CHAPTER 2

Theory and computational details

2.1 Theoretical background of computational chemistry

Computational theoretical chemistry focuses on the numerical computation of electronic structures and molecular interaction, in which the formulation of analytical expressions for the properties of molecules and their reactions are given in the mathematic equation. Computational chemistry is often referred to when chemists use a quantum calculation software to theoretically investigate their systems of interest through solving the equations that contain important information.

Computational chemistry is employed in all divisions of chemistry particularly in physical chemistry, organic chemistry, and inorganic chemistry. All chemists want to understand all properties of their interested systems in molecular level. Particularly, they are interested in molecular design of new materials using computational chemistry tools which is an effective method prior to actual synthesis. Computational tools such as quantum chemistry software can help chemist reduce the number of trial and error of synthesis of molecules that they design. Moreover, computational chemistry tools can help in understanding their designed materials when some important information cannot be obtained directly from experimental method. There are some properties of a molecule that can be obtained computationally more easily than by experimental means. The tools can provide more insights into molecular level in terms of chemical bonding between elements in the composition of synthesized molecules. With these advantages of using computational chemistry tool, thus now, experimental chemists have been using computational tools to gain additional understanding of the compounds being examined in the laboratory.

2.1.1 Schrödinger equation

Schrödinger equation is the basic equation of quantum chemistry [42] that can contain information of a given system in term wave function. The ultimate target of the most quantum chemical methods is to solve solution of the time-independent and non-interaction Schrödinger equation given in equation 2.1 by the approximate approaches

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

where Ψ is the many-electron wave function and $\hat{\mathrm{H}}$ is the Hamilton operator for a molecular system including electrons and nuclei in the lack of magnetic or electric fields. Generally, Schrödinger equation with the detailed Hamiltonian is expressed as;

$$(T_n + T_e + V_{en} + V_{ee} + V_{nn})\Psi = E\Psi \tag{2.2}$$

T_n: kinetic energy of nuclei

T_e: kinetic energy of electron

V_{en}: electron-nuclei interaction Coulomb potential

V_{nn}: repulsive Coulomb potential of nuclear-nuclei

V_{ee}: repulsive Coulomb potential of electron-electron

in which $\hat{\mathrm{H}}$ is a differential operator playing the total energy:

$$\hat{\mathrm{H}} = -\sum_{\mathrm{A}}^{\mathrm{nucclei}} \frac{\hbar^2}{2\mathrm{M_A}}\nabla_{\mathrm{A}}^2 - \frac{\hbar^2}{2m}\sum_{\mathrm{i}}^{\mathrm{electrons}} \nabla_i^2 - \sum_{\mathrm{i}}^{\mathrm{electrons}}\sum_{\mathrm{A}}^{\mathrm{nuclei}} \frac{\mathrm{Z_A}e^2}{4\pi\varepsilon_0 \mathrm{r_{iA}}} + \sum\sum_{\mathrm{i>j}}^{\mathrm{electrons}} \frac{e^2}{4\pi\varepsilon_0 \mathrm{r_{ij}}} + \sum\sum_{\mathrm{A<B}}^{\mathrm{nuclei}} \frac{\mathrm{Z_A Z_B}e^2}{\mathrm{R_{AB}}} \tag{2.3}$$

Here, Z is defined as nuclei charge, $\mathrm{M_A}$ is the mass of nucleus A, *m* is the mass of the electron, $\mathrm{R_{AB}}$ is the distance between nuclei A and B, $\mathrm{r_{ij}}$ is the distance between electrons *i* and *j* and $\mathrm{r_{iA}}$ is the distance between electron *i* and nucleus A, ε_0 is the permittivity of free space and ħ is the Plank constant.

The many-electron Schrödinger equation cannot be solved exactly even for a simple two-electron system example of hydrogen molecule (H_2) or helium atom (He). Approximations as practical methods are necessary to be used to solve for wave function and energy of a given system.

2.1.2 Born-Oppenheimer approximation

To make the Schrödinger equation easy for molecular systems one must suppose that fixed the nuclei does not move. Absolutely, nuclei can be moved, but their movement is slower than electrons whose speed is equal to speed of light. So, this estimation is called the Born-Oppenheimer approximation (BOA). Because of nucleus-nucleus repulsion is just a constant, therefore, it is feasible to get solution from the exact Hamiltonian provided in equation 2.3 which can be reduced to electronic Hamiltonian [42, 43].

$$\hat{H}_{el}\Psi_{el} = E_{el}\Psi_{el} \tag{2.4}$$

$$\hat{H}_{\mathrm{el}} = T_e + V_{Ne} + V_{ee} \tag{2.5}$$

$$\hat{H}_{\mathrm{el}} = -\frac{\hbar^2}{2m}\sum_{\mathrm{i}}^{\mathrm{electrons}} \nabla_i^2 - \sum_{\mathrm{i}}^{\mathrm{electrons}}\sum_{\mathrm{A}}^{\mathrm{nuclei}} \frac{Z_{\mathrm{A}}e^2}{4\pi\varepsilon_0 r_{\mathrm{iA}}} + \sum\sum_{\mathrm{i>j}}^{\mathrm{electrons}} \frac{e^2}{4\pi\varepsilon_0 r_{\mathrm{ij}}} \tag{2.6}$$

$$\mathrm{E} = \mathrm{E}^{\mathrm{el}} + \sum\sum_{\mathrm{A>B}}^{\mathrm{nuclei}} \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{R_{\mathrm{AB}}} \tag{2.7}$$

From formula above, it can be clearly seen that the last term of equation 2.3 which explains the nuclear kinetic energy is absent and the repulsive Coulomb potential of nuclear-nuclear is a constant providing equation 2.6. The approximate solution into Schrödinger equation can be obtained by using the BOA. In the BOA formula, nuclei mass term does not appear in the electronic Schrödinger equation. Therefore, the extent of the BOA is usable for one electron system but not for all case.

2.1.3 *Ab initio* method

The *ab initio* is Latin word for "from the beginning". This name is given to computations that are proposed directly from theoretical principles. This method can predict molecular structure and properties of molecules and their reaction types either exothermic or endothermic can be predicted as well. *Ab initio* is beginning from Schrödinger equation supported by properly approximated theory. This process can evaluate more than one-electron system.

1) Hatree-Fock approximation

Hatree-Fock (HF) method uses the variational method to solve the solution of the electronic Schrödinger equation. The first assumption is that the movements of electrons are independent from each other. Therefore, each electron is constrained to a function called molecular orbitals in which each of them moves in the average field of other electrons. The correct wave function can be written using a Slater determinant to ensure the anti-symmetry characteristic as shown below.

$$\Psi = \frac{1}{\sqrt{N!}}\begin{bmatrix} \chi_{1(1)} & \chi_{2(1)} & \cdots & \chi_{n(1)} \\ \chi_{1(2)} & \chi_{2(2)} & \cdots & \chi_{n(2)} \\ \vdots & \vdots & \vdots & \vdots \\ \chi_{1(N)} & \chi_{2(n)} & \cdots & \chi_{n(N)} \end{bmatrix} \tag{2.7}$$

Where, χ_i is the product of spatial and spin wave functions in which a spin function can be either α or β but the way to put a spin up or down must follow the Pauli principle. The wave function with lowest energy can be solved with a self-consistent field or SCF process. This SCF is normally called HF method that includes density functional methods. The SCF provides the wave function as follow which is called Fock operator:

$$f(i)\chi(x_i) = \varepsilon\chi(x_i) \tag{2.8}$$

Here, the Fock operator f(i) can be written in a shorter form as:

$$f(i) = -\frac{1}{2}\nabla_i^2 + \upsilon^{eff}(i) \tag{2.9}$$

x_i are the coordinates of the electron i both spatial and spin, χ are the spin orbitals and υ^{eff} is the effective potential of each electron i in the field of other electrons. Normally, this effective potential is dependent on SCF procedure.

2) Post HF approximation

Because HF method has a serious problem in term ignoring the electron correlation. There are improved methods that account the electron correlation by using the HF as the starting equation and expand the wave function and the Hamilton. These methods are called post HF. By taking correlation between electrons into account the wave function and the energy of a considered system can be improved. Post HF methods include configuration interaction (CI), perturbation theory (MPn), coupled-cluster method (CC) and quantum Monte Carlo (QMC) [44]. Normally, post-HF methods give more accurate energy than HF method however with expanded wave function, all post HF methods are very expensive in term of time consumption compared to HF. However, there is another different approach that can provide a comparable accuracy with cost effective which is presented in the next section.

2.1.4 Density functional theory (DFT)

DFT has become a powerful and popular method among the physicists and chemists because of its accuracy and cost effect. DFT uses a concept of the electron probability density, ρ(r), as assumed to the many-electron wave function [45]. DFT results are most of the time in good agreement with experimental data and more accurate than HF method. Computational costs (time) are relatively low when compared with HF theory and post-HF that includes electron correlation.

Originally, theoretical framework of DFT was first proposed by Hohenberg-Kohn theorem and then Kohn-Sham developed the theory that formulated a method considering systems with two electrons with different spin sign (up or down) which are in the same spatial one-electron orbitals in the ground-state and its corresponding energy (E) is given as following expression:

$$\mathrm{E}[\rho] = \mathrm{E_T}[\rho] + \mathrm{E_V}[\rho] + \mathrm{E_J}[\rho]) + \mathrm{E_{XC}}[\rho] \tag{2.10}$$

where, E_T represents the kinetic energy, E_V represents the interaction energy between electron and nuclei, E_J represents the Coulomb energy, and the E_{XC} represents the exchange-correlation energy. All energies are dependent of the total electron density, ρ(r), except the E_T. Thus, the exact electron density in the ground-state is written as

$$\rho(\mathrm{r}) = 2 \sum_{\mathrm{i}}^{\mathrm{orbitals}} |\Psi_{\mathrm{i}}(\mathrm{r})|^2 \tag{2.11}$$

where ρ (r) is the total electron density at a specific point r in space for a given system of n electrons and Ψ_{i} is Kohn-Sham orbitals and the summation accounts for all pair electrons. The accuracy of DFT methods depends on the choice of E_{xc} functionals. The most widely used method among physicists and theoretical chemists is hybrid three parameters of Beck and Lee-Yang-Parr correlation functional (B3LYP).

Hybrid functional is one of approximations to the exchange correlation energy functional in DFT. This approximation is extensively utilized because it provides very excellent results compared to available experimental data. The distinguishing feature of such hybrid approximations is that it mixes in a certain amount of the exact HF exchange energy into the exchange and correlation received from others functional. This observation of Becke's leads to conclusion that a fraction of exact exchange should be mixed with GGA exchange and correlation. The simplest such hybrid functional is given as following:

$$E_{XC}^{hyb} = aE_X^{exact} + (1-a)E_X^{GGA} + E_C^{GGA} \tag{2.12}$$

where the constant a can be fitted and theoretically evaluated as around 0.2 for molecules. One of the most commonly used versions is B3LYP, which stands for two parts; the first part, B3 is Becke 3 parameter exchange correlation functional which uses 3 parameters to mix in the 20% HF exchange correlation and the second part, LYP is the Lee Yang and Parr correlation functional that recovers dynamic electron correlation. B3LYP has now become the most widely used alternative [46] method and its formulation is shown in equation 2.13.

$$E_{xc}^{B3LYP} = 0.2E_x^{HF} + 0.8E_x^{LDA} + 0.72E_x^{B88} + 0.81E_x^{LYP} + 0.9E_x^{VWN} \tag{2.13}$$

B3LYP is generally not only faster than most Post HF techniques and usually yields comparable results but it also shows excellently great performance in the calculation of structures, energies and properties of molecules.

2.1.5 Time-dependent density functional theory (TD-DFT)

The time-dependent density functional theory (TD-DFT) is the generalization of stationary DFT to time-dependent potentials and electron densities, ρ (r, t). TD-DFT is very popular tool for electronic excitation energies and ocsillator strength. It is a powerful tool in studying photochemistry because its computation cost is not expensive compared to the post HF methodes. The time-dependent Kohn-Sham equation in TD-DFT is shown in the following equaiton:

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

2.1.6 Basis set

To solve Schrödinger equation using a computational chemistry tool, one needs to have a hamiltonian and a wave function which are denoted by a method and basis set, respectively. Each method is unique with different accuracy, and basis set has also a unique set to approximate Schrödinger equation. Choosing a suitable method and basis set for a given system normally depends on accuracy and computational cost. However, more accurate methods and larger basis sets results in an expensive cost (much longer time).

Principally, the correct wave function is Slater determinant which is a set of basis functions to represent the spin-orbitals [47]. Normally, basis function is the Slater-type orbitals (STOs) with all permitted integral values of n, *l*, and m_l and all positive values of the orbital exponents of the STO. However, taking full STOs is numerically difficult to be solved. Therefore, in a real calculation only a small number of all possible functions are used. Another choice to overcome the difficult calculation is to use Gaussian-type orbitals (GTOs) to make *ab initio* calculations computationally feasible. The simplest basis set is a minimal basis set in which one function is used to represent the orbitals of valence theory, for example 1s-orbital for one function however, the electrons of most elements are not only in s but also in p, d, f orbital depending on its number of atomic number. Therefore, a significant improvement is required by adopting a bigger basis set such as double-zeta basis set (DZ basis set) and a triple-zeta basis set (TZ basis set) to describe each of the orbitals encountered in valence theory. Moreover, there are other types of basis function describing changing in size and shape of molecular orbitals [48] such as split valence, polarized and diffusion function. However, to use the accurate basis set for a given system, one has to carry out a systematic comparison of difference basis set and also compare the results with experimental results or theoretical data in case there is no experiment available.

2.1.7 Adiabatic dynamics

Molecular dynamics is a technique for computer simulation of molecular process at the atomic level. The equations of motion are solved numerically to follow the time evolution of the system, allowing the derivation of kinetic and thermodynamic properties. The main challenge in molecular dynamic simulations of molecules is to obtain information of the time-dependent Schrödinger equation (TD-SE) for a given system [49].

$$\left(i\hbar\frac{\partial}{\partial t} - H\right)\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = 0 \tag{2.14}$$

Where Ψ is the wavefunction depending of time (t) and **R** is the coordinates of nuclei. the molecular wave function depended on time *t*. The electronic coordinates are represented in **r** and *H* is the total Hamiltonian. In terms of motions of nuclei, it can be estimated by the molecular wave function using a Born-Oppenheimer expansion.

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{j} \Phi_{\mathrm{j}}(\mathbf{r}, \mathbf{R}))\chi_i(\mathbf{R}, \mathrm{t}) \tag{2.15}$$

Where χ_i represents the nuclei wave function and Φ_{j} represents the electronic wave function, for electronic state *j*.

1) Initial conditions

The initial conditions for each representative for nuclei must be set up before being integrated by Newton’s equation. In general, the initial condition is sampled with a phase space distribution in the ground state before going to the excite-state. The distribution in ground state can be prepared both by a ground state trajectory simulation and from a probabilistic sampling. Nevertheless, due to the classical nature of the trajectory simulations in the ground state and the quantum nature of typical distributions like that given by the Wigner function, the two sets may differ substantially.

2) Wigner distributions

Assuming that potential energy surface in the ground-state as a quadratic estimation is the minimum, the $3N_{at}-6$ internal coordinates can be defined in terms of normal modes Q and the nuclear wave function which can be solved using a harmonic oscillator [50]. The classical phase space distribution can be approximated by a Wigner distribution.

$$P_W\left(Q^i, P^i\right) = (\pi\hbar)^{-1} \int d\eta \chi_{HO}^0\left(Q^i + \eta\right)^* \chi_{HO}^0(Q^i - \eta) e^{2i\eta P^i/\hbar} \tag{2.16}$$

Here, χ_{HO}^0 is the harmonic oscillator wavefunction for the vibration of ground state and P^i is the momentum associated with the normal coordinate Q^i. This integral of evolution gives

$$P_W\left(Q^i, P^i\right) = (\pi\hbar)^{-1}\, exp\left(-\mu^i \omega_{HO}^i Q^{i2}/\hbar\right)\, exp\left(P^{i2}/\left(\mu^i \omega_{HO}^i \hbar\right)\right) \tag{2.17}$$

where μ^i represent the reduced mass and ω_{HO}^i representthe harmonic frequency and i is normal mode of the equilibrium distance.

To sample coordinates and momentum, independent randomly choose values are determined to Q^i and P^i and then the acceptance of the pair is evaluated according to the probability given by equation 2.17. Due to uncorrelated value of Q^i and P^i, this process will result in a Gaussian distribution in the (Q^i and P^i) space. The distribution of initial energy occurs around the harmonic zero-point value. This procedure takes place repeatedly for each normal mode and then the normal momentum and coordinates have been converted back into Cartesian coordinates.

When equation 2.16 is estimated for a vibrationally excited level χ_{HO}^n instead for the vibrational ground state, the Wigner function can suppose negative values and cannot be used as a distribution. To obtain this main cause, it can be written as

$$P_W(Q^i, P^i) = \left|\chi^o_{HO}(Q^i)\right|^2 \left|\xi^0_{HO}(P^i)\right|^2 \tag{2.18}$$

where ξ^0_{HO} represents the harmonic oscillator wavefunction. Although the equation X is exact only for the ground vibrational level, therefore, the excited vibrational states is

$$P_W(Q^i, P^i) = \left|\chi^o_{HO}(Q^i)\right|^2 \left|\xi^n_{HO}(P^i)\right|^2 \tag{2.19}$$

the initial conditions are used by sampling for example, to create biased distributions leading to specific normal modes

2.2 Computational details

2.2.1 Static calculation

For the theoretical calculations, ground state (S_0) and excited state (S_1) structure optimizations were carried out using the DFT and TD-DFT at B3LYP with TZVP basis set, respectively. Optimizations were performed without constraints of bond, angle or dihedral. Vibrational frequencies were calculated using optimized structures to confirm that these structures correspond to characteristic of the local minimum by the absence of an imaginary mode. The simulated infrared (IR) spectra were computed to investigate vibrational frequencies involved in PT process. The vertical excitation energy calculations were computed from the S_0 state optimized structure using TD-DFT with five low-lying absorbing transition. To further investigate the occurrence of ESPT, the potential energy curves (PECs) on proton transfer (PT) coordinates of S_0 and S_1 state were scanned by constrained optimizations in their relevant electronic state keeping distance of bond O1–H1 at a series of values. All electronic calculations were performed using Gaussian09 program [51].

2.2.2 Dynamic simulations

Classical dynamics simulations were carried out for 3HF and 3HF with solvents on the first singlet excited state (S_1) energy surface. The initial conditions were generated using harmonic-oscillator Wigner distribution for each normal mode as implemented with the NEWTON-X [52] interfaced with TURBOMOLE program [53]. The Velocity-Verlet algorithm [54] was applied to solve the Newton's equations of nuclear motion. The Born-Oppenheimer energies and gradients computed at TD-DFT approach using B3LYP functional with TZVP basis set. Fifty trajectories were simulated using a time step of 0.5 fs and up to a maximum of 300 fs, enough to cover pre- and post-PT process. In addition, each trajectory was classified into two types of reactions: ESPT (ESIntraPT and ESInterPT) and no PT. All active ESPT trajectories were analyzed. Furthermore, details of dynamics simulations such as energy difference between S_0 and S_1 state, probabilities and time evolutions in the excited state were ascribed by a statistical analysis.