

CHAPTER 2

THEORITICAL BACKGROUND

The purpose of this chapter is to briefly discuss quantum mechanical (QM) approaches that are three methods, which include semi-empirical, ab initio and density functional theory (DFT) methods. It can be widely used in computational studies to calculate molecular structures, chemical and physical properties of chemical systems and reactions. Prior to 1920s, E. Fermi and L. H. Thomas developed their work by using the concept of density functional, which is a function of total electron density for expressing the energy of the chemical system. Later, J. C. Slater generated the HF-Slater method to report the energy and other properties of the system, using the same concept into development of his method in 1951. These ideas were confirmed by P. Hohenberg and W. Kohn. They published a theorem which uses the electron density of system to describe the ground state energy of a non-degenerate electronic system and the correspondent electronic properties. Recently, DFT has become known as an effective methodology for simulation of the chemical system.

2.1 The DFT method

The main problem of DFT concept [41] is difficult to explain kinetic energy systems of interacting electron. So, W. Kohn and L. Sham introduced the way to solve this problem in 1965 [42].

2.1.1 The Kohn-Sham energy



The kinetic energy functional of a system can be divided into two parts: one is the part of non-interacting particles that can be calculated exactly. The other is a small correction term for electron-electron interaction. The electronic energy of ground state of the system is followed by the Kohn-Sham formalism can be written as

$$E[\rho] = -\frac{1}{2} \sum_{i=1}^n \int \Psi_i^*(r_i) \nabla_i^2 \Psi_i(r_i) dr_i - \sum_{x=1}^N \int \frac{Z_x}{r_x} \rho(r_i) dr_i + \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 + E^{xc}[\rho] \quad (2.1)$$

The system comprises n electrons and N nuclei. $\Psi_i (i=1,2,3,\dots,n)$ are the Kohn-Sham orbitals, the kinetic energy of non-interacting electrons are accounted in the first term, the nuclear-electron interactions are shown in the second term, the Coulombic repulsions between the total charge distributions at r_1 and r_2 are regarded in the third term, and the last term corresponds to the exchange-correlation which represents the correction of kinetic energy from electron-electron repulsion energy.

As set of one-electron orbitals, the ground state electron density $\rho(r)$ at location r can be written as

$$\rho(r) = \sum_{i=1}^n |\Psi_i(r)|^2 \quad (2.2)$$

The Kohn-Sham orbitals are calculated by solving Kohn-Sham equations

$$\hat{h}_i \Psi_i(r_i) = \varepsilon_i \Psi_i(r_i) \quad (2.3)$$



where \hat{h}_i is the Kohn-Sham Hamiltonian, ε_i is the Kohn-Sham orbital energy

The Kohn-Sham Hamiltonian can be written as

$$\hat{h}_i = -\frac{1}{2}\nabla_1^2 - \sum_{X=1}^N \frac{Z_X}{r_{X1}} + \int \frac{\rho(r_2)}{r_{12}} dr_2 + V^{xc}(r_1) \quad (2.4)$$

In equation (2.4), V^{xc} is functional derivative of the exchange-correlation energy, given by

$$V^{xc}[\rho] = \frac{\delta E^{xc}[\rho]}{\delta \rho} \quad (2.5)$$

The exchange-correlation energy (E^{xc}) consists of exchange term (E^x) and correlation term (E^c) which are functional of the electron density. The exchange term is represented interaction between electrons of the same spin, while correlation term is described interaction between electrons of opposite spin.

$$E^{xc}[\rho] = E^x[\rho] + E^c[\rho] \quad (2.6)$$

The exchange-correlation energy can be split into two groups which are local functional and gradient corrected.

2.1.1.1 Local Density Approximation

At any point in space, the local density approximation (LDA) depends only on electron density. The exchange-correlation energy is a function of the



electron density at that point in space and can be given the same density in homogeneous electron gas. Thomas-Fermi-Dirac method is presented as LDA to the exchange energy which was employed together with the Thomas-Fermi model by P. A. M. Dirac, in 1930.

$$E_{LDA}^{X,Dirac}[\rho] = -C_x \int \rho^{\frac{4}{3}}(r) dr \quad (2.7)$$

C_x is a constant that can be given by

$$C_x = -\frac{3}{4} \cdot \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \quad (2.8)$$

Whereas, the correlation energy is performed by using suitable formula which was calculated for a number of different densities in homogeneous electron gas. Many different formulations were developed such as Vosko –Wilk-Nusair and Perdew.

2.1.1.2 Generalized Gradient Approximation

The generalized gradient approximation (GGA) [43] represents the exchange-correlation functional which depend not only on the electron density (ρ), but also on its gradient, $\Delta\rho(r)$. Perdew-Wang (PW), Becke88 (B88), OptX (O) were developed for using as exchange functional. Examples of the correlation functionals include Becke 88 (B88), Perdew 86 (P86), Perdew-Wang 91 (PW91) and Lee-Yang-Parr (LYP).



2.1.1.3 Hybrid Density Functional Methods

The exchange-correlation of GGA method is increased with a term of HF exchange calculated from HF theory, in the so-called hybrid density functional method (H-GGA) [43]. HF orbital give an expression for the HF exchange energy that can be written as

$$E_x^{HF} = -\sum_{i=1}^n \sum_{j=1}^n \left\langle \Psi_i(1)\Psi_j(2) \left| \frac{1}{r_{ij}} \right| \Psi_i(2)\Psi_j(1) \right\rangle \quad (2.9)$$

For many molecule properties, H-GGA has become an extremely popular option in quantum calculation and widely used because it has allowed an important improvement over GGA. Many different functionals were developed such as B3P86, B3PW91, O3LYP, B97-1, B97-2 and B3LYP.

2.2 Gaussian basis sets

The molecular orbitals are created by using a set of function called the basis set, which is expanded as a linear combination atomic orbital with coefficient. There are two major types of basis set which include minimal and extended basis sets.

2.2.1 Minimal basis set



Minimal basis set [44] is a basis set that is constructed by using one basis function for each atomic orbital in the atom to describe only the most aspects of orbitals. Commonly used minimal basis sets of this type are Slater type orbital (STO), and Gaussian type orbital (GTO).

2.2.1.1 Slater type orbital (STO)

J. C. Slater developed the basis set which were fitted with linear least-square. The expression of STO basis function for s-orbital is given as

$$\phi^{STO} = N \cdot e^{(-\epsilon r)} \quad (2.10)$$

where

$$N = \left(\frac{\epsilon^3}{\pi} \right)^{0.5} \text{ is normalization constant}$$

ϵ is orbital exponent

r is a radius in angstrom unit

2.2.1.2 Gaussian type orbital (GTO)

STOs can be approximated as linear combinations of Gaussian orbital that called Gaussian primitive. The product of its primitive can be obtained from the GTO of r^2 . The expression of GTO basis function for s-orbital is given as



$$\phi^{GTO} = N \cdot e^{(-\gamma r^2)} \quad (2.11)$$

where $N = \left(\frac{2\gamma}{\pi}\right)^{0.75}$ is normalization constant

γ is orbital exponent

r is a radius in angstrom unit

All basis set equations are in the form STO-nG (where n represents the number of GTOs combined to the STO).

2.2.2 Extended basis sets

The extended basis set is basis set with more details. They accounted the higher orbital of the molecule and described for shape and size of molecular charge distributions. There are several types of extended basis sets consist of Double-Zeta, Triple-Zeta, Quadruple-Zeta, Split-Valence, Polarized Sets and Diffuse Sets [42, 45].

2.2.2.1 Double-Zeta, Triple-Zeta, Quadruple-Zeta

Each atomic orbital, the double-zeta basis set is calculated by the sum of two STOs. The equation can be written as

$$\phi_{2s}(r) = \phi_{2s}^{STO}(r, \xi_1) + d\phi_{2s}^{STO}(r, \xi_2) \quad (2.12)$$



The zeta value (ξ) shows diffusion of the orbital. The constant (d) accounts for the number of each STO which counts to the last orbital. So, each STO shows a different size of the orbital because of the different of its zeta. In the same way, the sum of three and four STOs is called as Triple-Zeta and Quadruple-Zeta, respectively.

2.2.2.2 Split-Valence

A split-valence basis set is the method that inner-shell electrons are considered to describe with a single STO. The examples of split-valence basis sets are 3-21G, 4-31G and 6-31G. In case of 6-31G basis set, it comprise of 6 gaussians for inner-shell orbital, 3 gaussians for the first STO of valence orbital and 1 gaussian for the second STO.

2.2.2.3 Polarized Sets

Polarization effect can be occurred when some orbitals share qualities of its orbitals to each other. The charge distribution between positive and negative charge cause the distortion of the shape of atomic orbital. To solve this problem, polarized basis sets are utilized. One asterisk (*) at the end of basis set implies that polarized basis set has been taken into consider in the p orbital which was modified by adding a d orbital. Two asterisks (**) imply that polarized basis set has been taken into consider in the s orbital which was modified by adding a p orbital.



2.2.2.4 Diffuse Sets

The diffuse function is used to compensate the loosely bond electron when an atom is in an anion or in an excited state. One (+) implies that p orbital was being accounted, while (++) signs imply that both p and s orbital was being accounted

2.2.2.5 Effective core potentials

Using of effective core potentials (ECP) have been the highly performance in the molecular orbital calculations that is suitable for transition metals. ECP is a group of potential functions that is used to replace the inner electrons of atomic and molecular systems, and calculate only the valence electrons explicitly in quantum molecular calculations. Following this approach, LanL2DZ (a split valence basis) is one of ECP basis sets which consist of double-zeta basis set and effective core potential for calculating valence electrons and inner shell electrons, respectively. This basis was confirmed the accuracy of calculation data comparing with experimental results as well as those from an expensive all electron basis sets.

2.3 The chemical indices

The chemical indices are obtained by density calculation. These indices show the specific properties of a chemical species [46].



2.3.1 Electronic chemical potential

The chemical potential of the DFT [47], which is variational the principle of equation (2.13), is a very small one-electron energy that is smaller than the total electronic energy. It gets into the variational principle of traditional quantum chemistry.

$$\delta\{E[\eta(r)] - \mu[N[n(r)]]\} = 0 \quad (2.13)$$

Where μ is a electronic chemical potential, η is a chemical hardness and N is a electron molecular system.

It has to solve this equation for every μ , then taking the μ value that makes the correct number of electrons for the system of interest. According to the Lagrangian multipliers, μ determines how sensitive the extreme E is to change in N

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{V(\bar{r})} \quad (2.14)$$

Approximate of μ can be computed by the equation (2.15) which ionization potential is IP and electron affinity is EA .

$$\mu \approx -\frac{1}{2}(IP + EA) \quad (2.15)$$



2.3.2 Mulliken electronegativity

The Milliken electronegativity (χ) [46] is a negative of chemical potential in DFT, shown by equation as:

$$\chi = -\mu \quad (2.16)$$

2.3.3 Chemical hardness

The hardness (η) [48-50] can be described of as a resistance to charge transfer. E versus N plot is not straight lines but is generally convex upward. Their curvatures define another property of substantial importance.

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{r(\bar{r})} \quad (2.17)$$

The finite-difference approximation is expressed in equation [67]. It can be written as

$$\eta \approx -\frac{1}{2}(IP - EA) \quad (2.18)$$



2.3.4 Electrophilicity

The electrophilicity (ω) index [51] is used to describe a reliable property of a chemical system and may be used as quantum chemical descriptor. The operational definition is expressed by term of electrophilicity index may be written as

$$\omega = \frac{\mu^2}{2\eta} \quad (2.19)$$

2.3.5 Dipole moment

The asymmetry of a charge distribution is determined by the physical property which is the dipole moment. The dipole moment is shown as the product of the total amount of positive or negative charge and the distance between their centroids. The unit for dipole moments is called a Debye.

2.4 Thermodynamic properties

The basic equations used to describe thermochemical quantities [52] such as enthalpy, free energy and rate of reaction.



2.4.1 Enthalpies and Gibbs free energies of reaction

The different of the sums of heats of formation is taken to calculate the enthalpies of reaction using this equation

$$\Delta_r H^\circ(298K) = \sum_{prod} \Delta_f H^\circ_{prod}(298K) - \sum_{react} \Delta_f H^\circ_{react}(298K) \quad (2.20)$$

However, there is the way to simply take different of the sums of heats of formation for reactant and the products. Gaussian program provides the short cut to calculate the enthalpy of reaction is defined as

$$\Delta_r H^\circ(298K) = \sum_{prod} (\varepsilon_0 + H_{corr}) - \sum_{react} (\varepsilon_0 + H_{corr}) \quad (2.21)$$

where ε_0 for the total electronic energy. H_{corr} is correction to the enthalpy due to internal energy which can be calculated by

$$H_{corr} = E_{tot} + k_B T \quad (2.22)$$

where E_{tot} (total internal energy) is the sum of E_t, E_r, E_v, E_e (internal energy due to translation, rotational, vibrational and electronic motion, respectively).

$$E_{tot} = E_t + E_r + E_v + E_e \quad (2.23)$$



Likewise, Gibbs free energies of reaction can be calculated by the same short cut:

$$\Delta_r G^\circ(298K) = \sum_{prod} (\epsilon_0 + G_{corr}) - \sum_{react} (\epsilon_0 + G_{corr}) \quad (2.24)$$

where the correction to the Gibbs free energy due to internal energy (G_{corr}) can be calculated by

$$G_{corr} = H_{corr} - TS_{tot} \quad (2.25)$$

$$S_{tot} = S_t + S_r + S_v + S_e \quad (2.26)$$

where S_{tot} (total internal entropy) is the sum of S_t, S_r, S_v, S_e (entropy due to translation, rotational, vibrational and electronic motion, respectively).

2.4.2 Rate of reaction

The rate of reaction ($k(T)$) is defined by equation:

$$k(T) = \frac{k_B T}{hc^\ddagger} e^{-\Delta G^\ddagger / RT} \quad (2.27)$$

where k_B is the Boltzmann's constant, h is Plank's constant, T is the absolute temperature, R is the gas constant, $c^\ddagger = 1$ for the concentration.

