CHAPTER 2

Theoretical and computational detail

2.1 Theoretical background of computational chemistry

Computational chemistry has been immediately developed over the last 50 years, and has vividly changed the way of research. One of the first ways in 1998, Sir John Anthony Pople recognized the importance of turning a computer program into an everyday tool that bench chemists can use to complement their experimental work. After that, he was a Nobel Prize winning theoretical chemist, and was awarded the Nobel Prize in Chemistry with Walter Kohn in the year 1998. The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry". And recently, Martin Karplus, Michael Levitt, and Arieh Warshel won the 2013 Nobel Prize in Chemistry for work that they did in the 1970s. They successfully developed methods that combined quantum and classical mechanics to calculate the courses of chemical reactions using computers.

Computational chemistry is one of the branches of chemistry concerning with high performance computing in theoretical studies. The results of the calculation can help develop and find new materials, which reducing laboratory costs. The computational chemistry covers the topics of cheminformatics, molecular mechanics, statistical mechanics, *ab initio* quantum chemistry, and semi-empirical methods.

2.1.1 Quantum mechanics

In the 20th century, quantum mechanics (QM) and relativity are the most significant class in science. They are used in a variety of many fields such as physics, chemistry, biochemistry, medicinal chemistry, and material of science. In chemistry, the Schrödinger equation is the fundamental principle in quantum mechanics [52]. The QM is an expansion of the electrons behavior by corrected mathematical formula. The QM principle can predict the property of an individual atom or a molecule. The solution of QM has been solved for single electron systems only [53].

2.1.2 Schrödinger equation

The Schrödinger equation is an equation that is fundamental to quantum mechanics. It is also based on the physical situation. The common forms are the time-dependent and time-independent Schrödinger equation, which give a description of a system evolving with time and without time, respectively. Here, we will present only the time-independent Schrödinger equation. The time-independent Schrödinger equation is

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

where H is the Hamiltonian operator, the wavefunction or eigenfunction in term of mathematics is ψ, and E is the energy or eigenvalue. The H operator is a matrix and the eigenfunction can be a vector, but this is not always the case. The ψ is a function of electron and nuclear positions, this is the description of an electron as a wave. The wavefunction obtains the electron part of the Schrödinger equation for fixed nuclear coordinates.

The H is separated into the kinetic energy (T) operator and the potential energy (V) operator as shown in equation (2.2). A stationary key of the Schrödinger equation corresponds to a constant energy. In this case, it is the quantum mechanical equivalent of the energy conservation law.

$$H = T + V \tag{2.2}$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z) \tag{2.3}$$

$$H = -\sum_{i}\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{\left|r_i - R_I\right|} + \frac{1}{2}\sum_{\substack{i,j \\ (i\neq j)}}\frac{e^2}{\left|r_i - r_j\right|} - \sum_{I}\frac{\hbar^2}{2M}\nabla_I^2 + \frac{1}{2}\sum_{\substack{I,J \\ (I\neq J)}}\frac{Z_I Z_J e^2}{\left|R_I - R_J\right|} \tag{2.4}$$

The many electron H operator that manages the behavior of an interacting of electrons and nuclei in atomic units are shown in equation (2.4) where the overall value of i and j is represented to electrons, and the overall value of I and J is represented to nuclei. The T terms is the spatial differential operator or ∇ where the I nuclei, with atomic number Z_i, has a mass ratio of MI to that of an electron. The three-dimensional vector positions of the i electron and I nuclei are implied to r_i and R_I, respectively [53].

2.1.3 Born-Oppenheimer approximation

To elucidate both nuclei and electrons of atom. An observation in employing quantum mechanics to atoms is that proton or neutron in nuclei has more than 1800 times the mass of an electron [54]. So, that means the nuclei respond slower to changes than electrons which is represented by the equations (2.5) that describes the movement of electron. The ground state of the electrons is known as the lowest energy state and the separation of the nuclei and electrons splits into the mathematical problems. This is called Born-Oppenheimer approximation.

$$H = -\sum_{i} \frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{\left|r_i - R_I\right|} + \frac{1}{2}\sum_{\substack{i,j \\ (i\neq j)}} \frac{e^2}{\left|r_i - r_j\right|} \tag{2.5}$$

Here, the kinetic energy of the electrons shows at the first term of eq. (2.5). The second term is the attraction of electrons to nuclei, and the last term is the repulsion of electrons. The repulsion energy of nuclei is added at the end of the calculation. The potential energy term describes the movement of nuclei [53].

2.1.4 *Ab initio* calculations

The term *ab initio* (from Latin “from first principle”) was first used in quantum chemistry. This method solves the Schrödinger equation for a molecule and gives us the molecule’s energy and wavefunction. The wavefunction is a mathematical function that can be used to calculate the electron distribution. The *ab initio* calculations can describe chemical phenomena such as geometry prediction, electronic structure, and molecular properties.

2.1.4.1 Hartree-Fock Approximation

The Hartree-Fock (HF) approximation is the simple kind of *ab initio* calculation [55]. The HF approximation is exact only for a one electron system. The HF problem occurs from the true data for any atoms or molecules with more than one electron, so the Schrödinger equation (2.1) cannot describe such system with many electrons because of the term of repulsion between electrons. The HF ground state energy (E_{HF}) will be an upper bound to the exact ground state energy (E_{exact}).

$$E_{corr} = E_{exact} - E_{HF} \tag{2.6}$$

The correlation energy (E_{corr}) is the difference between the exact energy and HF approximation energy. This energy is often large enough to be discarded. To calculate $E_{corr,}$ it needs to use what is known as post-Hartree-Fock approximation.

2.1.4.2 Post Hartree-Fock Approximation

For the high level of electron correlation occurring from repulsion of electron, the method is called post HF approximation. Post-HF methods are the set of methods developed to improve on the HF or self-consistent field (SCF) method. The term of electron correlation is added to improve the accuracy by including the electron-electron repulsions which is different from the HF method. Normally, the post-HF methods give more accurate calculation results than HF method, but time and computational cost are also higher. The higher-level methods including the electron correlation are for examples Configuration interaction (CI), Møller–Plesset (MP) perturbation theory, Coupled cluster (CC), Quantum Montecarlo (QMC), *etc*.

2.1.5 Density function theory

In many electron systems, it is unworkable to solve the Schrödinger equation. Clearly, we must use some approximations to solve the equation. Here, the density functional theory (DFT), it has simplest definition. A DFT theory obtains an approximate solution to the Schrödinger equation of a many electron systems.

To date, DFT is one of the most popular and successful quantum mechanical approaches. The DFT theory is based on probability of electron or electron density function ($\rho(x,y,z)$) in ground state [55], which is used to describe physical properties and electronic properties of atoms and molecules as well as simple crystals in both gas and liquid phase. Moreover, the DFT has become a first-principles calculation to describe or predict the properties of molecules systems.

2.1.5.1 Hohenberg-Kohn theorems

Hohenberg-Kohn theorem is the heart of DFT theory. Firstly, Hohenberg-Kohn theorem applies the ground state density to determine the external potential energy, the Hamiltonian (H) and the wavefunction (ψ). Generally, it has a system of electrons moving in an external field $v(r)$ generated by the nuclei. The external field, $v(r)$ is a unique functional of the electron density. In addition, since $v(r)$ assigns the H, the full many-particle in ground state, the wavefunction ($\psi\,(r_1,\ldots,r_N)$) is a unique functional of $\rho(r)$. The integral of the exact ground state density is related to the number of n electrons. Secondly, Hohenberg-Kohn theorem is an important and variational principle for the electron density in ground state. The correct ground state density minimizes the total energy. Therefore, the Hohenberg-Kohn theorems prove the existence of an energy functional $E(\rho)$.

$$E[n(r)] = \int v(r)n(r)dr + \frac{1}{2}\int\int \frac{n(r)n(r')}{|r-r'|}drdr' + G[n(r)]$$ ((7.2

Where the first term $v(r)$ is the potential of nuclear charges, next term is the electrons-electrons repulsion, and the last term $G[n(r)] = -\frac{1}{2}\sum_i \nabla_i^2$ is the kinetic energy of the electrons.

$$H = -\frac{1}{2}\sum_i \nabla_i^2 + \int v(r)n(r)dr + \frac{1}{2}\int\int \frac{n(r)n(r')}{|r-r'|}drdr'$$ ((8.2

2.1.5.2 Kohn-Sham equation

The Kohn-Sham approach to the electrons-electrons interacting is to modify the Hohenberg-Kohn theorem for the energy functional corresponding to the ground state. The term of exchange-correlation (xc) potential interprets the difference between the interacting and non-interacting between electron-electron systems. So, the electronic energy in the ground state is obtained by

$$E_{KS} = E_T + E_v + E_{coulomb} + E_{xc} \tag{2.9}$$

where E_T represents the kinetic energy, E_v represents the energy of electron and nuclei interaction, $E_{coulomb}$ indicates the Coulomb self-interaction, and E_{xc} indicates the term of exchange-correlation energy.

2.1.5.3 Hybrid three parameters of Beck and Lee-Yang-Parr correlation functional (B3LYP)

Hybrid functional is one kind of approximations to the exchange-correlation DFT, which amalgamates a section of exchange from HF method with exchange-correlation from *ab initio* or empirical sources. The exchange energy functional is exhibited in the Kohn-Sham equation, thus the exact exchange energy functional is a certain density functional. The most popular approximation is Becke-3-LYP or B3LYP method. The B3LYP which means Becke, 3-parameter, Lee-Yang Parr is well-known because it provides the best results on predicting some important properties of the organic molecules compared to experimental data. The hybrid model of B3LYP is expressed in equation 2.9:

$$\begin{aligned} E_{XC} = {} & 0.2 * E_X(HF) + 0.8 * E_X(LSDA) + 0.72 * DE_X(B88) \\ & + 0.81 * E_C(LYP) + 0.19 * E_C(VWN) \end{aligned} \tag{2.10}$$

2.1.5.4 Basis set

The atomic orbitals or AOs depend on a set of functions which are combined in linear combinations, so for computational chemistry they are called basis set. Basis functions can be mathematic functional. Three types of basis functions are used in the scientific method. Slater-type functions (STFs) [52] was the first basis function. The STFs was efficient in representing the AOs in one electron system only. After that in 1950, Boys [56] used Gaussian-type functions (GTFs), whose exponent term is difference from the STFs function. The GTFs function is less accurate compared with the STFs function when the equal number of functions are used in linear least-squares fittings. The third basis function is plane wavefunctions, this basis function does not depend on the positions of nuclei. A minimal basis set is the simplest type of basis set, which would include one function for 1s-orbital such as H and He atoms. When used a higher basis set, the result will be more accurate. Consequently, the development of minimal basis set replaced by two basis functions for each AOs (double-zeta or DZ basis set) and three basis functions for each AOs (triple-zeta or TZ basis set) was introduced. A split-valence basis set (SV basis set) changes the size and shape of atomic orbitals of molecules. This basis set can give inner-shell atomic orbital and valence atomic orbital by one and two basis functions, respectively [1].

2.1.6 Time-dependent density functional theory

Time-dependent density functional theory or TD-DFT is the augmentation of stationary DFT and electronic density ($\rho(r,t)$). TD-DFT uses the quantum mechanical to explore the properties and dynamics of many electron systems. Moreover, this theory calculates the photon of absorption spectra for fixed nuclei or recurrence subordinate reaction properties. TD-DFT theory is a famous tool for studying about electronic excitation energies and oscillator strength. It is a powerful tool in studying photochemistry. The time-dependent Kohn-Sham equation in TD-DFT is

$$\rho(r,t) = \sum_{i=1}^{N} \left|\psi_i(r,t)\right|^2 \tag{2.11}$$

2.1.7 Dynamics simulation

Dynamics simulations are concerned with the time-dependent behavior of a system. In this way, chemical processes can be directly observed and more information is gained then just by considering the stationary points or other cuts out of the potential energy surface. In principle, the time-dependent Schrödinger equation (2.25) has to be solved.

$$H(\psi(R,r,t)) = i\hbar\frac{\partial}{\partial t}\psi(R,r,t) \tag{2.12}$$

2.1.7.1 Initial condition

For assembling the Newton's conditions for the nuclei, it needs to arrange the initial conditions [57]. Normally, the problem of initial conditions represents a classical phase space as the initially excited quantum wave packet is approached by building a phase space distribution in ground state and then projecting it in the excited-states. The ground state trajectory simulation or from a probabilistic sampling is used to arrange the ground state distribution. In addition, the quantum nature of typical distributions is given by the Wigner function.

2.1.7.2 Wigner distributions

Wigner distribution is used to approximate the classical phase space distribution. Assuming a quadratic approximation for the ground state potential energy surface around the minimum, the 3N−6 internal coordinates can be described in terms of normal modes Q and the nuclear wave function can be approximated as that of a quantum harmonic oscillator [57].

$$P_w(Q^i, P^i) = (\pi\hbar)^{-1}\int d\eta\, \chi_{HO}^0(Q^i+\eta)^*\, \chi_{HO}^0(Q^i-\eta)\, e^{2i\eta P^i/\hbar}, \tag{2.13}$$

where the term of χ_{HO}^0 is the wave function quantum harmonic oscillator for ground state and term of P^i is the momentum associated with the Q^i (Q^i is normal coordinate).

$$P_w(Q^i, P^i) = (\pi\hbar)^{-1}\exp(-\mu^i\omega_{HO}^i Q/\hbar)\exp(-P^{i2}/(\mu^i\omega_{HO}^i\hbar)), \tag{2.14}$$

where the term of μ^i and ω_{HO}^i are the reduced mass, and the harmonic frequency and the equilibrium distance of i normal mode, respectively.

To sample coordinates and momentum, independent random values are assigned to P^i and Q^i, then, the acceptance of the pair is evaluated according to the probability given by equation (2.13). To solve the problem, the equation (2.12) can be written in equation. (2.14).

If equation (2.12) is evaluated for a vibrationally excited level χ^{n}_{HO} instead for the ground vibrational state, the Wigner function can assume negative values and cannot be used as a distribution. To solve this problem, note that equation (2.13) can be written as

$$P_{W}(Q^{i}, P^{i}) = \left|\chi^{0}_{HO}(Q^{i})\right|^{2} \left|\xi^{0}_{HO}(P^{i})\right|^{2} \tag{2.15}$$

where ξ^{0}_{HO} is the representation of harmonic oscillator wave function in the momentum. Even though equation (2.14) is usable for the ground vibrational level, it activates to compose a quasi-Wigner distribution for the excited vibrational states.

$$P_{QW}(Q^{i}, P^{i}) = \left|\chi^{n}_{HO}(Q^{i})\right|^{2} \left|\xi^{n}_{HO}(P^{i})\right|^{2} \tag{2.16}$$

2.1.7.3 Sampling with Trajectory Simulations

From equation (2.15) is a sampling of initial conditions. For the random sampling, this method should play out a classical ground state trajectory reproduction and selection is focused from it to start the excited-state dynamics [57]. The main process to create the initial conditions for large systems using a normal mode analysis is not possible. One problem with this process is that it takes a long time to find sampling of the phase space. Furthermore, the energy distribution of the degrees of freedom also be regarded. Therefore, using Wigner distribution as the sampling of trajectory simulations is more appropriate and practical.

2.2 Computational detail in this study

2.2.1 Static calculations

Geometry optimizations of HBQ and its derivatives; (1a) HBQ, (1b) 9-Hydroxy-3H-benzo[*g*]indole (HBID), (1c) 5H-indeno[1,2-*b*]pyridine-9-ol (IPDO), (1d) 3,4-dihydro indene[1,2-*b*]pyrrole-8-ol (IPRO), (1e) 2-(Pyridin-2-yl)phenol (PDP), and (1f) 2-(4H-pyrrol-2-yl)phenol (PRP), as depicted in Figure 1 were performed using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) descriptions for the electronic structures for ground state (S_0) and the first excited-state (S_1), respectively. Becke's three-parameter hybrid exchange functional with Lee-Yang-

Parr gradient-corrected correlation (B3LYP functional) was used in both the DFT and TD-DFT calculations [58-62]. The triple-ζ valence quality with one set of polarization functions (TZVP) [61] was chosen as the basis set for all atom types, which is an appropriate basis set for all systems. Bond lengths, angles or dihedral angles were not constrained during the geometry optimization calculations. All the local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations. The simulated infrared (IR) spectra of all compounds both in the S_0 and S_1 states were computed. In addition, the simulated absorption and emission spectra were calculated using optimized structures from the S_0 and S_1 states, respectively. For the S_0 and S_1 states potential energy curves, PT coordinates of all compounds were scanned by constrained optimizations in their corresponding electronic state fixing the O–H bond distance at a series of values. All calculations were performed using the Gaussian 09 program suite [63].

2.2.2 Dynamics simulations

Classical dynamics simulations were performed for HBQ and its derivatives on the S1 energy surface. The Velocity-Verlet algorithm [64] was applied to solve the Newton's equations of nuclear motion. The Born–Oppenheimer energies and gradients were obtained by means of the TD-DFT (B3LYP) approach, which has been employed in previous studies [47, 65, 66]. The twenty-five trajectories as a representative set for each system were simulated at TD-DFT/B3LYP/TZVP level with a time step of 1 fs with maximal duration of 300 fs, enough to cover the pre- and post-PT regimes. The initial conditions for each trajectory were generated by sampling the coordinates and momenta so as to reproduce the ground-vibrational quantum harmonic distribution of the electronic ground state by means of a Wigner distribution. The classical dynamic simulations were performed in NEWTON-X interfaced [67, 68] with Turbomole 6.3 program package . As results in classical dynamic simulation details such as average breaking and forming bonds showing time evolutions, energy difference of S_1 and S_0 states (S_1-S_0), and average C1C2C3N torsion angles between phenyl and pyridinic nitrogen groups were described by statistical analysis.