CHAPTER II

ELECTRONIC STRUCTURE CALCULATION

Quantum mechanical methods can be divided into two categories: *ab initio* and semiempirical methods. *Ab initio* methods include Hartree-Fock (HF), configuration interaction (CI) and also density functional theory (DFT). The discipline of *ab initio* quantum chemistry aims at studying systems at molecular level. However, a drawback is that *ab initio* calculations are extremely demanding in computer resources, especially for large systems. Semiempirical methods (*e.g.*, AM1, PM3 and NNDO) lie between *ab initio* and molecular mechanics (MM) methods. These calculations are computationally fast because many of the difficult integrals are neglected.

2.1 The Hartree-Fock Theory

The wave function Ψ is postulated to illustrate the state of a system in quantum mechanics and is a function of 3N coordinates of all particles. Systems of electrons can be described by their wave functions which are the solutions of the Schrödinger equation. The non-relativistic time-independent Schrödinger equation has a general form of

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

where E is the energy of the system and $\hat{H}$ is the Hamiltonian. The physical meaning of Ψ, given by Max Born, is that $|\Psi(r)|^2 dr$ is the probability of finding the particle in volume dr and then $\int_\infty |\Psi(r)|^2 dr = 1$, where r is the position vector of the particle.

The Hamiltonian operator for systems of n electrons and K nuclei is

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ext} + \hat{V}_{ee} + \hat{V}_{nn}$$

$$\hat{H} = -\sum_{i=1}^{n}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{K}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{n}\sum_{A=1}^{K}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j<i}\frac{1}{r_{ij}} + \sum_{A=1}^{K}\sum_{B<A}\frac{Z_A Z_B}{R_{AB}}, \tag{2.2}$$

where A and B designate nuclei, and i and j electrons. M_A is the mass, and Z_A is the atomic number of nucleus A. the ∇_i^2 and ∇_A^2 operators involve differentiation with respect to the coordinates of the ith electron and Ath nucleus. r_{iA} is the distance between the ith electron and nucleus A and r_{ij} is the distance between the ith and jth electrons, the distance between nucleus A and B represents by R_{AB}. The Hamiltonian operator in Equation 2.2 contains the kinetic energy of the electrons $\hat{T}_e$ and of the nuclei $\hat{T}_n$, the Coulomb repulsions among all the molecule's electrons $\hat{V}_{ee}$, the Coulomb attractions among the electrons and all of the molecule's nuclei $\hat{V}_{ext}$, and the Coulomb repulsions $\hat{V}_{nn}$ among all of the nuclei. The wave function and energy are determined by solving the Schrödinger equation.

2.2 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation (BO) is made when trying to solve Schrödinger's equation (Equation 2.1) for more complex systems than one or two electrons. Since nuclei are much heavier than electrons, they move much slower. To a good approximation, the electrons can adjust themselves almost simultaneously to changes in the position of the nuclei (R_A). So, we consider electrons in a molecule to be moving in the field of fixed nuclei. The electronic wave functions thus depend only on the positions but not on the momenta of nuclei. Therefore, the motion of electrons can be decoupled from the motion of the nuclei

$$\Psi\left(\{r_i\};\{R_A\}\right) = \psi_{elec}\left(\{r_i\};\{R_A\}\right)\psi_{nucl}\left(\{R_A\}\right). \tag{2.3}$$

In the BO approximation, the kinetic energy of the nuclei can be neglected and the repulsion between the nuclei can be considered to be constant. The electronic wave function ψ_{elec}, which describes the motion of electrons and depends parametrically on the coordinates of the nuclei, is the solution to a Schrödinger equation involving the electronic Hamiltonian,

$$\hat{H}_{elec}\psi_{elec} = E_{elec}\psi_{elec}. \tag{2.4}$$

Therefore, only the $\hat{T}_e$, $\hat{V}_{ext}$ and $\hat{V}_{ee}$ terms remain in the electronic Hamiltonian operator $\hat{H}_{elec}$, describing the motion of n electrons in the field of nuclei, *i.e.*,

$$\hat{H}_{elec} = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{n} \sum_{A=1}^{K} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{n} \sum_{j<i}^{n} \frac{1}{r_{ij}}.$$

(2. 5)

From now on the electronic problem of Equation 2.4 will be the only focus and therefore electronic Hamiltonian $\hat{H}$ and the electronic wave functions ψ will be written without subscript labels.

The wave functions ψ can be solved exactly only for one electron systems, *e.g.*, hydrogen and H_2^+. Such a many-electron wave function is termed a Hartree product. The electron-one is described by the spin orbital ϕ_1 and then electron-two being described by the orbital ϕ_2, *etc*. In the Hartree Approximation the *n*-electron wave function Ψ^H is written as a product of one-electron wave functions ϕ_i,

$$\psi^H (x_1, x_2, ... x_n) = \phi_1(x_1)\phi_2(x_2)..\phi_n(x_n)$$

(2. 6)

Using the Hartree product, the energy, E, is just the sum of the orbital energies ϵ_i.

$$E = \epsilon 1 + \epsilon 2 + ... + \epsilon_n$$

(2. 7)

Hartree product wave functions suffer from several major flaws that serve to make them physically unrealistic. Hartree products take no account of the indistinguishability of electrons.

Introducing the Pauli Exclusion Principle, the wave function of electrons must be antisymmetric with respect to the interchange of any two electrons. One general way to ensure that this happens is to write the wave function as a Slater determinant of spin orbitals, $\phi_i(x_i)$,

$$\psi(x_1, x_2, \ldots x_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \cdots & \phi_n(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \cdots & \phi_n(x_1) \\ \vdots & \vdots & & \vdots \\ \phi_1(x_n) & \phi_2(x_n) & \cdots & \phi_n(x_n) \end{vmatrix} \qquad (2.8)$$

The factor $\frac{1}{\sqrt{n!}}$ is normalization constant. The antisymmetric property of a Slater determinant is $\left| \ldots \phi_i \ldots \phi_j \ldots \right\rangle = - \left| \ldots \phi_j \ldots \phi_i \ldots \right\rangle$.

2.3 The Hartree-Fock Equations

The Hartree-Fock method is based on the variational theorem in quantum mechanics. Hartree-Fock considers a single determinant formed from electrons's orbitals as a possible approximation to the ground state of the n-electron system described by an electronic Hamiltonian $\hat{H}$. According to the variation principle, the best orbitals are those which minimize the electronic energy E, which is defined by

$$\begin{aligned} E &= \langle \psi | \hat{H} | \psi \rangle \\ &= \sum_a^N \langle a | \hat{h} | a \rangle + \frac{1}{2} \sum_{a,b}^N \left(\langle ab | ab \rangle - \langle ab | ba \rangle \right) \cdot \\ &= \sum_a^N h_{aa} + \tfrac{1}{2} \sum_{a,b}^N \left(J_{ab} - K_{ab} \right) \end{aligned} \qquad (2.9)$$

here $\hat{h}$ is a core-Hamiltonian for an electron, describing its kinetic energy and potential energy in the field of the nuclei and J_{ab} and K_{ab} are the Coulombic energy and exchange energy, respectively.

For a given single determinant $|\psi\rangle \equiv |\phi_1 \phi_2 \ldots \phi_a \phi_b \ldots \phi_n\rangle$ the energy is a function of the orbitals $\{\phi_i\}$. We need to minimize E with respect to the orbitals, subject to the constraints that the orbitals remain orthonormal,

$$\int dx(1) \phi_a^*(1) \phi_b(1) = \langle \phi_a | \phi_b \rangle = \delta_{ab}, \qquad (2.10)$$

Using the variational principle, the best orbitals that minimize E are obtained from the Hartree-Fock equation written as

$$[\hat{h}(1) + \sum_{b \neq a} \hat{J}_b(1) - \sum_{b \neq a} \hat{K}_b(1)]\phi_a(1) = \epsilon_a \phi_a(1).$$

(2. 11)

The Coulomb operator, corresponding to the classical electrostatic interaction, is defined by

$$\hat{J}_b(1)\phi_a(1) = \left[\int dx_2 \phi_b^*(2) r_{12}^{-1} \phi_b(2)\right]\phi_a(1)$$

(2. 12)

and the exchange term is defined by

$$\hat{K}_b(1)\phi_a(1) = \left[\int dx_2 \phi_b^*(2) r_{12}^{-1} \phi_a(2)\right]\phi_b(1)$$

(2. 13)

So the Hartree-Fock equation (Equation 2.11) can be, then, re-written as

$$\hat{F}|\phi_a\rangle = \epsilon_a|\phi_a\rangle.$$

(2. 14)

The Fock operator, $\hat{F}$, is an effective one-electron operator, describing the kinetic energy of an electron, the attraction of all the nuclei and the repulsion induced from the mean field of all the other electrons,

$$\hat{F}(1) = \hat{h}(1) + \sum_{b=1}^{N} \hat{J}_b(1) - \hat{K}_b(1).$$

(2. 15)

Since the Fock operator has a functional dependence, through the Coulomb and exchange operators, on the solution of $\{\phi_i\}$ of the pseudo-eigenvalue equation, thus the Hartree-Fock equations are really nonlinear equations and will need to be solved by iterative procedures.

Introducing the MO-LCAO approach, a spatial Molecular Orbital (MO) is expanded as a linear combination of Atomic Orbitals (AO).

$$\phi_i = \sum_{\nu}^{M} c_{\nu i} \chi_{\nu} \qquad (2.16)$$

In Equation 2.16, the unknown HF orbitals ϕ_i are written as a linear expansion in M known basis function χ_{ν}. If the set of χ_{ν} is complete, it would be an exact expansion. Inserting this linear combination into the Fock equation, we obtain

$$\hat{F} \sum_{\nu}^{M} c_{\nu i} \chi_{\nu} = \epsilon_i \sum_{\nu}^{M} c_{\nu i} \chi_{\nu} \qquad (2.17)$$

Multiplying from the left by a specific basis function and integrating yields the *Roothaan-Hall equations* which can be written as

$$\sum_{\nu} c_{\nu i} \int dr_1 \chi_{\mu}^{*}(1) \hat{F}(1) \chi_{\nu}(1) = \epsilon_i \sum_{\nu} c_{\nu i} \int dr_1 \chi_{\mu}^{*}(1) \chi_{\nu}(1) \qquad (2.18)$$

The Roothaan equations can be written in a short form of

$$\sum_{\nu} F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i} \quad i = 1, 2, 3 \dots M \qquad (2.19)$$

Two matrices are defined here as the overlap matrix **S** and the Fock matrix **F**,

$$F_{\mu\nu} = \int dr_1 \chi_{\mu}^{*}(1) \hat{F} \chi_{\nu}(1) = \langle \chi_{\mu} | \hat{F} | \chi_{\nu} \rangle \qquad (2.20)$$

$$S_{\mu\nu} = \int dr_1 \chi_{\mu}^{*} \chi_{\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle. \qquad (2.21)$$

If a system is closed-shell and n electrons, the sum over N occupied spin orbitals includes an equal sum over those with the α spin function and those with the β spin function, *i.e.*, $\sum_{b}^{N} \rightarrow \sum_{b(\alpha)}^{N/2} + \sum_{b(\beta)}^{N/2}$, the Fock operator, then, has a form of

$$\hat{F}(1) = \hat{h}(1) + \sum_{a=1}^{N/2} 2\hat{J}_a(1) - \hat{K}_a(1).$$ (2. 22)

The Fock matrix, F, is the matrix representation of the Fock operator in the basis $\{\chi_\mu\}$, i.e.,

$$F_{\mu\nu} = \int dr_1 \chi_\mu^*(1)\hat{h}(1)\chi_\nu(1) + \sum_a^{N/2} \int dr_1 \chi_\mu^*(1)[2\hat{J}_a(1) - \hat{K}_a(1)]\chi_\nu(1)$$

$$= H_{\mu\nu}^{core} + \sum_a^{N/2} 2\langle \mu a | \nu a \rangle - \langle \mu a | a \nu \rangle$$ (2. 23)

where a core-Hamiltonian matrix is involving the one-electron operator describing the kinetic energy and the nuclear attraction of an electron. By including the LCAO, then

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_a^{N/2} \sum_{\lambda\sigma} c_{\lambda a} c_{\sigma a}^* \left[2\langle \mu\sigma | \nu\lambda \rangle - \langle \mu\sigma | \lambda\nu \rangle \right]$$

$$= H_{\mu\nu}^{core} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[\langle \mu\sigma | \nu\lambda \rangle - \tfrac{1}{2} \langle \mu\sigma | \lambda\nu \rangle \right]$$ (2. 24)

$$\mathbf{P}_{\mu\nu} = 2\sum_a^{N/2} c_{\mu a} c_{\nu a}^*$$ (2. 25)

P is the density matrix. The Roothaan equations are nonlinear and can be written in a matrix form of

$$\mathbf{FC} = \mathbf{SC\epsilon}$$ (2. 26)

where C is an $M \times M$ square matrix of the expansion coefficients $c_{\nu i}$, and ϵ is a diagonal matrix of the orbital energies ϵ_i. The procedure used to solve for the MO coefficients $c_{a i}$ is called the Self-Consistent-Field (SCF) method which is presented in Figure 2.1. By making an initial guess at the spin orbitals, one can calculate the average field seen by each electron and then solve the eigenvalue equation for a new set of spin orbitals.

Using these new spin orbitals, one can obtain new fields and repeat the procedure until self-consistency is reached.

The SCF procedure can be, then, summarized as follow:

1. Specify a molecule and a basis set $\{ \chi_v \}$.

2. Calculate all required integrals ($S_{\mu v}$, $H_{\mu v}^{core}$ and $\langle \mu \lambda | v \sigma \rangle$).

3. Orthogonolize the overlap matrix S.

4. Obtain a guess at the density matrix P.

5. Calculate the Fock matrix and P, and two electron integrals $\langle \mu \lambda | v \sigma \rangle$.

6. Diagonalize the Fock matrix to obtain C and ϵ.

7. Form a new density matrix P from C.

8. Determine whether the procedure has converged. If not, return to step (5) with a new P.

If the procedure has converged, use the resultant solution to calculate expectation values.

By repeating the calculation for different nuclear coordinates the potential energy surface for nuclear motion can be explored. The equilibrium geometry of a molecule can be determined by finding a set of nuclei's positions which minimize the total energy
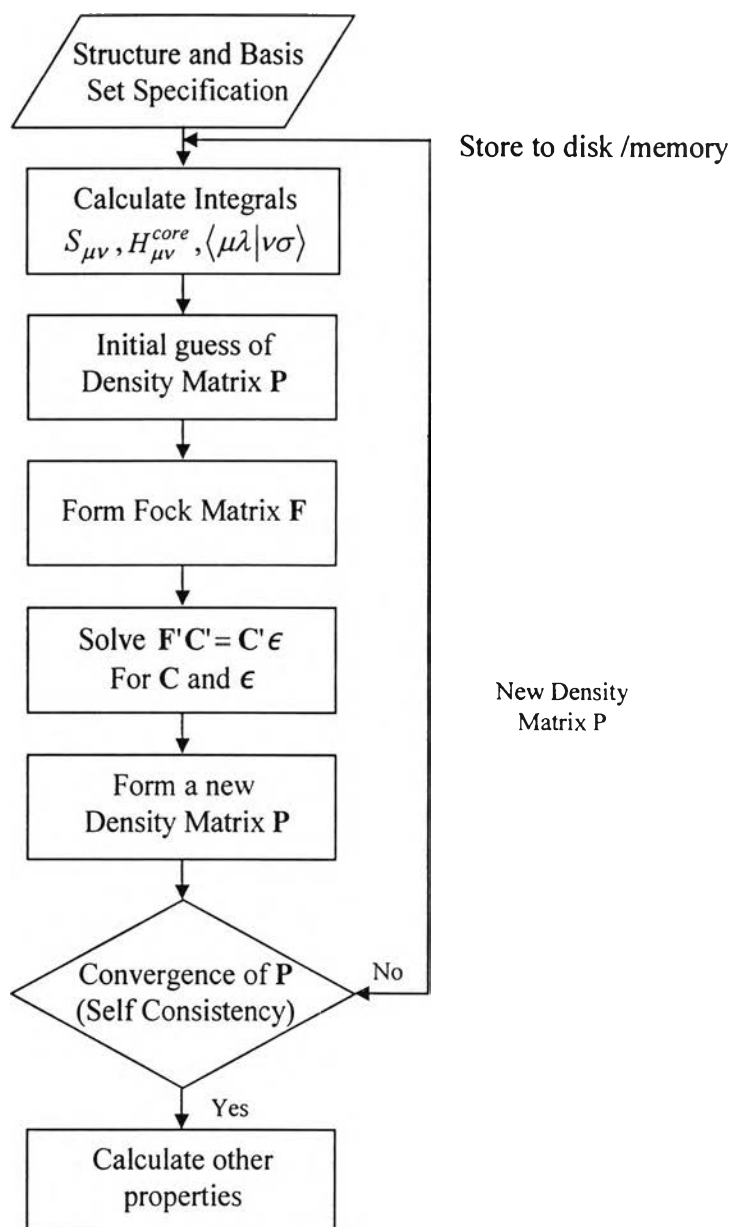
Figure 2.1 A self-consistent field procedure used to solve the wave functions of the Schrödinger equation.

2.4 Semiempirical

Semiempirical methods are simplified versions of Hartree-Fock theory using empirical corrections in order to improve performance. Within this construction, certain pieces of information, such as two electron integrals, are approximated or completely omitted. In order to correct for the errors introduced by omitting part of the calculation, the method is parameterized, by curve fitting in a few parameters or numbers, in order to give the best possible agreement with experimental data.

The most frequently used methods are MNDO, AM1, and PM3. They are all based on the *Neglect of Differential Diatomic Overlap (NDDO)* [63] integral approximation, while older methods use simpler integral schemes such as CNDO and INDO. A number of additional approximations are made to speed up calculations and a number of parameterized corrections are made in order to correct for the approximate quantum mechanical model. How the parameterization is performed to characterize the particular semiempirical method. For the MNDO, AM1, and PM3 the parameterization is performed such that the calculated energies are expressed as heats of formations instead of total energies.

The approximation in NDDO is only neglect differential overlap between atomic orbitals on different atoms. So, all of the two-electron integrals of the form $\langle \mu\sigma|\nu\lambda \rangle$ where μ and ν are on the same atom and λ and σ are also the same atom are retained. The Fock matrix elements become

$$F_{\mu\mu} = H_{\mu\mu}^{core} + \sum_{\lambda\, on\, A} \sum_{\sigma\, on\, A} \left[P_{\lambda\sigma}\langle \mu\sigma/\mu\lambda \rangle - \frac{1}{2}P_{\lambda\sigma}\langle \mu\sigma/\lambda\mu \rangle \right]$$
$$+ \sum_{B\neq A} \sum_{\lambda\, on\, B} \sum_{\sigma\, on\, B} P_{\lambda\sigma}\langle \mu\sigma/\mu\lambda \rangle \qquad (2.27)$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda\, on\, A} \sum_{\sigma\, on\, A} \left[P_{\lambda\sigma}\langle \mu\sigma/\nu\lambda \rangle - \frac{1}{2}P_{\lambda\sigma}\langle \mu\sigma/\lambda\nu \rangle \right]$$
$$+ \sum_{B\neq A} \sum_{\lambda\, on\, B} \sum_{\sigma\, on\, B} P_{\lambda\sigma}\langle \mu\sigma/\nu\lambda \rangle \quad ; \mu \text{ and } \nu \text{ both on A} \quad (2.28)$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} - \frac{1}{2} \sum_{\lambda\, on\, B} \sum_{\sigma\, on\, B} P_{\lambda\sigma}\langle \mu\lambda/\sigma\nu \rangle \, ; \mu \text{ on A and } \nu \text{ on B} \quad (2.29)$$

AM1, or Austin Model 1, is based on the NDDO integral approximation. It is a generalization of the modified neglect of differential diatomic overlap approximation. AM1 was developed by Michael Dewar and co-workers [64] and published in 1985. AM1 is an attempt to improve the MNDO model by reducing the repulsion of atoms at close separation distances. The atomic core-atomic core terms in the MNDO equations were modified through the addition of off-center attractive and repulsive Gaussian functions.

The advantage of semiempirical calculations is that they are much faster than the *ab initio* calculations.

The disadvantage of semiempirical calculations is that the results can be inconsistent. If the molecule being computed is similar to molecules in the data base used to parameterize the method, then the results may be very good. If the molecule being computed is significantly different from anything in the parameterization set, the answers may be very poor.

Semiempirical calculations have been very successful in the description of organic chemistry, where there are only a few elements used extensively and the molecules are of moderate size. However, semiempirical methods have been devised specifically for the description of inorganic chemistry as well.