CHAPTER 2

QUANTUM MECHANICS THEORY ; AB INITIO

Many attempts have been made to obtain reliable approximated solutions to the nonrelativistic Schroedinger equation, resulting several levels of quantum mechanics calculations such as CI (Configuration Interaction), ab initio, CNDO (Completely Neglect of Differential Overlap), INDO (Intermediately Neglect of Differential Overlap) etc. In this chapter, one of the most popular approximation in field of quantum chemical, namely the Hartree-Fock-Roothaan " LCAO-MO-SCF " procedure (32,33) will be presented The term "ab initio" is synonymous for this method.

Ab Initio Molecular Orbital Theory

Any physically observable quantity can be calculated quantum mechanically if the corresponding Schroedinger equation can be solved.

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

According to this equation the total energy is obtained by

$$E = \langle \Psi | \hat{H} | \Psi \rangle \tag{2.2}$$

where is normalized total wave function of the system.

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

a) Define an approximate Hamiltonian operator (H) for the system.

b) Select some mathematical function $\Psi(q_1,q_2,q_3,...)$ as the trial wave functions, where $q_1,q_2,q_3,...$ are a finite number of variable parameters.

c) Minimize the total energy, (eq.2.2) with respect to variations of the parameters.

$$E = \frac{\int\Psi(q_1,q_2,q_3,...)\hat{H}\Psi(q_1,q_2,q_3,...)}{\int\Psi(q_1,q_2,q_3,...)\,\Psi(q_1,q_2,q_3,...)} \tag{2.3}$$

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

2.1 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 interactions plus the kinetic energy of the electrons and nuclei.

$$H = -\sum_{A} 1/2\, M_A \nabla_A^2 - 1/2\sum_{i} \nabla_i^2 - \sum_{A}\sum_{i} Z_A/r_{Ai} + \sum_{i<j}\sum 1/r_{ij} + \sum_{A<B}\sum Z_A Z_B/R_{AB} \tag{2.4}$$

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. The first term, the kinetic energy of the nuclei, can be neglected according to the Born-Oppenheimer approximation for fixed molecular geometry, since nuclei are much heavier than electrons and their motions are expected to be much slower. The last term, the replusion between the nuclei, is considered to be constant and can be put apart. Consequently, only the remaining terms should be considerd within the Hartree-Fock approximation.

$$H^{el} = H^{core}(i) + \sum_{i<j} 1/r_{ij} \qquad (2.5)$$

where

$$H^{core}(i) = -1/2\sum_{i} \nabla_i^2 - \sum_{A} Z_A/r_{iA}$$

H^{el} called the electronic Hamiltonian operator describing the motion of electrons in the field of the nuclei.

2.2 The Hartree-Fock Wave Functions

2.2.1 Independent Electron Model

The typical approximation to construct the many-electron wave function is the Independent Particle Approximation, based on one-electron spin orbitals (MOs) products of a spatial orbital and a one-electron orbital. The most convenient way to represent a trial wave function for a 2n-electron-closed shell system is to use a single-determinantal wave function, namely a Slater determinant (34-35) given in eq.(2.6), in order to serve the antisymetric principle.

$$\Psi = \frac{1}{\sqrt{2n!}} \left| \Psi_1(1)\bar{\Psi}_1(2)\Psi_2(3)\bar{\Psi}_2(4)\ldots\Psi_n(2n-1)\bar{\Psi}_n(2n) \right| \qquad (2.6)$$

the one electron spin orbital (MO) Ψ_i and $\bar{\Psi}_i$ respectively equal to $\Psi_i(\alpha)$ and $\Psi_i(\beta)$, where α and β being the spin functions.

This approximation automatically leads to a spin-up of the hamiltonian into a sum of one electron operators (Fock Operator)

$$H = \sum_i F_i = \sum_i H^c + \sum_{i<j} \sum (2J_i - K_j) \qquad (2.7)$$

where H^c is the core Hamiltonian and J_i and K_j are Coulomb and Exchange operators, respectively.

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

The approximate Hartree-Fock orbitals can be expanded in a set of basis functions (ϕ_μ) (36) as:

$$\psi_i = \sum_\mu c_{\mu i} \phi_\mu \qquad (2.8)$$

The functions are often associated with atomic orbitals of the component atoms and eq.(2.8) is then know as the Linear Combination of Atomic Orbital (LCAO) approximation. The optimal values of the coefficients $c_{\mu i}$ are determined by means of variation principle.

Basis Functions

As appearing in eq.(2.8), the accuracy of the MOs depends directly on number and quality of AOs , namely "basis set" in use. There are several types of atomic orbital-functions :

Slater Type Orbital (STO) is as follows :

$$\chi^{STO} = Nr^{(n-1)}\exp(-\beta r)Y_{l,m}(\theta,\phi) \qquad (2.9)$$

STO was originally introduced by Slater (37) as 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 is that only a few functions are needed for good description, STOs are more accurate representations of exact atomic orbitals but the integration of higher functions is largely time consuming.

Gaussian Type Orbital (GTO (38)) can be described as :

$$\chi^{GTO} = Nr^{(n-1)}\exp(-\beta r^2)Y_{l,m}(\theta,\phi) \qquad (2.10)$$

GTO is an alternative choice of STO and often used nowadays. The integration of this function is easier to solve. 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. Contraction is applied to avoid a too large size of the combined basis set. 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.

Gaussion Lobe Orbital (GLO(39,40)) are the most common form of basis functions ;

$$\chi^{GLO} = Nr^{(n-1)}\exp(-\beta r^{2}) \qquad (2.11)$$

Angular variables are omitted and GLOs located at different points in space are used to reproduce the conventional orbital symmetry. However, they also give sufficient accuracy.

The orbital reviews of basis set can be seen from ref.(63) and normally classified as:

a. Minimal basis sets

This size of basis set will contain only one basis function for an electron in each orbital of the system, for example, the basis set of NH_3 is 1s for H and 1s,2s and 2p for N

b. Extended basis sets

Extended basis sets are larger than minimal basis sets. The number of basis function respresenting each atomic orbital can be varied, higher than one. They may also include additional functions for existing electrons polarization functions, for example p for H or d and f functions for higher atoms. This functions give a more flexible shape to the molecular orbitals. If there are two functions for each such atomic orbital, then the basis is referred to as double-zeta quality. A basis which is of double-zeta quality and includes polarization functions is generally sufficient to give a close approximate to the " Hartree-Fock limit ".

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

Optimization of the total energy is performed by varying the values of the coefficients, $c_{\mu i}$, in eq.(2.8). The minimization procedure begins with the use of an initial guess of c 's to create a first matrix of the Fock operator F. The elements of the matrix F are :

$$F_{\mu\nu} = H^{core}_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) - 1/2(\mu\lambda|\nu\sigma) \qquad (2.12)$$

The matrix of the elements of the core hamiltonian, H^{core}, contains the one-electron hamiltonians, H^{c} , for electron moving in the field of nuclei :

$$H^{core}_{\mu\nu} = <\phi_{\mu}(i)|H^{c}|\phi_{\nu}(i)> \qquad (2.13)$$

The second term in eq.(2.12) is the two-electron part. The elements of the density matrix $P_{\lambda\sigma}$ and the two-electron integrals, $(\mu\nu|\lambda\sigma)$ and

$(\mu\sigma|\nu\lambda)$, are given by

$$P_{\lambda\sigma} = 2\sum_{i}^{occ} c_{\lambda i} c_{\sigma i} \qquad \text{(for closed shell system)} \qquad (2.14)$$

and

$$(\mu\nu|\lambda\sigma) = \iint \phi_{\mu}^{*}(1)\phi_{\nu}(1)\frac{1}{r_{12}}\phi_{\lambda}^{*}(2)\phi_{\sigma}(2)d\tau_{1}d\tau_{2} \qquad (2.15)$$

$$(\mu\sigma|\nu\lambda) = \iint \phi_{\mu}^{*}(1)\phi_{\sigma}(1)\frac{1}{r_{12}}\phi_{\nu}^{*}(2)\phi_{\lambda}(2)d\tau_{1}d\tau_{2} \qquad (2.16)$$

From the first approximation of Fock operator matrix F, a second approximation of C can be obtained by solving of the Roothaan equation

$$FC = SCE \qquad (2.17)$$

where F : Fock matrix

C : Coefficient

S : Overlap matrix

E : Eigen value matrix

S is containing the elements $<\phi_{\mu}|\phi_{\nu}>$. Since the coefficient matrix is contained in the Fock matrix, the equation cannot be solved straight forward. An iterative procedure is required. It is so-called SCF (Self Consistent Field) procedure.

The process is carried out iteratively until the total electronic energy of the system remain unchange. This is the core concept of the LCAO-MO-SCF procedure.