CHAPTER 2

THEORETICAL BACKGROUND

Quantum mechanics can describe, correlate, and predict with great accuracy the behavior of nature at the atomic levels [29]. A lot of experimental results have been given a satisfactory explanation by quantum mechanics, and its development has in turn suggested many new measurements.

The quantum mechanical calculations can be classified as *semi-empirical* and *ab initio* types [30]. The *ab initio* strictly means *from the beginning* or *from the first principles*, which would imply that the calculation using such an approach would require universal constants such as the speed of light, Planck's constant, the masses of elementary particles and so on as input and would not require any parameter from experiment. By contrast, the semi-empirical simplifies the calculations, using parameters from experiment to approximate some of integrals. The *ab initio* methods have risen in popularity in recent years because of its accuracy and the availability of high-speed digital computers and the development of theoretical and computational methods.

This chapter aims at setting the stage with a discussion of some of the essential concepts.

2.1 Schrödinger Equation [31-32]

According to quantum mechanics, the energy and many properties of a particles can be obtained by solution of the Schrödinger equation [33],

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

where $\hat{H}$ is the Hamiltonian operator, E is the energy of the system and Ψ is the total wavefunction of the system. The square of the wavefunction, Ψ^2 (or $|\Psi|^2$ if Ψ is complex) is interpreted as a measure of the probability distribution of the particles within the molecule.

The Hamiltonian $\hat{H}$ is sum of kinetic and potential parts,

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

where the kinetic energy operator $\hat{T}$ is a sum of differential operators and the potential energy operator $\hat{V}$ is the coulomb interaction.

The Hamiltonian described above is *nonrelativistic*. In cases of N noninteracting particles, the Schrödinger equation can be solved easily, but for a system containing N interacting particles no analytical solution is known. For a molecule consisting of n electrons and K nuclei, the kinetic energy operator and the potential energy operator are given by

$$\hat{T} = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{K} \frac{1}{2M_A} \nabla_A^2 \tag{2.3}$$

$$\hat{V} = -\sum_{i=1}^{n}\sum_{A=1}^{K}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} + \sum_{A=1}^{K}\sum_{B>A}^{K}\frac{Z_A Z_B}{r_{AB}} \tag{2.4}$$

where ∇^2, r, M, and Z are Laplacian operator, distance, mass of nuclei, and charge of nuclei, respectively. A and B represent nuclei while i, j represent electrons. So the nonrelativistic Hamiltonian (in atomic units) is expressed by

$$\hat{H} = -\sum_{i=1}^{n}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{K}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{n}\sum_{A=1}^{K}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} + \sum_{A=1}^{K}\sum_{B>A}^{K}\frac{Z_A Z_B}{r_{AB}} \tag{2.5}$$

The first and the second term in eq. (2.5) are the operators for the kinetic energy of the electrons and nuclei, respectively. The third term is the electron-nuclear attraction. The fourth term is the electron-electron repulsion. The last term is the nuclear-nuclear repulsion.

Due to the complexity of the Schrödinger equation for molecular systems involving both nuclear and electron coordinates, therefore an approximation is needed. Since nuclei are much heavier than electrons, they move more slowly. Hence, one can consider electrons in a molecule as moving in field of fixed nuclei. Within this approximation, the nuclear part which depends only on nuclear coordinates and the electronic part of wavefunction which depends on electron coordinates while treating nuclear coordinates as parameters can be solved separately. This approximation is called *Born-Oppenheimer approximation*. The Hamiltonian that omits the nuclear kinetic energy and nuclear-nuclear repulsion terms from eq. (2.5) is called *purely electronic Hamiltonian*, $\hat{H}^{el}$.

$$\hat{H}^{el} = -\sum_{i=1}^{n}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{n}\sum_{A=1}^{K}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} \tag{2.6}$$

When

$$\hat{H}^{core} = -\sum_{i=1}^{n} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{n}\sum_{A=1}^{K} \frac{Z_A}{r_{iA}} \qquad (2.7)$$

therefore

$$\hat{H}^{el} = \hat{H}^{core} + \sum_{i=1}^{n}\sum_{j>i}^{n} \frac{1}{r_{ij}} \qquad (2.8)$$

where $\hat{H}^{core}$ is a one-electronic Hamiltonian operator.

The solution of the Schrödinger equation involving the electronic Hamiltonian is given as

$$\hat{H}^{el}\Psi^{el} = E^{el}\Psi^{el} \qquad (2.9)$$

where Ψ^{el} is the electronic wavefunction, which describes the motion of electrons in the field of fixed nuclei. The total energy, E^{total}, for fixed nuclei must also include the nuclear repulsion energy and it is given as

$$E^{total} = E^{el} + \sum_{A=1}^{K}\sum_{B>A}^{K} \frac{Z_A Z_B}{r_{AB}} \qquad (2.10)$$

2.2 Hatree-Fock Wavefunction

From the eq. (2.6), the electronic Hamiltonian is the function of only spatial coordinates of the electrons. To describe the behavior of an electron, it is necessary to specify its spin. In the context of nonrelativistic theory, there are two spin functions, $\alpha(\omega)$ and $\beta(\omega)$, corresponding to spin up and spin down, respectively. These two spin functions form complete set and are orthonormal.

The wavefunction for an n-noninteracting-electron system or the Hartree product is given as

$$\Psi = \chi_1(1)\chi_2(2)........\chi_n(n) \qquad (2.11)$$

where $\chi_i(i)$ is the function of space and spin coordinate of electron i, $\chi_i(\bar{r},\bar{\omega}_i)$, called the spin orbital.

However, such a wavefunction is not acceptable, as it does not have the property of antisymmetry. If the coordinates of electron i and j are interchanged in this wavefunction, the product $...\chi_i(i)...\chi_j(j)...$ becomes $...\chi_i(j)...\chi_j(i)...$ which is not equivalent to multiplication by -1. To ensure antisymmetry, and to guarantee with Pauli exclusion principle, the Hartree-Fock wavefunction is written as *Slater determinant* [34] given in eq. (2.12),

$$\Psi = (\frac{1}{\sqrt{n!}}) \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_n(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(n) & \chi_2(n) & \cdots & \chi_n(n) \end{vmatrix} \qquad (2.12)$$

For the closed-shell ground state of molecule with n (even) electrons, doubly occupying n/2 orbitals, the Hartree-Fock wavefunction can be written as

$$\Psi = (\frac{1}{\sqrt{n!}}) \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \cdots & \psi_{n/2}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \cdots & \psi_{n/2}(2)\beta(2) \\ \vdots & \vdots & \vdots & & \vdots \\ \psi_1(n)\alpha(n) & \psi_1(n)\beta(n) & \psi_2(n)\alpha(n) & \cdots & \psi_{n/2}(n)\beta(n) \end{vmatrix} \qquad (2.13)$$

The $\chi_j(k)$ is the spin orbital j of electron k which is called one-electron spin orbital. It consists of spatial part called molecular orbital (ψ) and spin function (α or β). For the spatial part, two different assignments of orbital can be made *i.e.* the restricted orbital where the paired α and β electrons are assigned the same spatial part and the unrestricted orbital where the paired α and β electrons are assigned the different spatial part. The Hartree-Fock wavefunction using restricted orbital is called *Restricted Hartree-Fock (RHF)* and using unrestricted orbital is called *Unrestricted Hartree-Fock (RHF)*.

The molecular orbitals ψ_i can be expressed as linear combination of a set of orthogonal functions,

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i}\phi_\mu \qquad (2.14)$$

The functions ϕ_μ are known as *one-electron basis functions* or simply as *basis functions*, and $c_{\mu i}$ are the *molecular orbital expansion coefficients*, whose variation allows to minimize the energy.

2.3 Hartree-Fock Approximation [31,35]

The Hartree-Fock approximation is the heart and soul of the attempts in solving the problem of the many-electron system. If Φ is any antisymmetric normalized function of the electronic coordinates, then an expectation value of the energy corresponding to this function can be obtained from the integral

$$E' = \int \Phi * \hat{H}\Phi d\tau \qquad (2.15)$$

where integration is over the coordinates of all electrons. The asterisk again denotes complex conjugation. If Φ happens to be the exact wavefunction, Ψ, for the electron ground state, it will satisfy the Schrödinger equation (2.1). Since Ψ is normalized, E' will therefore be the exact energy E,

$$E' = E \int \Psi^* \Psi d\tau = E \tag{2.16}$$

However, if Φ is any other normalized antisymmetric function, it can be shown that E' is greater than E,

$$E' = \int \Phi^* \hat{H} \Phi d\tau > E \tag{2.17}$$

It follows then that if Φ is the antisymmetric molecular orbital function (eq. (2.13)), the energy E' calculated from eq. (2.15) will be upper bound of the exact energy.

The variational method may be applied to determine optimum orbitals in single-determinant wavefunctions. The resulting value of E' will then be as close to the exact energy E as is possible within the limitations imposed by the single-determinant wavefunction.

By minimizing E' using technique of Lagrange multiplier, the Hartree-Fock equation is earned as follow,

$$f(i)\chi(x_i) = \varepsilon\chi(x_i) \tag{2.18}$$

where f(i) is an effective one-electron operator called Fock operator express as

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{K}\frac{Z_A}{r_{iA}} + v^{HF}(i) \qquad (2.19)$$

where $v^{HF}(i)$ is the average potential experienced by the ith electron in the field of other electrons. The $v^{HF}(i)$ is given by $\sum_b \left(J_b(i) - K_b(i)\right)$ where J_b and K_b are Coulomb and exchange operators, respectively, expressed as

$$J_b(i) = \int dx_2 \chi_b^*(x_2)\frac{1}{r_{12}}\chi_b(x_2) \qquad (2.20)$$

$$K_b(i) = \int dx_2 \chi_b^*(x_2)\frac{1}{r_{12}}P_{12}\chi_b(x_2) \qquad (2.21)$$

where P_{12} is the permutation operator which interchanges all the coordinates of particles1 and 2.

The complicated many-electron problem is then now reduced to a one-electron problem in which the electron-electron repulsion is treated in an average way. Protecting out the spin part, the Hartree-Fock equation for a closed-shell system is then

$$f(r_1)\psi(r_1) = \varepsilon\psi(r_1) \qquad (2.22)$$

where ψ is the molecular orbital, ε is the orbital energy and

$$f(r_1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{K}\frac{Z_A}{r_{1A}} + \sum_b^{n/2}\int dr_2 (2J_b(r_2) - K_b(r_2)) \qquad (2.23)$$

where

$$J_b(r_2) = \int dr_2 \psi_b^*(r_2) \frac{1}{r_{12}} \psi_b(r_2) \tag{2.24}$$

$$K_b(r_2) = \int dr_2 \psi_b^*(r_2) \frac{1}{r_{12}} P_{12} \psi_b(r_2) \tag{2.25}$$

By substitution the molecular orbital expansions (eq. (2.14)) into the Hartree-Fock equation (eq. (2.22)), gives

$$f(1) \sum_{v=1}^{N} c_{vi} \phi_v(1) = \varepsilon_i \sum_{v=1}^{N} c_{vi} \phi_v(1) \tag{2.26}$$

then multiply by $\phi_\mu^*(1)$ and integrate

$$\sum_{v=1}^{N} c_{vi} \int \phi_\mu^*(1) f(1) \phi_v(1) = \varepsilon_i \sum_{v=1}^{N} c_{vi} \int \phi_\mu^*(1) \phi_v(1) \tag{2.27}$$

and define two matrices which are the overlap matrix **S**, has elements

$$S_{\mu v} = \int dr_1 \phi_\mu^*(1) \phi_v(1) \tag{2.28}$$

and the Fock matrix **F**, has elements

$$F_{\mu v} = \int dr_1 \phi_\mu^*(1) f(1) \phi_v(1) \tag{2.29}$$

Therefore, the integrated Hartree-Fock equation is written as

$$\sum_{v=1}^{N} F_{\mu v} c_{vi} = \varepsilon_i \sum_{v=1}^{N} S_{\mu v} c_{vi} \qquad (\mu = 1,2,...,N) \tag{2.30}$$

They are the Roothaan-Hall equation proposed by Roothaan [36] and Hall [37] which can be written as the single matrix equation

$$\mathbf{FC} = \mathbf{SC\varepsilon} \qquad (2.31)$$

Where **C** is a N x N square matrix of the expansion coefficients $c_{\mu i}$

$$\mathbf{C} = \begin{bmatrix} c_{11} & c_{12} & \cdots & c_{1N} \\ c_{21} & c_{22} & \cdots & c_{2N} \\ \vdots & \vdots & & \vdots \\ c_{N1} & c_{N2} & \cdots & c_{NN} \end{bmatrix} \qquad (2.32)$$

and ε is a diagonal matrix of the orbital energies ε_i

$$\varepsilon = \begin{bmatrix} \varepsilon_1 & & & 0 \\ & \varepsilon_2 & & \\ & & \ddots & \\ 0 & & & \varepsilon_N \end{bmatrix} \qquad (2.33)$$

and
$$F_{\mu\nu} = H_{\mu\nu}^{core} + G_{\mu\nu} \qquad (2.34)$$

where $H_{\mu\nu}^{core}$ is the core-Hamiltonian matrix

$$H_{\mu\nu}^{core} = \int dr_1 \phi_\mu^*(1) h(1) \phi_\nu(1) \qquad (2.35)$$

and
$$h(1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{K} \frac{Z_A}{r_{1A}} \qquad (2.36)$$

$G_{\mu\nu}$ is the two-electron part of the Fock matrix

$$G_{\mu\nu} = \sum_{\lambda=1}^{n/2} \sum_{\sigma=1}^{n/2} P_{\lambda\sigma} [(\mu\nu \mid \lambda\sigma) - \frac{1}{2}(\mu\lambda \mid \nu\sigma)] \qquad (2.37)$$

where $P_{\lambda\sigma}$ is density matrix,

$$P_{\lambda\sigma} = 2\sum_{i=1}^{n/2} c_{\lambda i}^* c_{\sigma i} \qquad (2.38)$$

and the quantities $(\mu\nu \mid \lambda\sigma)$ appearing in eq. (2.37) are two electron repulsion integrals,

$$(\mu\nu \mid \lambda\sigma) = \iint dr_1 dr_2 \phi_\mu^*(1)\phi_\nu(1)\frac{1}{r_{12}}\phi_\lambda^*(2)\phi_\sigma(2) \qquad (2.39)$$

The electronic energy, E^{el}, is now given

$$E^{el} = \frac{1}{2}\sum_{\mu=1}^{n}\sum_{\nu=1}^{n} P_{\mu\nu}(F_{\mu\nu} + H_{\mu\nu}^{core}) \qquad (2.40)$$

Accounting for the internuclear repulsion,

$$E^{nr} = \sum_{A}^{K}\sum_{A<B}^{K} \frac{Z_A Z_B}{r_{AB}} \qquad (2.41)$$

(see eq. (2.4) for Z_A, Z_B and r_{AB}) yields an express for the total energy (eq. (2.10)).

For solving the Roothaan-Hall equation, iterative process called *Self-Consistent Field (SCF)* procedure are required. The process is carried out iteratively until the total electronic energy or density matrix remains unchanged within given limits.

2.4. Mulliken Population Analysis

The *electron density function* or *electron probability distribution function*, $\rho(r)$, is a three-dimensional function defined such that $\rho(r)dr$ is the probability of finding an electron in small volume element, dr,

$$\int \rho(r)dr = n \tag{2.42}$$

where n is the total number of electrons. For a single-determinant wavefunction in which the orbitals are expanded in terms of a set of N basis function, ϕ_μ, $\rho(r)$ is given by expression (2.43),

$$\rho(r) = \sum_\mu^n \sum_v^n P_{\mu v} \phi_\mu \phi_v \tag{2.43}$$

According to the equation (2.28), suggestions about how to calculate the electron density, starting from the density matrix, $P_{\mu v}$, were made by Mulliken [38]. Integration of eq. (2.43) leads to

$$\int \rho(r)dr = \sum_\mu^N \sum_v^N P_{\mu v} S_{\mu v} = n \tag{2.44}$$

It is desirable to determine electron density at parts of a molecule (atoms, bonds, etc.). It will be useful, for example, to define a total electronic charge on a

particular atom in a molecule in order that quantitative meaning may be given to such concepts as electron withdrawing or donating ability. In addition, it will be used to represent the interaction potential of the Coulombic force.

2.5 Basis Functions

As appearing in eq. (2.14), the accuracy of the molecular orbitals depends directly on number and quality of atomic orbitals, namely *basis set* in use. There are two types of atomic orbital functions:

Slater Type Orbital (STO) is as follows,

$$\phi^{STO} = Nr^{n-1}e^{-\zeta r}Y_l^m(\theta,\Theta) \tag{2.45}$$

where r, θ, and Θ are spherical polar coordinate, while N, ζ, n, and $Y_l^m(\theta,\Theta)$ are the normalization constant, the positive orbital exponent, principle quantum number, and the angular part of the wavefunction, respectively.

The STO basis function, which was originally introduced by Slater [34], is based on approximations of hydrogen-like atomic orbitals. They were mostly used for the calculations of small molecules. Although, the advantage of using this type of orbital is that only a few functions are needed for good description, STOs are more accurate representations of atomic orbitals but the integration of higher functions is largely time consuming.

Gaussian Type Orbital (GTO) [39-41] can be described as

$$\phi^{GTO} = Nx^a y^b z^c e^{-\zeta r^2} \tag{2.46}$$

where x, y, and z are Cartesian coordinate and a, b, and c are nonnegative integers.

The GTO is an alternative choice of STO. The integration of this function is easier to compute. However, due to the different shape of the GTO from STO type functions, for a near region from nucleus, a combination of GTOs with different exponent is required to obtain equivalent results. For example, the symbol STO-3G for a basis means that each STO is approximated by a linear combination of three GTOs, the coefficients being chosen to minimize the difference between the STO and its STO-3G approximation. There are many GTO expansions in current use which have been optimized for molecular calculations.

The orbital reviews of basis set can be seen from ref. [42] and normally classified as:

(i) *Minimal basis sets*: The size of this basis set will contain just the number of functions that are required to accommodate all the filled orbitals in each atom. In practice, a minimal basis set normally includes all of the atomic orbitals in the shell. Thus, for hydrogen and helium, a single s-type function would be required. For elements from lithium to neon, the 1s, 2s and 2p functions are used and so on. The basis sets STO-nG, for example, STO-3G and STO-4G are all minimal basis set in which n Gaussian functions are used to represent a Slater orbital.

(ii) *Extended basis sets*: They are larger than minimal basis sets. The number of basis function representing each atomic orbital can be varied, higher than one. For STO, a basis set which doubles the number of functions in the minimal basis set is described as *double zeta basis*. The double, trible, or more of STO minimal basis function allows the linear combination of the *contracted* and the *diffuse* functions which gives an overall result that is intermediate between the both. In other words, the size of orbital can be modified during the course of calculation. An alternative to

the double zeta basis approach is to double the number of functions used to describe the valence electrons but to keep a single function for the inner shells called *split valence double zeta basis*. For GTO, the similar notation like STO can also be used. The 3-21G exemplifies the notation used for such split valence double zeta basis sets. In this basis set, three Gaussian functions are used to describe the core orbitals. The valence electrons are also represented by three Gaussian; the contracted part by two Gaussian and the diffuse part by one Gaussian. The most commonly used split valence basis sets are 3-21G, 4-31G, and 6-31G. Other type of extended basis set is Dunning basis set such as DZV and TZV.

(iii)*Polarize basis sets*: Just simply increasing the number of basis functions does not necessarily improve the model. In fact, this possibly leads to a wholly erroneous result, particularly for molecules with strongly anisotropy charge distribution. All of the basis sets employed in modern quantum chemical calculations usually use functions that are centered on atomic nuclei. The use of split valence basis sets can help to overcome the problems with non-isolated atom. For instance, the electron cloud in an isolated hydrogen atom is symmetrical, but when the hydrogen atom is present in a molecule the electrons are drew towards the other nuclei. This distortion can be considered to correspond to mixing p-type character into the 1s orbital of the isolated atom, to give a form of sp hybrid. In a similar manner, the unoccupied d orbitals introduce asymmetry into p orbital. In other words, the addition of p function for H atom and d function for heavier atom enable orbitals on nuclei to polarize and form bond. These functions, p for hydrogen and d for 1st and 2nd row element, have a higher angular momentum and they are called the *polarization* function. An asterisk (*) indicates the use of polarization basis functions. Thus, 6-31G* refers to a 6-31G basis set with polarization functions on the heavy (non-hydrogen) atoms. Two asterisks, such as 6-31G** indicate the use of polarization functions on hydrogen and heavy atoms. For Dunning's type basis sets,

the annexation of "P" at the end of basis set notation, for example DZVP and TZVP, is made to represent the polarized basis set.

2.6 Basic Set Superposition Error (BSSE)

In calculating the interaction energy for a complex system, which equal or greater than two interacting molecules, the basis set employed should be sufficiently large and correctly express the multipole moments and the polarizability of the system. In the case that an insufficient basis set is used, an artificial basis set improvement will take place in the complex, leading to an error which is known as *basis set superposition error*. In a complex consisting of two monomers A and B which represented by the basis set ϕ_A and ϕ_B, respectively, the error occurs when the basis set ϕ_A is contaminated by ϕ_B in computing the energy of A or conversely, when ϕ_B is contaminated by ϕ_A in computing the energy of B. In this case, the interaction energy of the complex is always overestimated [43].

The *counterpoise (CP) method* proposed by Boys and Bernardi [44] was carried out to estimate this error. The method is based on the determination of the monomer energies using the same basis set as for the determination of the complex energy and can be presented as follows. First, the energy of complex AB with basis sets ϕ_{AB} is computed, yielding an energy $E_{AB}(\phi_{AB})$. Second, the computation of the energy of A with ϕ_{AB}, disregarding the nuclear charge in B, is performed to obtain an energy $E_A(\phi_{AB})$. The operation is repeated for B with ϕ_{AB} as basis set, yielding the energy $E_B(\phi_{AB})$. The counterpoise correction, Δe, can be defined as

$$\Delta e = \left[E_A(\phi_A) - E_A(\phi_{AB}) \right] + \left[E_B(\phi_B) - E_B(\phi_{AB}) \right] \qquad (2.47)$$

where

$$\phi_{AB} = \phi_A \cup \phi_B \qquad (2.48)$$

$E_A(\phi_A)$ and $E_B(\phi_B)$ are energies of A and B resulted from the computations of A with ϕ_A alone and of B with ϕ_B alone, respectively, and the counterpoise corrected interaction energy, ΔE^{CP}, is

$$\Delta E^{CP} = \Delta E + \Delta e \qquad (2.49)$$

where ΔE is the interaction energy calculated from the truncated basis set,

$$\Delta E = E_{AB}(\phi_{AB}) - [E_A(\phi_A) + E_B(\phi_B)] \qquad (2.50)$$

It should be mentioned, however, that this correction gives the upper limit of a possible BSSE and hence can not be regarded as an absolutely correct value for the real BSSE occurring in the simulation of a specific complex.