

## CHAPTER II

### QUANTUM CHEMICAL CALCULATIONS

The commonly used molecular quantum chemical methods are classified as "*non-empirical and semi-empirical*" types. Semi-empirical methods use a simpler Hamiltonian and use parameters whose values are adjusted to fit experimental data or the results of empirical one. In contrast, the non-empirical calculation uses the full Hartree-Fock Hamiltonian and does not use experimental data other than the values of the fundamental physical constants. A Hartree-Fock calculation seeks the antisymmetrized product of one-electron functions,  $\Phi$ , that minimizes  $\int \Phi^* H \Phi d\tau$ , where  $H$  is the Hamiltonian operator.

*Ab initio* method received popularity in the past decade because of the availability of high speed digital computers and the development of theoretical and computational methods. The main factor determining the accuracy of the *ab initio* calculations is the size and type of the basis set used.

#### 2.1 Ab Initio Molecular Orbital Theory

Any physically observable molecular property can be calculated quantum mechanically if the corresponding Schrödinger equation

$$H\Psi = E\Psi \quad (2.1)$$

can be solved. According to this equation, total energy is obtained by

$$E = \langle \Psi | H | \Psi \rangle \quad (2.2)$$

where  $\Psi$  is the normalized total wave function of the system.

The principle of the *ab initio* approach is based on the following steps :

- (a) define an approximate Hamiltonian operator for the system,
- (b) select trial mathematical function  $\Psi(q_1, q_2, q_3, \dots)$  where  $q_1, q_2, q_3, \dots$  are finitely variable parameters,
- (c) minimize the total energy, with respect to variation of the parameters until the change of energy is lower than a given limit (e.g.  $10^{-5}$  Hartree).

More details of the above consecutive steps will be briefly summarized as the following.

### 2.1.1 The Molecular Hamiltonian Operator

If we are interested in molecular systems, the total Hamiltonian operator of the system will be given as sum of all possible Coulombic energy operators and kinetic energy operators of the electrons and nuclei of the form,

$$H = -\frac{1}{2M_A} \sum_A \nabla_A^2 - \frac{1}{2} \sum_i \nabla_i^2 - \sum_A \sum_i \frac{Z_A}{r_{Ai}} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{A < B} \frac{Z_A Z_B}{r_{AB}} \quad (2.3)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

A and B are nuclear centers, and i and j represent electrons.  $M_A$  is the ratio of the mass of nucleus A to the mass of an electron. r and Z are the distances and the atomic number, respectively. The first term, the kinetic energy of the nuclei, can be neglected according to the Born-Oppenheimer approximation for a fixed molecular geometry, since nuclei are much heavier than electrons and their motions are expected to be much slower. The last term, the repulsion between the nuclei, becomes a constant in this case and can be put apart. Consequently, only the remaining terms should be considered within the Hartree-Fock approximation.

The Hamiltonian operator is, then, reduced to

$$H^{\text{el}} = H^{\text{core}}(i) + \sum_{i < j} \sum \frac{1}{r_{ij}} \quad (2.4)$$

where

$$H^{\text{core}}(i) = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_A \sum_i \frac{Z_A}{r_{Ai}}$$

$H^{\text{core}}$ , frequently denotes as  $H$ , is a one-electronic Hamiltonian operator, and the total electronic Hamiltonian is composed of the one-electron operators for all electrons.

### 2.1.2 The Hartree-Fock Wave Function

#### a) Independent Electron Model

The typical approximation to construct the many-electron wave function,  $\Psi$ , is the *Independent Particle Approximation*, based on a factorization into one-electron spin orbitals, being themselves products of a spatial orbital and a spin function. The most convenient way to represent a trial wave function for a  $2n$ -electron closed shell system is to use a single-determinanted wave function, also called a Slater determinant [22] given in eq. (2.5), in order to satisfy the antisymmetry principle.

$$\Psi = \frac{1}{\sqrt{2n!}} \left| \begin{array}{c} \psi_1(1)\bar{\psi}_1(2)\psi_2(3)\bar{\psi}_2(4)\dots\psi_n(2n-1)\bar{\psi}_n(2n) \end{array} \right| \quad (2.5)$$

The spin orbitals  $\psi_i$  and  $\bar{\psi}_i$  correspond to  $\psi_i(j)\alpha(j)$  and  $\psi_i(j)\beta(j)$ , where  $\alpha(j)$  and  $\beta(j)$  denote by spin functions for the  $j$ th electron.

This approximation automatically leads to a split-up of the Hamiltonian into a sum of one-electron operators (Fock Operator)  $F$

$$H = \sum_i F_i = \sum_i H_i^c + \sum_{i < j} (2J_j - K_j) \quad (2.6)$$

where  $H_i^c$  is the core Hamiltonian and  $J_j$  and  $K_j$  are Coulomb and Exchange operators, respectively.

b) Molecular Orbitals and the Linear Combination of Atomic Orbitals (LCAO) Approximation

To construct molecular orbitals ( $\psi_i$ ) for electrons in a molecular system, a linear combination of atomic orbitals (basis functions) is used.

$$\psi_i = \sum_{\mu} c_{i\mu} \phi_{\mu} \quad (2.7)$$

where  $\phi_{\mu}$  are the atomic orbitals, and  $c_{i\mu}$  are the molecular orbital expansion coefficients, whose variation allows to minimize the energy. The orbitals used in the linear combination are called basis orbitals or basis functions. The optimal values of the coefficients  $c_{i\mu}$  are determined by means of the variation principle ( $\partial E / \partial c_{i\mu} = 0$ ).

### 2.1.3 Minimization of the Total Energy (Self-Consistent Field Procedure)

Minimization of the total energy is done by varying the value of the coefficients,  $c_{i\mu}$ , in eq. (2.7). The procedure starts with the use of an initial guess of  $c$ 's to calculate the first matrix of the total energy,  $\mathbf{E}$ . The elements of the matrix  $\mathbf{E}$  are :

$$E_{\mu\nu} = \sum_{\mu\nu} \mathbf{P}_{\mu\nu} \mathbf{H}_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\mu\nu} \sum_{\lambda\sigma} \mathbf{P}_{\mu\nu} \mathbf{P}_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \quad (2.8)$$

The matrix of the elements of the core Hamiltonian,  $\mathbf{H}^{\text{core}}$ , contains the elements for the core-electron Hamiltonian,  $\mathbf{H}^{\text{c}}$ , for electrons moving in the field of nuclei :

$$\mathbf{H}_{\mu\nu}^{\text{core}} = \left\langle \phi_{\mu}(i) \left| \mathbf{H}^{\text{c}} \right| \phi_{\nu}(i) \right\rangle \quad (2.9)$$

The elements of the density matrix  $\mathbf{P}_{\mu\nu}$  and the two-electron integrals,  $(\mu\nu|\lambda\sigma)$  and  $(\mu\lambda|\nu\sigma)$ , are given by

$$\mathbf{P}_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{\mu i}^* c_{\nu i} \quad (\text{for closed shell system}) \quad (2.10)$$

$$(\mu\nu|\lambda\sigma) = \iint \phi_{\mu}^*(1) \phi_{\nu}(1) \frac{1}{r_{12}} \phi_{\lambda}^*(2) \phi_{\sigma}(2) d\tau_1 d\tau_2 \quad (2.11)$$

and

$$(\mu\lambda|\nu\sigma) = \iint \phi_{\mu}^*(1) \phi_{\lambda}(1) \frac{1}{r_{12}} \phi_{\nu}^*(2) \phi_{\sigma}(2) d\tau_1 d\tau_2 \quad (2.12)$$

Create the first matrix of the Fock operator,  $\mathbf{F}$  using the first guess of  $c$ 's. The elements of the matrix  $\mathbf{F}$  are :

$$\mathbf{F}_{\mu\nu} = \mathbf{H}_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} \mathbf{P}_{\mu\nu} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \quad (2.13)$$

From the first approximation of the Fock operator matrix  $\mathbf{F}$ , a second approximation of  $\mathbf{C}$  can be obtained by solving the Roothaan-Hall equation.

$$\mathbf{FC} = \mathbf{SCE} \quad (2.14)$$

where

$$\mathbf{S}_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle. \quad (2.15)$$

- F : Fock matrix
- C : Coefficient matrix
- S : Overlap matrix
- E : Eigenvalue matrix.

Since the coefficient matrix is contained in the Fock matrix, the equation cannot be solved straight forward. A new total energy matrix, E, can be calculated from eq.(2.8), using a second approximation of the coefficient matrix, C. An iterative procedure is required which is the so-called " SCF (Self-Consistent Field) " procedure. The process is carried out iteratively until the total electronic energy of the system remains unchanged within given limits, usually  $10^{-5}$  Hartree.

## 2.2 Basis Functions

In all molecular quantum mechanical methods one has to choose, at the beginning of the calculation, the basis set. The use of an adequate basis set is an essential requirement for a success of the calculation. The quality of the molecular orbitals is also related to the quality of the basis set used.

The early STO (Slater Type Orbital) basis functions, introduced by Slater [23], is based on approximations of hydrogen-like atomic orbitals according to empirical rules. They were mostly used for the calculations of small molecules. Although the advantage of using a few functions of STO satisfies us for its simplicity and more accurate representation of atomic orbitals, the integrations of the functions are very time-consuming. The typical form of STO is denoted by the expression ;

$$\phi^{\text{STO}} = N r^{(n-1)} \exp(-\zeta r) Y_{l,m}(\Theta, \Phi) \quad (2.16)$$

where  $\zeta$ ,  $n$  and  $Y_{l,m}$  are the Slater orbital exponent, principle quantum number and the angular part of the wave function, respectively.  $N$  is the normalization constant.

An alternative to the STOs is the use of GTO (Gaussian Type Orbital) basis sets [24], which are defined as :

$$\phi^{\text{GTO}} = N \exp(-\alpha r^2) Y_{l,m}(\theta, \phi) \quad (2.17)$$

where  $\alpha$  is the Gaussian orbital exponent.

The GTO functions are more suitable and mostly used nowadays. The integration of such functions is easier and can be performed simply. However, due to the different shape of the GTO, for the region near the nucleus, a combination of GTOs with different exponents is required to obtain equivalent results. Contraction is applied to avoid a too large size of the combination basis set.

According to the series of minimal basis sets termed "STO-NG" consists of expansions of STOs in terms of  $N$  Gaussian functions. One starts with a minimal basis set of one STO per AO, with the STO orbital exponents ( $\zeta$ ) fixed at values found to work well in calculations on small molecules. Each STO is then approximated as a linear combination of  $N$  Gaussian functions, where the coefficients in the linear combination and the Gaussian orbital exponents are chosen to give the best least square fit to the STO. Most commonly,  $N = 3$ , giving a set of contraction of GTOs called "STO-3G". Since a linear combination of three Gaussians is only an approximation to an STO, the STO-3G basis set gives results not quite as good as a minimal basis set STO calculation.

Another type of atomic orbital is the GLO (Gaussian Lobe Orbital) [25,26] which is the simplest form of basis functions. Its form is

$$\phi^{\text{GLO}} = N \exp(-\alpha r^2) \quad (2.18)$$

The angular part is omitted. Instead, GLOs are combined together to reproduce the conventional orbital shapes.

### 2.3 Basis Set Superposition Error (BSSE)

In calculation of the interaction energy for complex systems, the basis set employed should be sufficiently large and correctly express the multipole moments and the polarizability of the systems. In the case that insufficient basis set are used, an artificial basis set improvement will take place in the supersystem, leading to an error which is known as "*basis set superposition error*". In a system consisting of two molecules A and B which have the basis set  $\{\alpha\}$  and  $\{\beta\}$ , respectively, the error occurs when the basis set  $\{\beta\}$  contaminates  $\{\alpha\}$  in computing the energy of A or conversely, when  $\{\alpha\}$  contaminates  $\{\beta\}$  in computing the energy of B. This causes the interaction energy of the supersystem to be overestimated.

A method proposed by Boys and Bernardi [18] was carried out to estimate this error - the counterpoise (CP) method. The method is based on the determination of the subsystem energies using the same basis set as for the determination of the supersystem energy and can be presented as follows. Firstly, one computes the supermolecule AB with basis sets  $\{\alpha\}$  and  $\{\beta\}$  yielding an energy  $E(AB)$ . Secondly, one computes the energy of A with both  $\{\alpha\}$  and  $\{\beta\}$  obtaining an energy  $E'(A)$ . The operation is repeated for B computed with  $\{\beta\}$  and  $\{\alpha\}$  yielding the energy  $E'(B)$ . The counterpoise correction,  $\Delta e$ , can be defined as

$$\Delta e = [ E(A) - E'(A) ] + [ E(B) - E'(B) ] \quad (2.19)$$

where  $BSSE = \Delta e$

where  $E(A)$  and  $E(B)$  are simply the computations of A with  $\{\alpha\}$  alone and of B with  $\{\beta\}$  alone, respectively. And the counterpoise corrected interaction energy is

$$\Delta E^{CP} = \Delta E + \Delta e \quad (2.20)$$

where  $\Delta E$  is the interaction energy calculated from truncated basis set. It should be mentioned, however, that this correction gives the upper limit of a possible BSSE and hence cannot be regarded as absolutely correct value for the real BSSE occurring in a specific supermolecule system.