

CHAPTER II

QUANTUM CHEMICAL METHODS

The theoretical model discussed in this chapter is based on *molecular orbital (MO) theory*. This treats the electron distribution and motion of individual electrons using one-electron functions termed *spin orbitals*. The spin orbitals are allowed to spread freely throughout the molecule. These orbitals are then brought together to form a suitable *many-electron wavefunction* Ψ which is the simplest MO approximation. It is described as the *linear combination of atomic orbitals (LCAO) approximation*. The *variational theorem* is employed in minimizing the total electronic energy from the many-electron wavefunction. This results in the optimal energy which is as close as possible to the energy corresponding to the exact values.

2.1 The Schrödinger Equation

It should be noted that any physically observable molecular properties can be calculated quantum mechanically when such properties are obtained by solving the Schrödinger partial differential equation (30),

$$H\Psi = E\Psi \quad [2.1],$$

where H is the *Hamiltonian* operator for a system. It is a sum of all possible Coulombic energy operators and kinetic energy operators of both nuclei and electrons, and Ψ is the *wavefunction* of the system.

The only solutions of [2.1] that are physically acceptable are those with the appropriate symmetry under interchange of identical particles. For electrons, which are fermions, the wavefunction must be *antisymmetric* with respect to the interchange of the coordinates of any pair of electrons. This is termed the *antisymmetric principle*, which is a statement of the familiar *Pauli exclusion principle* (31).

The total Hamiltonian in equation [2.1] is simplified and known as the *Born-Oppenheimer approximation* (32). The approximation involves (i) considering the repulsion between the nuclei as a constant and (ii) separating the kinetic energy of the nuclei due to the much slower movement of the nuclei relative to electrons.

In the framework of the Born-Oppenheimer approximation, the molecular wavefunction is written as the product of a nuclear wavefunction and an electronic wavefunction which depends on the nuclear coordinates, R . The many-electrons wavefunction is obtained by solving the Schrödinger equation for electrons in the field of fixed nuclei,

$$H^{\text{elec}} \Psi^{\text{elec}}(r, R) = E^{\text{elec}}(R) \Psi^{\text{elec}}(r, R) \quad [2.2].$$

Here, Ψ^{elec} is the electronic wavefunction, which depends on the electronic coordinates, r , as well as on the nuclear coordinates. In atomic units, the electronic Hamiltonian operator, H^{elec} , corresponds to motion of electrons only in the field of fixed nuclei and is

$$H^{\text{elec}} = -\frac{1}{2} \sum_i^{\text{electrons}} \nabla_i^2 - \sum_i^{\text{electrons}} \sum_s^{\text{nuclei}} \frac{Z_s}{r_{is}} + \sum_i^{\text{electrons}} \sum_{<j}^{\text{electrons}} \frac{1}{r_{ij}} \quad [2.3].$$

2.2 Molecular Orbital Theory

Molecular orbital theory is an approach to molecular quantum mechanics which uses one-electron wavefunctions or *orbitals* to approximate the full wavefunction. To describe the distribution of an electron completely, the dependence on the spin coordinates also has to be included. The complete wavefunction for a single electron known as *spin orbital* is the product of a molecular orbital and a spin wavefunction.

For a $2n$ -electron system in its ground state, with n orbitals doubly occupied, the simplest type of closed-shell wavefunction appropriate for the description can be written as a sum of products of spin orbitals of the form,

$$\Psi_{\text{product}} = \chi_1(1)\chi_2(2)\dots\chi_{2n}(2n) \quad [2.4],$$

or as the product of *spatial wavefunctions* and *spin wavefunctions* of the form,

$$\Psi_{\text{product}} = \varphi_1(1)\alpha(1)\varphi_1(2)\beta(2)\dots\varphi_n(2n-1)\alpha(2n-1)\varphi_n(2n)\beta(2n) \quad [2.5],$$

where $\chi_i(i)$ is the i th spin orbital of electron i , $\varphi_i(j)$ is the i th spatial orbital of electron j , and $\alpha(i)$ and $\beta(j)$ are the spin-up and spin-down wavefunctions of electron i and j , respectively. The spin orbitals may be arranged in a *determinantal wavefunction*

$$\Psi = \left(\frac{1}{\sqrt{(2n)!}} \right) \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \dots & \varphi_n(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \varphi_1(2)\beta(2) & \dots & \varphi_n(2)\beta(2) \\ \vdots & \vdots & & \vdots \\ \varphi_1(2n)\alpha(2n) & \varphi_1(2n)\beta(2n) & \dots & \varphi_n(2n)\beta(2n) \end{vmatrix} \quad [2.6].$$

Such determinants of spin orbitals are referred to as a *Slater determinant* (33).

In practice, a further restriction is imposed, requiring that the individual molecular orbitals be expressed as linear combinations of a finite set of N prescribed one-electron functions known as *basis functions*. An individual orbital φ_i can be written as

$$\varphi_i = \sum_{\mu=1}^N c_{\mu i} \Phi_{\mu} \quad [2.7].$$

where $c_{\mu i}$ are the *molecular orbital expansion coefficients*.

In molecular orbital theory, atomic orbitals of constituent atoms are used as basis functions. This treatment is called as the *linear combination of atomic orbitals (LCAO) method* (34).

In carrying out numerical calculations with molecular orbitals, it is necessary to have a convenient analytical form for the atomic orbitals of each type of atom in the molecule. There are two types of atomic basis function popularly in

use. They are the *Slater Type Orbital* (STO) (35) and the *Gaussian Type Orbital* (GTO) (36). The STO function has the form,

$$u_{\alpha,n,l,m}(r, \theta, \varphi) = [(2n)!]^{-1/2} (2\alpha)^{n+1/2} r^{n-1} e^{-\alpha r} Y_{l,m}(\theta, \varphi) \quad [2.8],$$

where α is the orbital exponent, n is the principle quantum number and $Y_{l,m}(\theta, \varphi)$ is a spherical harmonic. And the GTO's function is,

$$g(\alpha, n, l, m)(r, \theta, \varphi) = N r^{n-1} e^{-\alpha r^2} Y_{l,m}(\theta, \varphi) \quad [2.9].$$

In this form the electron-electron integrals can be evaluated more easily. Using the GTO functions but omitting their angular part and locating the functions off-center leads to the *Gaussian Lobe Orbitals* (GLO) which allow a simple analytical integral calculation with sufficient accuracy for large systems (37,38).

2.3 Self-Consistent Field Procedure

This procedure allows molecular orbitals to be derived from their own effective potential. This involves the use of the variational method that may be applied to determine optimum orbitals in single-determinant wavefunctions. The variational equations are

$$\frac{\partial E'}{\partial c_{\mu i}} = 0 \quad (\text{all } \mu, i) \quad [2.10].$$

A procedure of successive approximation is described as follows:

- (1) A guess is made for the set of molecular orbital expansion coefficients $c_{\mu i}$ (as in equation 2.7) to construct a trial molecular orbitals.
- (2) The first matrix of the *Fock operator*, F , is constructed using the first guess of c 's. The elements of the matrix, $F_{\mu\nu}$, are

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda=1}^N \sum_{\sigma=1}^N P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \quad [2.15].$$

The matrix of the elements of the core Hamiltonian, $H_{\mu\nu}^{\text{core}}$, contains the elements for the core-electron Hamiltonian, $H^{\text{core}}(1)$, for electrons moving in the field of nuclei:

$$H_{\mu\nu}^{\text{core}} = \int \Phi_{\mu}^*(1) H^{\text{core}}(1) \Phi_{\nu}(1) dx_1 dy_1 dz_1, \quad ,$$

where

$$H^{\text{core}}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}} \quad [2.12].$$

While the elements of one-electron *density matrix*, $P_{\lambda\sigma}$ are defined as

$$P_{\lambda\sigma} = 2 \sum_{i=1}^{\text{occ}} c_{\lambda i}^* c_{\sigma i} \quad [2.13],$$

the summation is over *occupied* molecular orbitals only. The quantities $(\mu\nu|\lambda\sigma)$ appearing in [2.11] are *two-electron repulsion integrals*:

$$(\mu\nu|\lambda\sigma) = \iint \Phi_{\mu}^*(1) \Phi_{\nu}(1) \frac{1}{r_{12}} \Phi_{\lambda}^*(2) \Phi_{\sigma}(2) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \quad [2.14].$$

- (3) From the first approximation of the Fock operator matrix \mathbf{F} , the new matrix of \mathbf{C} can be obtained by solving the *Roothaan-Hall equations* (34,39) that are

$$\sum_{\nu=1}^N (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0 \quad (\mu = 1, 2, 3, \dots, N) \quad [2.16],$$

with the normalization conditions,

$$\sum_{\mu=1}^N \sum_{\nu=1}^N c_{\mu i}^* S_{\mu\nu} c_{\nu i} = 1 \quad [2.17],$$

where $S_{\mu\nu}$ are the elements of *overlap matrix*,

$$S_{\mu\nu} = \int \Phi_{\mu}^*(1) \Phi_{\nu}(1) dx_1 dy_1 dz_1 \quad [2.18],$$

The Roothaan-Hall equations [2.16] can be written more compactly as the single matrix equation

$$\mathbf{FC} = \mathbf{SCE} \quad [2.19],$$

which \mathbf{C} is a $N \times N$ square matrix of the expansion coefficients $c_{\mu i}$ and \mathbf{E} is a diagonal matrix of the orbital energies ε_i .

The whole process is repeated until there is a consistency in the coefficients \mathbf{C} within a given limit, usually 10^{-7} Hartree. Since the effective potential for every orbital change with every iteration. The effective field corresponding to this cycle is called the self consistent field for the orbital, and this powerful method of tackling the many electron problem is called the *Self-Consistent Field procedure*.

2.4 Mulliken Population Analysis

Using the final set of linear expansion coefficients, the electronic distribution of constituent atoms can be analyzed. Here, we employed the *Mulliken population analysis* (40) since all terms needed in the analysis have also already been obtained from methods described earlier. The total number of electrons in the system can be written as

$$2n = \sum_{\mu, \nu}^{\text{occ}} P_{\mu\nu} S_{\mu\nu} \quad [2.21].$$

The quantity $P_{\mu\nu} S_{\mu\nu}$ may be considered to represent the electronic population of the atomic overlap distribution $\Phi_{\mu} \Phi_{\nu}$, and diagonal terms such as $P_{\mu\mu} S_{\mu\mu}$ may be associated with the net electronic charges residing in the orbital Φ_{μ} . An indication of contributions to chemical binding is given by off-diagonal terms $P_{\mu\nu} S_{\mu\nu}$ with Φ_{μ} and Φ_{ν} centered on different atoms.

2.5 Basis Set Superposition Error (BSSE)

In calculating the interaction energy for a complex system, 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 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 sets $\{\alpha\}$ and $\{\beta\}$, respectively, the error occurs when the basis set $\{\alpha\}$ contaminates $\{\beta\}$ in computing the energy of A or conversely, when $\{\beta\}$ contaminates $\{\alpha\}$ in computing the energy of B. This causes the interaction energy of the supersystem to be overestimated.

The counterpoise (CP) method proposed by Boys and Bernardi (41) was carried out to estimate this error. 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. First, the energy of

supermolecule AB with basis sets $\{\alpha\}$ and $\{\beta\}$ is computed, yielding an energy $E(AB)$. Second, the computation of the energy of A with both $\{\alpha\}$ and $\{\beta\}$, disregarding the nuclear charge in B, is performed to obtain an energy $E'(A)$. The operation is repeated for B with $\{\alpha\}$ and $\{\beta\}$ as basis set, yielding the energy $E'(B)$. The counterpoise correction, Δe , can be defined as

$$\Delta e = [E(A) - E'(A)] + [E(B) - E'(B)] \quad [2.22],$$

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

$$\Delta E^{CP} = \Delta E + \Delta e \quad [2.23],$$

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

$$\Delta E = E(AB) - E(A) - E(B) \quad [2.24].$$

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