



CHAPTER II

QUANTUM MECHANIC THEORY

The key for theoretical chemistry is molecular mechanics. This is the science relating molecular properties to the motion and interactions of electrons and nuclei. Soon after its formulating in 1925 (13), it became clear that solution of the Schrödinger differential equation could, in principle, lead to direct quantitative prediction of most chemical phenomena. Such a procedure constitutes an *ab initio* approach to chemistry, independent of any experimental determinations.

The most commonly used molecular quantum mechanical methods can be classified as either *ab initio* or *semi-empirical* types. The *semi-empirical* methods use a simpler Hamiltonian and use parameters whose values are adjusted to fit experimental data or the results of *ab initio* calculations. In contrast, an *ab initio* calculation uses the full Hartree-Fock Hamiltonian and does not use experimental data other than the values of the fundamental physical constants.

In practice, the Schrödinger equation has to be replaced by approximate mathematical models for which the possibility of solution exists. The advent of powerful digital computers and of increasingly efficient computer programs has led to significant progress in recent years, both in the development of ever more sophisticated approximate quantum mechanical models and in the application of these models to problems of chemical significance. It is fair to say that theory has now advanced sufficiently far as to provide the chemist with an alternative independent approach to his subject.

Ab Initio Calculation Method

2.1 The Schrödinger Equation

The energy and many properties of a stationary state of a molecule can be calculated quantum mechanically by solution of the Schrödinger partial differential equation.

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

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.

An *ab initio* computation has been concerned with the determination of molecular wavefunctions and properties in the framework of the Born-Oppenheimer approximation, the molecular wavefunction Φ is written as the product of a nuclear wavefunction X and an electronic wavefunction Ψ which depends on the nuclear coordinates R as parameters.

$$\Phi(r, R) = \Psi(r, R)X(R) \quad (2.2)$$

The many-electrons wavefunction is obtained by solving the time-independent electronic Schrödinger equation.

$$H^{\text{elec}} \Psi^{\text{elec}}(r, R) = E^{\text{elec}}(R) \Psi^{\text{elec}}(r, R) \quad (2.3)$$

Where Ψ^{elec} is the electronic wavefunction, which depends on the electronic coordinates, r , as well as on the nuclear coordinates R ; E^{elec} is the electronic energy and H^{elec} is the electronic Hamiltonian operator.

2.2 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 kinetic energy of the electrons and nuclei.

$$H = -\sum_A^{\text{nuclei}} \frac{1}{2M} \nabla_A^2 - \frac{1}{2} \sum_i^{\text{electrons}} \nabla_i^2 - \sum_i^{\text{electrons}} \sum_A^{\text{nuclei}} \frac{Z_A}{r_{iA}} + \sum_i^{\text{electrons}} \sum_{<j}^{\text{electrons}} \frac{1}{r_{ij}} + \sum_A^{\text{nuclei}} \sum_{<B}^{\text{nuclei}} \frac{Z_A Z_B}{R_{AB}} \quad (2.4)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (2.5)$$

According to the *Born-Oppenheimer approximation* (14), the total Hamiltonian in equation (2.4) will be simplified. *The first term*, the kinetic energy of the nuclei, can be neglected due to the much slower motions of the nuclei relative to electrons, since nuclei are much heavier than electrons. *The last term*, the repulsion between the nuclei, is considered as a constant in this case and can be put apart. Consequently, only the remaining terms should be considered within the Hartree-Fock approximation.

$$H^{\text{elec}} = -\frac{1}{2} \sum_i^{\text{electrons}} \nabla_i^2 - \sum_i^{\text{electrons}} \sum_A^{\text{nuclei}} \frac{Z_A}{r_{iA}} + \sum_i^{\text{electrons}} \sum_{<j}^{\text{electrons}} \frac{1}{r_{ij}} \quad (2.6)$$

when

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



therefore

$$H^{\text{elec}} = H^{\text{core}}(i) + \sum_i^{\text{electrons}} \sum_{<j}^{\text{electrons}} \frac{1}{r_{ij}} \quad (2.8)$$

H^{core} is a one-electronic Hamiltonian operator, and H^{elec} called the electronic Hamiltonian operator describing the motion of electrons in the field of the nuclei.

2.3 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. A molecular orbital, $\varphi(x,y,z)$, is a function of the cartesian coordinates x,y,z of single electron. The square of the wavefunction, φ^2 , is interpreted as a measure of the probability distribution of the particles within the molecule. To describe the distribution of an electron completely, the dependence on the spin coordinates, ξ , also has to be included.

The complete wavefunction for a single electron is the product of a molecular orbital and a spin wavefunction, $\varphi(x,y,z)\alpha(\xi)$ or $\varphi(x,y,z)\beta(\xi)$. It is termed a *spin orbital*, $\chi(x,y,z,\xi)$.

It might appear that the simplest type of closed-shell wavefunction appropriate for the description of an n -electron system could be written as a sum of a product of spin orbitals.

$$\Psi_{\text{product}} = \chi_1(1)\chi_2(2)\dots\dots\dots\chi_n(n) \quad (2.9)$$

where $\chi_i(i)$ is written for $\chi_i(x_i, y_i, z_i, \xi_i)$, the spin orbital of electron i .

However, such a wavefunction is not acceptable, as it does not have the property of antisymmetry if the coordinates of electrons i and j are interchanged in this wavefunction. To ensure antisymmetry and to guarantee with Pauli exclusion principle, the electronic wavefunction is written as Slater determinant (15).

$$\Psi = \left(\frac{1}{\sqrt{n!}} \right) \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_{n/2}(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_{n/2}(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(n) & \chi_2(n) & \dots & \chi_{n/2}(n) \end{vmatrix} \quad (2.10)$$

For the closed-shell ground state of a molecule, with n (even) electrons, doubly occupying $n/2$ orbitals, can be written down a full many-electron molecular orbital wavefunction.

$$\Psi = \left(\frac{1}{\sqrt{n!}} \right) \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \dots & \varphi_{n/2}(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \varphi_1(2)\beta(2) & \dots & \varphi_{n/2}(2)\beta(2) \\ \vdots & \vdots & & \vdots \\ \varphi_1(n)\alpha(n) & \varphi_1(n)\beta(n) & \dots & \varphi_{n/2}(n)\beta(n) \end{vmatrix} \quad (2.11)$$

To construct molecular orbitals for electrons in a molecular system, a linear combination of atomic orbitals (LCAO-MO method) , known as *basis functions*, is used. An individual orbital φ_i can be written as

$$\varphi_i = \sum_{\mu=1}^N c_{\mu i} \Phi_{\mu} \quad (2.12).$$

where Φ_{μ} are the atomic orbitals, and $c_{\mu i}$ 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 $c_{\mu i}$ are determined by means of the variation principle.

2.4 Self-Consistent Field Procedure

The variational method starts with the selection of the basis set in order to construct a suitable molecular orbitals. Then the molecular orbital expansion coefficients $c_{\mu i}$ (as in equation 2.12) may then be adjusted to minimize the expectation value of the energy E' , which is always greater than the exact energy. The resulting value of E' will then be as close to the exact energy E as is possible within the limitations imposed by: (a) the single-determinant wavefunction, and (b) the particular basis set employed. Hence, the *best* single-determinant wavefunction, in an energy sense, is found by minimizing E' with respect to the coefficients $c_{\mu i}$. This implies the variational equations

$$\frac{\partial E'}{\partial c_{\mu i}} = 0 \quad (\text{all } \mu, i) \quad (2.13).$$

For closed-shell system, the variational condition (2.13) leads to a set of algebraic equations for $c_{\mu i}$ that were derived independently for the closed-shell wavefunction (2.6) by Roothaan (16) and by Hall (17). The *Roothaan-Hall equations* are

$$\sum_{\nu=1}^N (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0 \quad (\mu = 1, 2, 3, \dots, N) \quad (2.14)$$

with the normalization conditions

$$\sum_{\mu=1}^N \sum_{\nu=1}^N c_{\mu i}^* S_{\mu\nu} c_{\nu i} = 1 \quad (2.15)$$

Here, ε_i is the *one-electron energy* of the molecular orbital φ_i , $S_{\mu\nu}$ are the elements of an $N \times N$ matrix named the *overlap matrix*,

$$S_{\mu\nu} = \int \Phi_{\mu}^*(1) \Phi_{\nu}(1) dx_1 dy_1 dz_1 \quad (2.16)$$

and $F_{\mu\nu}$ are the elements of another $N \times N$ matrix, the *Fock matrix*,

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda=1}^N \sum_{\sigma=1}^N P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \quad (2.17)$$

In this expression, $H_{\mu\nu}^{\text{core}}$ is a matrix representing the energy of a single electron in a field of "bare" nuclei. Its elements are

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

$$H^{\text{core}}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}} \quad (2.18)$$

Here Z_A is the atomic number of atom A, and summation is carried out over all atoms.

The quantities $(\mu\nu|\lambda\sigma)$ appearing in (2.17) are *two-electron repulsion integrals*:

$$(\mu\nu|\lambda\sigma) = \iint \Phi_\mu^*(1)\Phi_\nu(1) \frac{1}{r_{12}} \Phi_\lambda^*(2)\Phi_\sigma(2) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \quad (2.19)$$

They are multiplied by the elements of the one-electron *density matrix*, $P_{\lambda\sigma}$,

$$P_{\lambda\sigma} = 2 \sum_{i=1}^{\text{occ}} c_{\lambda i}^* c_{\sigma i} \quad (2.20)$$

The summation is over *occupied* molecular orbitals only. The factor of two indicates that *two electrons occupy* each molecular orbital. The electronic energy, E^{ee} , is now given

$$E^{\text{ee}} = \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N P_{\mu\nu} (F_{\mu\nu} + H_{\mu\nu}^{\text{core}}) \quad (2.21)$$

Accounting for the internuclear repulsion

$$E^{\text{nr}} = \sum_A^M \sum_{<B}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.22)$$

(where Z_A and Z_B are the atomic numbers of atoms A and B, respectively, and R_{AB} is their separation) yields an express for the total energy.

The Roothaan-Hall equations (2.14) can be written more compactly as the single matrix equation

$$FC = SCE \quad (2.23)$$

where

- F** is a Fock matrix
- C** is a coefficient matrix
- S** is an Overlap matrix
- E** is an 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 equation (2.21), 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.

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

$$\int \rho(r)dr = n \quad (2.24)$$

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 functions, Φ_μ , $\rho(r)$ is given by

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \Phi_{\mu} \Phi_{\nu} \quad (2.25)$$

According to the equation (2.16), suggestions about how to calculate the electron density, starting from the density matrix, $P_{\mu\nu}$, were made by *Mulliken* (18)

$$n = \sum_{\mu,\nu} P_{\mu\nu} S_{\mu\nu} \quad (2.26)$$

It is desirable to allocate the electrons in some fractional manner among the various 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.

Basis Functions

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

The are two types of atomic orbital (basis set) popularly in use.



2.5 Slater Type Orbital (STO)

The Slater Type Orbital basis functions, introduced by Slater (15), 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

$$u_{\alpha,n,l,m}(r, \theta, \varphi) = [(2n)!]^{-1/2} (2\alpha)^{n+1/2} r^{n-1} e^{-\alpha r} Y_{l,m}(\theta, \varphi) \quad (2.27)$$

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

2.6 Gaussian Type Orbital (GTO)

The Gaussian Type Orbital (19) are defined as

$$g_{\alpha,n,l,m}(r, \theta, \varphi) = N r^{n-1} e^{-\alpha r^2} Y_{l,m}(\theta, \varphi) \quad (2.28)$$

The GTO function 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- n G" 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 fixed at values found to work well in calculation 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.

In general, one distinguishes minimal and extended basis sets or classifies them according to the STO representations per valence electron type, for instance, Single zeta uses 1 STO per s,p,d, ... function and Double zeta must use 2 STO per s,p,d,... function. For extended basis sets usually contain also polarization functions, for example, p-functions for hydrogen, d and f functions for higher atoms. These functions give a more flexible shape to the molecular orbitals and help them to describe polarization effects related to chemical binding.

Basis Set Superposition Error (BSSE)

When insufficient basis sets are used, an artificial set improvement will take place in the complex, leading to an error which has been known as basis set superposition error,

and the interaction energies are always overestimated (20). The intermolecular interaction ΔE is obtained as the difference of the separately calculated complex and constituent energies

$$\Delta E = E_{AB}(\chi_{AB}) - [E_A(\chi_A) + E_B(\chi_B)] \quad (2.29)$$

where

$$\chi_{AB} = \chi_A \cup \chi_B \quad (2.30)$$

Here E_A , E_B and E_{AB} are energies of constituent monomers A , B and the complex AB respectively. χ_A and χ_B represent basis sets of monomers A and B . The intermolecular interaction acquired from equation (2.29) will contain, in addition to the "real interaction", the "non-physical" energy contribution called as "basis set superposition error", which arises from the lack in completeness of the basis set.

One method which has been widely used to estimate BSSE is the "counterpoise (CP) correction" proposed by Boys and Bernardi (21). The counterpoise correction is evaluated from the energy improvement for a free fragment (monomer) of a molecule (complex) when a "ghost" basis for the other fragment is added to the calculation. In other word, the monomer energies are evaluated in a dimer basis set, and exactly the same basis is used for both the monomers and dimer as in the following

$$\Delta e = [E_A(\chi_A) - E_A(\chi_{AB})] + [E_B(\chi_B) - E_B(\chi_{AB})] \quad (2.31)$$

The counterpoise corrected interaction energy is determined from

$$\Delta E^{CP} = \Delta E + \Delta e \quad (2.32)$$

where ΔE is interaction energy which calculate from truncated basis set.