depends on only 3 spatial coordinates. The N particle system electron density is given by,

$$\rho(\vec{r}_1) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_N \quad (2.12)$$

The electron density ρ is a function of position only, that is, of just three variables, x , y and z coordinates, no matter how large is the molecule. The DFT ground state energy of a molecule, which is a function of the ground state electron density, can be expressed as,

$$E_0 = - \sum_{nuclei} Z_A \int \frac{\rho_0(\vec{r}_1) d\vec{r}_1}{r_{1A}} - \frac{1}{2} \sum_{i=n}^{2n} \langle \Psi_i^{KS} | \nabla_i^2 | \Psi_i^{KS} \rangle + \frac{1}{2} \iint \frac{\rho_0(\vec{r}_1) \rho_0(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 E_{XC}[\rho_0] \quad (2.13)$$

The first term is the potential energy signifies the nuclei-electron attraction; the second term is the non-interaction electronic kinetic energy; the third term is the classical repulsion energy term; the fourth term is defined as exchange correlation energy. Once we know the density function $\rho_0(\vec{r})$ and the exchange-correlation energy functional $E_{XC}[\rho_0]$, we can get the exact energy. By comparing with the equations of

wave mechanics and assuming the Born–Oppenheimer approximation, it is clear that the functional can be divided into three parts, a term for kinetic energy ($E^T[\rho]$), one for columbic attraction between nuclei and electrons ($E^V[\rho]$) and one for interactions between electrons which in turn can be readily divided into coulomb ($E^J[\rho]$) and exchange ($E^{XC}[\rho]$) terms. Thus,

$$E[\rho] = E^T[\rho] + E^V[\rho] + E^J[\rho] + E^{XC}[\rho] \quad (2.14)$$

The density function $\rho_0(\vec{r})$ can be calculated using equation (2.12) where the wave function can be obtained by solving the Kohn-Sham equation [17]

$$\left[-\frac{1}{2} \nabla_i^2 - \sum_{nuclei A} \frac{Z_A}{r_{1A}} + \int \frac{\rho_0(\vec{r}_2) d\vec{r}_2}{r_{12}} + v_{XC} \right] \psi_i^{KS} = \varepsilon_i^{KS} \psi_i^{KS} \quad (2.15)$$

In Eq.(2.15), the ψ_i^{KS} is the Kohn-Sham (KS) spatial orbital function, ε_i^{KS} is the KS energy level and v_{XC} is the exchange correlation potential which is defined as the functional derivative of $E_{xc}[\rho(\vec{r})]$ with respect to $\rho(\vec{r})$:

$$v_{XC}(\vec{r}) = \frac{\delta E_{XC}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \quad (2.16)$$

The strength of DFT is that only the total electron density needs to be considered. If the exact $E_{xc}[\rho(\vec{r})]$ is known, DFT would provide the exact total energy including electron correlation. Various approximations are made to $E_{xc}[\rho(\vec{r})]$ to use DFT methods in different calculations.

2.4.4.1 Local Density Approximation (LDA)

Local density approximation (LDA) is the simplest approximation to the exchange correlation function $E_{xc}[\rho(\vec{r})]$ which assumes that the exchange correlation energy at a certain point in space depends on the density at the same point. $E_{xc}[\rho(\vec{r})]$ can be expressed in a simple form as:

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r}) \varepsilon_{XC}[\rho(\vec{r})] d\vec{r} \quad (2.17)$$

Where $\epsilon_{XC} [\rho(\vec{r})]$ is the exchange-correlation energy per particle of a uniform electron gas of density, $\rho(\vec{r})$. The exchange correlation energy, $\epsilon_{XC} [\rho(\vec{r})]$, is composed of two parts:

$$\epsilon_{XC} [\rho(\vec{r})] = \epsilon_X[\rho(\vec{r})] + \epsilon_C[\rho(\vec{r})] \quad (2.18)$$

The first part is the exchange part representing the exchange of an electron in a uniform gas and was approximated by Bloch [18]:

$$\epsilon_X = -\frac{3}{4} \sqrt{\frac{3\rho(\vec{r})}{\pi}} \quad (2.19)$$

The second part in Eq. (2.18) is the correlation part that has been studied by various workers using sophisticated interpolation schemes. The most popular $\epsilon_{XC} [\rho(\vec{r})]$ functional is developed by Vosko, Wilk and Nussair abbreviated as (VWN) [19]. A recent and accurate expression of $\epsilon_{XC} [\rho(\vec{r})]$ is PW density functional given by Perdew and Wang [20].

The presence of the exchange correlation term made LDA approximations more accurate than HF approximation having similar computational cost. It was found that LDA is successful to predict the optimized geometries [21] and vibrational frequencies [22] with a higher degree of accuracy. However, the assumption of a homogeneous electron gas in the system results a rather poor calculated energy in LDA functional.

2.4.4.2 Generalized gradient approximation (GGA)

The reason for failure of the LDA functional in calculating the ground state energy of a molecular system is the assumption of a uniform electron density. For obtain a further accurate approximation of the exchange-correlation energy, GGA functionals are developed which not only include the electron density but also the electron density gradient. Generally, E_{XC}^{GGA} is composed of two parts (i) exchange and (ii) correlation

$$E_{XC}^{GGA} = E_X^{GGA} + E_C^{GGA} \quad (2.20)$$

The most widely used exchange functional was developed by Becke in 1988 and termed as B88 [23]. One of the most popular correlation functionals developed by Lee, Yang and Parr called the LYP functional [24]. The other most common choices are Perdew 1986 (P86) [25], Perdew-Wang correlation functional (PW91) [21],

combination of B88 with LYP (BLYP) and Perdew-Becke-Ernzerhof exchange-correlation functional (PBE) [26].

2.4.4.3 Hybrid Functionals

To obtain an accurate expression for the exchange functional from DFT, the concept of hybrid functional was introduced. It is a combination of Hartee-Fock exchange with and DFT functional and can be expressed as,

$$E_X = E_X^{\text{HF}} + E_{xc}^{\text{DFT}} \quad (2.21)$$

The most popular hybrid model is the B3LYP method based on Becke's 3-parameter-functional (B3) and is given by,

$$E_{XC}^{\text{B3LYP}} = (1-a)E_x^{\text{LDA}} + aE_x^{\text{HF}} + bE_x^{\text{B88}} + cE_c^{\text{LYP}} \quad (2.22)$$

Where the parameters a, b, and c are determined by fitting experimental data and calculated data for the atomization energies, ionization potentials and proton affinities of second and third period elements and results in values of a=0.20, b=0.72 and c=0.81 [15,27].VWN is the Vosko, Wilk and Nusair functional [11] and LYP is Lee, Yang and Parr functional [16]. Varius functional has been generated in the same way by varying the component functional. For example another functional is devised by substituting the Perdrew-Wang [28] gradient-corrected correlation function for LYP and by adjusting other three parameters.

2.5 BASIS SETS

A basis set is a mathematical representation of the molecular orbitals within a molecule. The basis set can be interpreted as restricting each electron to a particular region of space [29]. For the ab inito molecular orbital approach, we can consider the molecular orbitals formed by the linear combination of atomic orbitals which can be expressed as:

$$\Psi_i = \sum_{\mu=1}^n c_{\mu i} \varphi_{\mu} \quad (2.23)$$

Where Ψ_i is the i -th molecular orbital, $c_{\mu i}$ are the coefficients of the linear combination, φ_{μ} is the μ -th atomic orbitals, n is the number of atomic orbital [30]. There are mainly two types of basis functions:

2.5.1 Slater Type Orbitals

Slater Type Orbitals (STO) are first introduced in the field of computation chemistry by J. C. Slater. They are characterized by an $\exp(-\xi r)$ radial dependence. STOs are the exact solutions to the hydrogen atom problem and hence can provide a good description of atomic wave functions and more importantly produce the correct behavior at the nucleus as well [31]. However, STOs have computational difficulties. To overcome this problem, Gaussian type orbitals (GTO) are derived as alternatives.

2.5.2 Gaussian Type Orbitals

Gaussian-type orbitals (GTOs) [32] are characterized by an $\exp(-\xi r^2)$ radial dependence and are most commonly used basis functions. A Gaussian-type orbital has the following form:

$$\chi_{\xi,a,b,c}(x,y,z) = N_{a,b,c,\xi} x^a y^b z^c e^{-\xi r^2} \quad (2.24)$$

Where N is the normalization constant, a , b and c are quantum numbers describing the angular shape and direction of orbital. Exponent ξ applies to the radial size of the orbital. In order to improve the properties of an individual basis function, Gaussian-type basis functions are often expressed as a linear combination of Primitive Gaussian Functions.

$$\Phi_{\mu} = \sum_i d_{\mu_i} g_i \quad (2.25)$$

The coefficient (d_{μ_i}) for each of the Primitive Gaussians (g_i) are chosen so as to better represent a true atomic orbital. This type of basis function (Φ_{μ}) is known as contracted Gaussian. There are different types of basis function. The most general classes are:

2.5.3 Minimal Basis Sets

A minimal basis set is the smallest number of basis functions needed to

accommodate all the electrons for each atom. It approximates all the orbitals to be the same shape. A minimal basis set consists of one STO for each inner-shell and valence-shell atomic orbital of each atom. STO-3G is an example of minimal basis set which uses three Gaussian primitives per basis functions and is a Slater type orbital.

2.5.4 Split Valence Basis Sets

Minimal basis sets are not able to alter the basis functions with reference to the molecular environment. Therefore, split valence basis sets are developed where the atomic orbitals are split into two parts- an inner compact orbital and an outer more diffuse orbital. It model each valence orbital by two or more basis functions. Double split valence or valence double zeta (VDZ) basis sets have one basis function per inner orbital and two basis functions per valence orbital. An example is 3-21G where core orbitals are represented by three Gaussians whereas inner and outer valence orbitals are represented by two and one Gaussians, respectively. The triplesplit valence or valence triple zeta (VTZ) basis sets have one basis function for each core electron and three basis functions per valence orbital. Example of VTZ basis set is 6-311G where the inner valance orbitals are represented by three Gaussians and middle and outer valence orbitals are represented as single Gaussians.

2.5.5 Polarization Functions

Polarization of the electron distribution around the nucleus is not considered in VDZ and VTZ basis sets. Thus polarization functions are introduced which allow the shift of the centre of an orbital away from the centre of the nucleus due to charge polarization. Here s orbitals possess a little p behavior and p orbitals have little d behavior. The purpose of adding the polarization function is to provide additional angular flexibility to the linear combination of atomic orbitals in forming bonding orbitals. They have the effect of showing angular electron correlation i.e. allow for non-spherical distributions of the electrons around a nucleus. Examples are 3-21G* or 3-21G(d) , 6-311G** or 6-311G(d,p) etc, where one asterisk (*) at the end of basis set represent the polarization of p orbitals whereas two asterisks (**) denotes the polarization of s orbitals in addition to p orbitals.

2.5.6 Diffuse Functions

Diffuse functions are used to properly describe the outlying regions of the molecules which are particularly important for the anions or excited states. They improve the basis sets by considering the larger distances from the nuclei and thus describe better the barely bound electrons. Diffuse basis sets are represented by '+' signs and are written as 3-21+G and 6-31+G(d). Double diffuse basis sets are also used and these are represented as 6-31++G(d).

2.5.7 Effective Core Potentials

Effective core potential is an approach to consider the relativistic effect of heavier elements. The inner electrons in the heavier elements have movement at a significant fraction of speed of light and as a result their relative masses increase. Due to gain in mass, the inner electrons cause their orbitals to contract and screen the outer electrons highly. Hence the outer, valence d and f orbitals expand, gain higher energy and also become more reactive. The effect of the core electrons is minimized by a collective way by considering an average potential known as effective core potential (ECP). It is the most satisfying way to carry out relativistic molecular calculations. The common basis sets applied to consider ECP are LANL2DZ, LANL2TZ etc.

2.6 QUANTUM THEORY OF ATOMS IN MOLECULES (QTAIM)

The nature of chemical bonding of a system can be calculated by using Bader's quantum theory of atoms in molecules [33-35]. The basis of this theory is the three dimensional electron density functions, $\rho(r)$. The topological analysis is the investigation of critical points of this function, $\rho(r)$. The commonly used parameters to describe the nature and extent of bonding between two atoms are the electron density, ρ and the Laplacian of electron density, $\nabla^2\rho$ at the bond critical point (BCP). Generally, a large value of $\rho(r)$ (>0.2 au) and large and negative value of $\nabla^2\rho$ indicates a covalent or open shell interaction, whereas a small value of $\rho(r)$ (<0.10 au) and a positive value of $\nabla^2\rho$ indicates an ionic or closed-shell interaction. However, for transition metal based systems, this view can't be extended since the electron distribution of these elements are diffuse in nature. Hence, in transition metal complexes, the rule is slightly modified

and it is observed that a small value of ρ and a small and positive value of $\nabla^2\rho$ imply a covalent interaction. Two additional parameters are also used to describe the bonding nature more appropriately. These two parameters are local electronic energy density function, $H(r)$ and relative kinetic energy density, $G(r)/\rho$, where, $H(r)$ is the sum of local kinetic $G(r)$ and potential $V(r)$ energy densities, i.e., $H(r) = G(r) + V(r)$. Cremer and Kraka [36] proposed that a value of $H(r) < 0$ at the BCP indicates the presence of significant covalent character or an open-shell interaction and lowering of potential energy of electrons at the BCP, whereas a value of $H(r) > 0$ at the BCP generally refers to a closed shell interaction, i.e., ionic, van der Waals, or hydrogen bonding. Similarly, value of $G(r)/\rho < 1$ at the BCP indicates a covalent interaction, whereas $G(r)/\rho > 1$ indicates the ionic nature of the bond [37].

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