CHAPTER 2

Theoretical and Computational Details

Basic concept of computational chemistry starts with the solving of Schrödinger equation (2.1). There are many description to explain the motion of particles. One of the descriptions is the wave function concept in which the wave function (Ψ) for an interested system governed by a Hamiltonian ($\hat{H}$) is determined by Schrödinger equation as given below.

$$\hat{H}\Psi = E\Psi \tag{2.1}$$

Where $\hat{H}$ is the Hamiltonian operator, Ψ is the wave function and E is the total energy. Unfortunately, the Schrödinger equation can be solved exactly for the one electron system. Therefore, the numerical method can be used to approximate the wave function and the theoretical approximations include *ab initio* method, semi empirical method, density functional theory and etc.

The *ab initio* method (means "the method form the beginning" in Latin) is the approximation from Schrödinger equation in order to find an approximate solution without an inclusion of experimental data. The well-known type of *ab initio* calculation is Hartree-Fock (HF) approximation. There are several ways in which we can proceed with the derivation of HF equations (2.2).

$$\hat{h}^F\Psi_I = \varepsilon_I \Psi_I \tag{2.2}$$

Where the HF operator $\hat{h}^F$ depends only on the coordinates of any electron, but allows for the averaging over their interactions. [91, 92]

2.1 Density Functional Theory [93, 94]

Density Functional Theory (DFT) is one of the most popular and successful quantum mechanics approaches to apply in many research topics. The basic for DFT is the very useful proof by Hohenberg and Kohn that the ground state electronic energy is determined completely by the electron density. The result of the proof has resulted in a much less variables needed in the computation compared to directly solving the Schrodinger equation as shown in Figure 2.1.
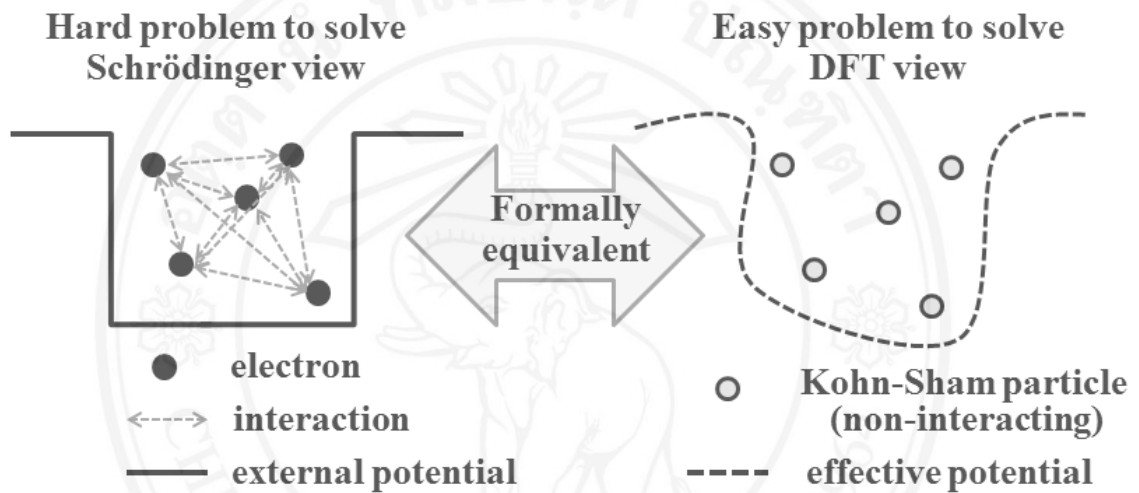

Figure 2.1 Basic concept for the Density Functional Theory.

2.1.1 The Hohenberg-Kohn theorem

Solving the problem using the single electron wave function, this method uses one of functions which represents the entire electron density of the molecule represented as $\rho(r)$. Electronic energy of electron density is represented as

$$E(\rho) = E_T[\rho] + E_V[\rho] + E_U[\rho] \tag{2.3}$$

where $E_T[\rho]$ is the kinetic energy, $E_V[\rho]$ is the potential energy, $E_U[\rho]$ is the external perturbation and Coulomb repulsive force between pairs of electrons.

2.1.2 Kohn-Sham Equations

A density functional is used to obtain the energy for the electron density. The advantage of using electron density is that integrals for Coulombic repulsion need to be done only over the electron density which is a three-dimensional function. The exact ground-state electron density is given by

$$\rho(r) = \sum_{i=1}^{n}|\Psi_i(r)|^2 \tag{2.4}$$

The electronic energy can be written in a simple form as

$$E(\rho) = E_T[\rho] + E_V[\rho] + E_{XC}[\rho] \tag{2.5}$$

where the sum is overall energy of the occupied Kohn-Sham orbitals. $E_T[\rho]$ represents the kinetic energy of the electron, $E_V[\rho]$ is the potential energy including electron-nucleus attraction and coulomb repulsive interaction between electros and $E_{XC}[\rho]$ is the exchange-correlation term that is often split into two parts. The first part is for exchange effects and the second part is for correlation effects, in which both parts must be the functional of the electron density.

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho] \tag{2.6}$$

Therefore, exchange-correlation potential, V_{XC} can be presented as the functional derivatives of the exchange-correlation energy:

$$V_{XC}[\rho] = \frac{\delta E_{XC}[\rho]}{\delta_p} \tag{2.7}$$

2.1.3 Hybrid Functional

B3LYP [95-98]

B3LYP is a hybrid functional, which includes the combination of Becke's parameter exchange correlation functional mixing (B3) in the exact HF exchange correlation. LYP is the Lee Yang and Parr correlation functional that recovers dynamic electron correlation. The introduction of the B3LYP hybrid exchange correlation

functional was a turning point for DFT. The B3LYP functional can be described as follow;

$$E_{XC}^{B3LYP} = E_X^{LDA} + a_0 \left(E_X^{HF} - E_X^{LDA}\right) + a_X(E_X^{GGA} - E_X^{LDA}) + E_C^{LDA} + \tag{2.8}$$
$$a_C(E_C^{GGA} - E_C^{LDA})$$

When $a_0 = 0.20$, $a_X = 0.72$, $a_C = 0.81$

PBE0 [99]

PBE0 is sort of similar functional to B3LYP except that it does not contain any empirically fitted parameters and has 25% HF exchange (vs 20% for B3LYP). Kieron Burke (the B of PBE) claims that it is popular in the physics community because it has no empirically fitted parameters (and is thus more *"ab-initio"*).

$$E_{XC}^{PBE0} = \frac{1}{4} E_X^{HF} + \frac{3}{4} E_X^{PBE} + E_C^{PBE} \tag{2.9}$$

M06 and M06-2X [100]

M06 is a hybrid functional which combines parameter of transition metal and non-metal. While, M06-2X is high-nonlocality functional which using the parameter od non-metal only. M06 and M06-2X functional are represented as follows;

$$E_X^{M06} = \sum_\sigma \int dr \left[F_{X\sigma}^{PBE}(\rho_\sigma, \nabla_{\rho\sigma}) f(W_\sigma) + \varepsilon_{X\sigma}^{LSDA} h_X(X_\sigma, Z_\sigma) \right] \tag{2.10}$$

When $X_\sigma = \dfrac{|\nabla_{\rho\sigma}|}{\rho_\sigma^{4/3}}$ $\quad \sigma = \alpha, \beta$ $\tag{2.10.1}$

$$\tau_\sigma = \frac{1}{2} \sum_i^{occup} |\nabla \Psi_{i\sigma}|^2 \tag{2.10.2}$$

$$Z_\sigma = \frac{\tau_\sigma}{\rho_\sigma^{5/3}} - C_F \quad, C_F = \frac{3}{5}(6\pi^2)^{2/3} \tag{2.10.3}$$

$$\gamma(X_\sigma, Z_\sigma) = 1 + \alpha(X_\sigma^2 + Z_\sigma) \tag{2.10.4}$$

$$h(X_\sigma, Z_\sigma) = \left(\frac{d_0}{\gamma(X_\sigma, Z_\sigma)} + \frac{d_1 X_\sigma^2 + d_2 Z_\sigma}{\gamma_\sigma^2(X_\sigma, Z_\sigma)} + \frac{d_3 X_\sigma^4 + d_4 X_\sigma^2 Z_\sigma + d_5 X_\sigma^2}{\gamma_\sigma^3(X_\sigma, Z_\sigma)} \right) \tag{2.10.5}$$

$$\varepsilon_{X\sigma}^{LSDA} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\rho\sigma^{4/3} \tag{2.10.6}$$

$$f(w_\sigma) = \sum_{i=0}^{m} a_i w_\sigma^i \tag{2.10.7}$$

$$w_\sigma = (t_\sigma - 1)/(t_\sigma + 1) \tag{2.10.8}$$

$$t_\sigma = \tau_\sigma^{LSDA}/\tau_\sigma \tag{2.10.9}$$

$$\tau_\sigma^{LSDA} \equiv \frac{3}{10}(6\pi^2)^{2/3}\rho\sigma^{5/3} \tag{2.10.10}$$

2.1.4 Long-Range Corrected Hybrid Functionals

The long range corrected functionals are a non-coulomb part of exchange functionals which typically dies off too rapidly and becomes very inaccurate at large distances, making them unsuitable for modeling processes such as electron excitations to high orbitals.

ωB97XD [101]

This functional is proposed by Head-Gordon and coworkers, which includes empirical dispersion. These functionals also include long range corrections.

CAM-B3LYP [102, 103]

CAM-B3LYP is the mix functional between B3LYP and long-range correction, which is represented in equation 2.11.

$$E_{XC}^{CAM-B3LYP} = E_X^{LR} + E_X^{SR} \text{ [Becke88]} + 0.81E_c^{LYP} + 0.19E_c^{VWN} \tag{2.11}$$

LC-BLYP [104]

Prefixed LC- may be added to any pure functional to apply the long-range correction of Hirao and coworkers. The general form of the long-range corrected functional is given as;

$$E_{XC}^{LC-DFT} = E_C^{DFT} + (1 - C_{HF})E_X^{SR-DFT} + C_{HF}E_X^{SR-HF} + E_X^{LR-HF} \tag{2.12}$$

2.1.5 Basis Set [105]

A basis set is a set of functions used to approximate the exact wave functions and create the molecular orbitals, which are expanded as a linear combination with coefficients to be determined. The equation 2.13 shows the general form of basis set of Gaussian type functions.

$$g_p(\alpha, r) = Cx^n y^m z^l e^{-\alpha r^2} \tag{2.13}$$

The radial dependence is modulated by the exponent (α) and r is the electronic position vector with coordinates (x, y, z). In this work, we use the 6-311G(d,p) for all calculations and the detailed basis function is given in Table 2.1.

Table 2.1 Spitting scheme of 6-311G(d,p) basis set.

Atomic number	1-2		3-10	
Basis functions	Basis functions	Constructed of	Basis functions	Constructed of
	1s	3 gaussians	1s	6 gaussians
	1s′	1 gaussians	2s, 2p$_x$, 2p$_y$, 2p$_z$	3 gaussians
	1s″	1 gaussians	2s′, 2p$_x$′, 2p$_y$′, 2p$_z$′	1 gaussians
	2p$_x$, 2p$_y$, 2p$_z$	1 gaussians	2s″, 2p$_x$″, 2p$_y$″, 2p$_z$″	1 gaussians
			3d$_{xx}$, 3d$_{yy}$, 3d$_{zz}$, 3d$_{xy}$, 3d$_{xz}$, 3d$_{yz}$	1 gaussians
Total number	6	8	19	32

Therefore, the full wavefunctions were approximated by 6 independent Gaussian functions for core electrons, and 3+1+1 Gaussian functions for valence electron. One additional Gaussian function beyond the valence was also added for a more accurate approximation. This approximation is sufficient and accurate enough for predicting the investigated molecules in this research, where the valence electrons of the studied molecules are only in s and p orbitals.

2.2 Time-Dependent Density Functional Theory [106]

Time-dependent density functional theory (TD-DFT) is the postulate of stationary DFT into time-dependent potential and electron densities. For example, in the case of photo absorption spectra for fixed nuclei, the electric field constitutes a small perturbation that can be treated using linear response theory. TDDFT is a very popular tool for electronic excitation energies and oscillator strength. It is a powerful tool in studying photochemistry because its computation cost is not expensive and it gives reasonable accuracy of calculated results compared with experimental data. The excited-state electron density is given by Runge-Gross theorem as

$$\rho(r,t) = \sum_{i=1}^{n} |\Psi_i(r,t)|^2 \tag{2.14}$$

As mentioned before, the exchange-correlation potential, V_{XC} can be presented as the functional derivatives of the exchange-correlation energy:

$$V_{XC}[\rho] = \frac{\delta A_{XC}[\rho]}{\delta_p}\bigg|_{\rho=\rho(r,t)} \tag{2.15}$$

From excitation energy, the procedure starts with the construction of many particles with good symmetry, Ψ_i, by taking a finite superposition of states

$$\Psi_i = \sum_{\alpha} c_{i\alpha}\Phi_\alpha \tag{2.16}$$

Where Φ_α is the Slater determination of Kohn-Sham orbitals, and the coefficients $c_{i\alpha}$ can be determined from group theory. Simply, we can express the determinants as linear combinations of the many body wave functions.

$$\Phi_\beta = \sum_j a_{\beta j}\Psi_j \tag{2.17}$$

By taking the expectation value of the Hamiltonian in the state Φ_β we reach here

$$\langle\Phi_a|\hat{H}|\Phi_\beta\rangle = \sum_j |a_{\beta j}|^2 E_j \tag{2.18}$$

Where E_j is the energy of the many body state Ψ_j and Φ_β is built from n Kohn-Sham orbitals.

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2.3 Molecular Orbitals of Benzene Derivatives [107, 108]

Molecular orbital (MO) of benzene provides a more satisfying and more general treatment of aromaticity of benzene. In addition, MO can describe π-bonding in organic molecules (Figure 2.2 (a) displays the MO of benzene). Benzene ring has a planar hexagonal structure in which all carbon atoms are sp^2 hybridization and all the carbon-carbon bonds are equal in length. While, the effect of heteroatom on benzene ring such as the nitrogen heteroatom on pyridine is shown in Figure 2.2(b). The hybridization of nitrogen atom is sp^2 hybridization whereas two of the three sp^2 orbitals form sigma overlaps with the sp^2 orbitals of neighboring carbon atoms and the third nitrogen sp^2 orbital contains the lone pair. While, the unhybridized p orbital contains a single electron, which is part of the 6 π-electron system delocalized around the pyridine ring. From the previous study, the lone pair electrons of nitrogen affect the delocalization of π-electron. They stabilize the HOMO or LUMO energy levels because of the lone pair of electron in the substituted hetero nitrogen is involved in π-conjugation which might help lower the HOMO-LUMO energy gap [57-59].

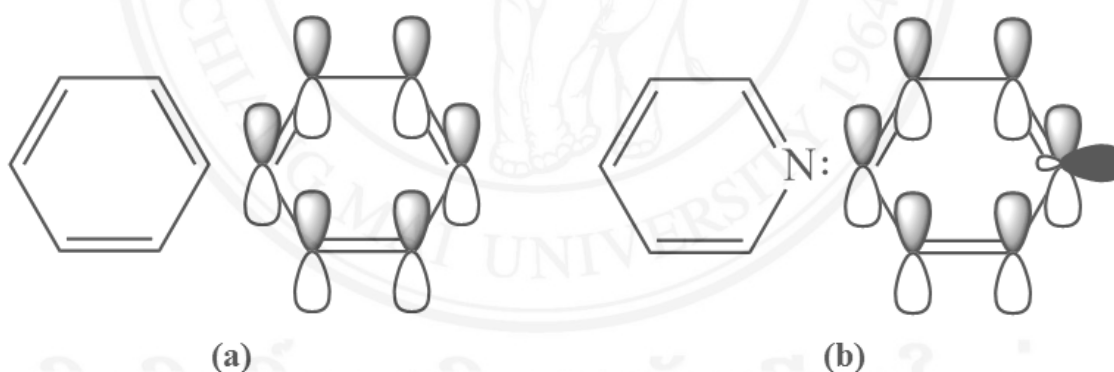(a)   (b)

Figure 2.2 The molecular orbital of Benzene (a) and Pyridine (b).

In summary, the effect of heteratom on aromaticity of benzene can disrupt the delocalization of π-electron of the aromatic compounds, and thus effect in the photophysical and photochemical properties.