



Chapter I

Self Consistent Field Molecular Orbital Theory

In principle, any physically observable quantity can be calculated quantum mechanically if the corresponding Schrödinger equation can be solved.

However, the Schrödinger equation can be solved exactly only for the hydrogen atom, the simplest system. For more complicated systems, some approximations are needed.

If we are interested in molecular systems, the total Hamiltonian of the system will be given as sum of all possible coulombic interactions plus the kinetic energy of the electrons and nuclei.

$$H_{\text{tot}} = \sum_{A < B} \sum Z_A Z_B / R_{AB} - \sum_A \sum_i Z_A / r_{Ai} + \sum_{i < j} \sum 1 / r_{ij} - \sum_i 1/2 \nabla_i^2 - \sum_A 1/2 M_A \nabla_A^2 \quad 1.1$$

where A and B are nuclear centers, and i and j represent electrons. The first term represents the nuclear repulsions, the second electron repulsion and the two last terms the kinetic energy of electrons and nuclei, respectively.

According to Schrödinger equation the total energy will be

$$E_{\text{tot}} = \langle \Psi | H_{\text{tot}} | \Psi \rangle \quad 1.2$$

where Ψ is the normalized total wave function of the system.

To solve the Schrödinger equation which includes the Hamiltonian of equation 1.1 exactly is mathematically impossible. Further approximations must be introduced.

The Born-Oppenheimer approximation

The first approximation in solving the non-relativistic Schrödinger equation of molecular systems is the Born-Oppenheimer approximation.

This approximation is based on the fact that the nuclei are much heavier than electrons, and move more slowly. As a good approximation, one can consider, therefore, the electrons in a molecule to be moving in a field of fixed nuclei. Within this approximation, the kinetic energy of the nuclei in equation 1.1 can be neglected, and the repulsion between the nuclei can be considered to be constant. The remaining terms in equation 1.1 are called the Electronic Hamiltonian or Hamiltonian describing the motion of electrons in the field of nuclear point charges.

$$H_{el} = - \sum_A \sum_i Z_A / r_{iA} - \sum_i 1/2 \nabla_i^2 + \sum_{i < j} 1/r_{ij} \quad 1.3$$

The Schrödinger equation involving the electronic Hamiltonian is

$$H_{el} \phi_{el} = E_{el} \phi_{el} \quad 1.4$$

The electronic wave function is

$$\phi_{el} = \phi_{el} (q_i, q_A) \quad 1.5$$

which describes the motion of the electrons, explicitly depends on the electronic coordinates, and depends parametrically on the nuclear coordinates as does the electronic energy:

$$E_{\text{el}} = E_{\text{el}}(q_A) \quad 1.6$$

Parametric dependence implies that, for different arrangements of the nuclei, ψ_{el} is a function of the electronic coordinates and the nuclear coordinates do not appear explicitly in ψ_{el} . The total energy for fixed nuclei must also include the constant nuclear repulsion.

$$E_{\text{tot}} = E_{\text{el}} + \sum_{A < B} \sum Z_A Z_B / R_{AB} \quad 1.7$$

For the motion of the nuclei a similar equation can be constructed under the same assumptions as used to formulate the electronic problem. As the electrons move much faster than the nuclei, it is reasonable to approximate equation 1.1 by replacing the electronic coordinates by their average values, averaged over the electronic wave function. This then generates a nuclear Hamiltonian for the motion of the nuclei in the average field of the electrons.

$$\begin{aligned} H_{\text{nuc}} &= -\sum_A \frac{1}{2M_A} \nabla_A^2 + \sum_{A < B} \sum Z_A Z_B / R_{AB} + \left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_A \sum_i \frac{Z_A}{r_{Ai}} \right. \\ &\quad \left. + \sum_{i < j} \frac{1}{r_{ij}} \right] \\ &= -\sum_A \frac{1}{2M_A} \nabla_A^2 + \sum_{A < B} \sum Z_A Z_B / R_{AB} + E_{\text{el}}(q_A) \\ &= -\sum_A \frac{1}{2M_A} \nabla_A^2 + E_{\text{tot}}(q_A) \end{aligned} \quad 1.8$$

The total energy $E_{\text{tot}}(q_A)$ provides a potential for nuclear motion. This function constitutes a potential energy surface as shown in figure 1.1 Thus the nuclei in the Born-Oppenheimer approximation move on a potential energy surface obtained by solving the electronic problem.

$$H_{\text{nuc}} \psi_{\text{nuc}}(q_A) = E_{\text{nuc}} \psi_{\text{nuc}}(q_A) \quad 1.9$$

The solutions of a nuclear Schrödinger equation describe the vibration, rotation, and translation of a molecule. From the Born-Oppenheimer approximation, the approximate wave function of the total wave function is given hence as

$$\Psi(q_i, q_A) = \psi_{\text{el}}(q_i, q_A) \psi_{\text{nuc}}(q_A) \quad 1.10$$

and the corresponding total energy includes electronic, vibrational, rotational, and translational energy.

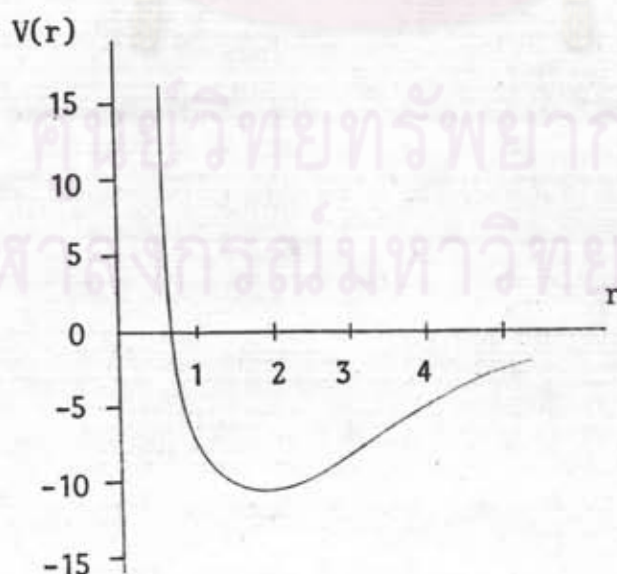


Figure 1.1 The potential energy surface of molecule

The Independent Electron Model.

The Schrödinger equation which involves electrons only, i.e. the many-electron Schrödinger problem, is approached for an N-electron system in the simplest way by constructing the total wave function as a product of one electron wave functions.

$$\psi(1, 2, \dots, n) = \psi_1(1) \psi_2(2) \dots \psi_n(n) \quad 1.11$$

Such one electron functions are called spin orbitals and the product function as such is known as the Hartree product.

In its physical meaning, this approximation of a many electron wave function by a product of one-electron functions means independent electrons in non-correlated motion. This leads to splitting up the Hamiltonian into effective one electron Hamiltonians:

$$H_{\text{tot}}(1, 2, \dots, n) = \sum_P F(p) = \sum_P \left[-1/2 \nabla_P^2 + V(p) \right] \quad 1.12$$

Due to the antisymmetry principle (electrons are fermions) the total wave function has to be antisymmetrized, which leads to new effective one-electron Hamiltonians of the form

$$F(1) = -1/2 \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} + \sum_j (2J_j - K_j) \quad 1.13$$

where $(2J_j - K_j)$ is an effective potential of the instantaneous field presents by the other $n-1$ electrons and J_j and K_j represent the coulomb and exchange operator, respectively.

Now, the one electron Schrödinger equation will be of the form:

$$F(1) \varphi(1) = \epsilon \varphi(1) \quad 1.14$$

where ϵ is the (not really observable) orbital energy.

The effective potential $V(p)$, has to be known before φ is constructed. In mathematical terms, this will lead to an iterative solution process.

This independent electron model can be applied to large systems, but the model neglects the electron correlation which will be of importance in some cases.

This electron correlation energy is defined as

$$E_{\text{corr}} = E_{\text{Born-opp}} - E_{\text{HF}} \quad 1.15$$

where E_{HF} means the energy which is calculated with the independent particle model under optimal conditions.

In general, to construct the form of the ψ function, an antisymmetric wave function, the well known Slater determinant, will be used:

$$\psi(1, 2, \dots, n) = [1/(n!)]^{1/2} | \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_n \bar{\psi}_n | \quad 1.16$$

which is written here in its diagonal form, where ψ_n and $\bar{\psi}_n$ are equal to $\psi_n(2n) \alpha(2n)$ and $\psi_n(2n) \beta(2n)$ respectively.

Molecular orbitals and the linear combination of atomic orbitals

(LCAO) approximation

We define an orbital as a wave function for a single particle, and we will use molecular orbitals for the wave functions for all

electrons in a molecular system.

The simplest way to construct such molecular orbitals is from atomic orbitals (basis functions). For example, we take the electronic equation associated with the hydrogen molecule ion:

$$\left(-\frac{1}{2} \nabla^2 + \frac{1}{R_{AB}} - \frac{1}{R_A} - \frac{1}{R_B}\right) \psi = E \psi \quad 1.17$$

At a point in the vicinity of the nucleus A, the potential $-1/R_A$ is more important than the potential $-1/R_B$. If the latter potential is neglected the solution of equation 1.17 is simply the wave function ψ_A of the hydrogen atom centered at point A. Similarly near B the function ψ must be analogous to the wave functions ψ_B of a hydrogen atom centered at point B. Therefore, it is reasonable to approximate the function as

$$\psi = c_1 \psi_A + c_2 \psi_B \quad 1.18$$

where c_1 , c_2 , are simple coefficients. This is called the LCAO-MO approximation. If a polyelectronic molecule is concerned, one must combine the formalism of the independent electron model and the LCAO approximation. The molecular wave function will be approximated by the Slater determinant built up of spin orbitals, and these molecular orbitals will be extended in terms of atomic orbitals(basis functions).

The general form of the LCAO-MO approximation is

$$\psi_i = \sum_k^n c_{ki} \psi_k \quad 1.19$$

for the i th spin orbital, where n is the total number of basis

functions in use.

Self consistent field molecular orbital theory

We have discussed all of the approximations which are needed for solving the approximate molecular Schrodinger equation. Now, we will consider the energy expectation value of a closed shell system (one space orbital is occupied by two electrons with different spin).

1. The Hamiltonian

According to the Born-Oppenheimer approximation, the total energy with fixed nuclei is:

$$E = \sum_{A < B} \sum Z_A Z_B / R_{AB} + \langle \psi | H_{el} | \psi \rangle \quad 1.20$$

The first term is the nuclear repulsion. The second term represents the electronic energy. The Hamiltonian H_{el} consists of two terms: H_1 , which includes the nuclear attraction operator and the kinetic operator, and H_2 which includes the electron-electron repulsion operator.

$$H_{el} = H_1 + H_2 \quad 1.21$$

$$\text{where } H_1 = - \sum_i \left(\sum_A Z_A / r_{Ai} + 1/2 \nabla_i^2 \right) \quad 1.22$$

$$H_2 = \sum_{i < j} \sum 1/r_{ij} \quad 1.23$$

Substituting H_{el} in equation 1.20 by equation 1.21 we obtain

$$E_{tot} = \sum_{A < B} \sum Z_A Z_B / R_{AB} + \langle \psi | H_1 | \psi \rangle + \langle \psi | H_2 | \psi \rangle \quad 1.24$$

In this equation, the total energy of the system is given as the sum of three terms, nuclear-nuclear repulsions, one-electron terms, and electron-electron interactions. The latter two terms represent the total electronic energy of the system. Using the LACOMO approximation, we obtain

$$\begin{aligned}
 E_1 &= 2 \sum_i \left\langle \sum_k C_{ki} \varphi_k(1) \middle| H_1 \middle| \sum_l C_{li} \varphi_l(1) \right\rangle \\
 &= 2 \sum_k \sum_l \sum_i C_{ki} C_{li} \langle \varphi_k(1) | H_1 | \varphi_l(1) \rangle
 \end{aligned} \tag{1.25}$$

when P_{kl} is defined as density matrix, with

$$P_{kl} = 2 \sum_i^{\text{occ}} (C_{ki} C_{li}) \tag{1.26}$$

and the integral $\langle \varphi_k(1) | H_1 | \varphi_l(1) \rangle$ is shortly written as H_{kl} . It represents the kinetic energy and the nuclear attraction of an electron residing in the k-l overlap region. Equation 1.25 may now be expressed as

$$E_1 = \sum_k \sum_l P_{kl} H_{kl} \tag{1.27}$$

The electron-electron repulsion can be treated in a similar way and gives:

$$\begin{aligned}
 E_2 &= 1/2 \sum_k \sum_l \sum_m \sum_n P_{kl} P_{mn} [\langle \varphi_k(1) \varphi_m(2) | H_2 | \varphi_l(1) \varphi_n(2) \rangle \\
 &\quad - 1/2 \langle \varphi_k(1) \varphi_m(2) | H_2 | \varphi_l(2) \varphi_n(1) \rangle]
 \end{aligned} \tag{1.28}$$

where the first integral, often written as $\langle kl|mn \rangle$ is the Coulomb repulsion between two electrons residing in the overlap regions $k-l$ and $m-n$, respectively. The second integral is written as $\langle kn|lm \rangle$ and is called the Exchange integral. Now we have

$$E_2 = \frac{1}{2} \sum_k \sum_l P_{kl} \sum_m \sum_n P_{mn} (\langle kl|mn \rangle - \frac{1}{2} \langle kn|lm \rangle) \quad 1.29$$

The final expression for the total energy thus becomes

$$E_{\text{tot}} = \sum_{A < B} \sum Z_A Z_B / r_{AB} + \sum_k \sum_l P_{kl} [H_{kl} + \frac{1}{2} \sum_m \sum_n P_{mn} (\langle kl|mn \rangle - \frac{1}{2} \langle kn|lm \rangle)] \quad 1.30$$

All of these terms are calculated in the so called ab initio method.

2. The Roothaan equation

To determine the best molecular orbitals, which yield the lowest possible energy, the variational principle is applied to minimize the total energy with respect to each coefficient

$$dE/dC_{ki} = 0 \quad \text{for each index } k \text{ and } i \quad 1.31$$

From equation 1.26 we obtain

$$d (\sum_k \sum_l P_{kl}) / dC_{ki} = 2 \sum_l C_{li} (1 - S_{kl} \sum_m \sum_n C_{mi} C_{ni}) \quad 1.32$$

Minimizing the total energy leads to a set of linear homogenous equations of the type

$$0 = dE/dC_{ki} = 2 \sum_l C_{il} (1 - S_{kl} \sum_m \sum_n C_{mi} C_{ni})$$

$$\times [H_{kl} + \sum_m \sum_n P_{mn} (\langle kl|mn \rangle - 1/2 \langle kn|lm \rangle)] \quad 1.33$$

We define the Fock matrix elements as

$$F_{kl} = H_{kl} + \sum_m \sum_n P_{mn} (\langle kl|mn \rangle - 1/2 \langle kn|lm \rangle) \quad 1.34$$

and the molecular orbital energy as

$$\epsilon_i = \sum_m \sum_n (C_{mi} C_{ni}) F_{kl} \quad 1.35$$

Under the condition of maintaining the orbitals orthonormalized the set of equations becomes:

$$\sum_l C_{li} (F_{kl} - \epsilon_i S_{kl}) = 0 \quad 1.36$$

This is the well-known Roothaan equation, in its matrix form:

$$F C = S C E \quad 1.37$$

where E is the diagonal matrix of the ϵ_i . By Löwdin transformation equation 1.37 is transformed to

$$F' C' = C' E \quad 1.38$$

where $F' = S^{-1/2} F S^{-1/2} \quad 1.39$

$$C' = S^{1/2}C \quad 1.40$$

Equation 1.38 is the standard eigenvalue problem of ab initio computation. The elements ϵ_i of E will be the roots of the determinant equation

$$|F'_{kl} - \epsilon_i \delta_{kl}| = 0 \quad 1.41$$

the lowest roots corresponding to the occupied molecular orbitals. For each root ϵ_i the coefficients C'_{li} can be found from the linear equations

$$\sum_l C'_{li} (F'_{kl} - \epsilon_i \delta_{kl}) = 0 \quad 1.42$$

and the coefficient is then determined from

$$C = S^{-1/2}C' \quad 1.43$$

The central field approximation and the self consistent field (SCF) procedure

Solving the Roothaan equation requires the evaluation of the Fock matrix elements (which themselves depend on the coefficients) through the elements P_{mn} . As mentioned above an iterative procedure is needed. By guessing an initial set of linear combination coefficients C_{li} and generating the corresponding density matrix P one computes the first F_{kl} elements. By diagonalizing F a new C matrix is obtained. The whole process is then repeated until the change in the total energy E_{tot} is smaller than a given energy limit (usually set at 10^{-5} hartree) .

The diagram of the SCF procedure is

$$C' \text{---->} P' \text{---->} F' \text{---->} E' \text{---->} C' \text{ } C^n \text{ } C^{n+1}$$

The basis set (atomic orbitals)

The type of basis set commonly used consists either of Slater-type orbitals (STO) or Gaussian-type orbitals (GTO). Nowadays most non-empirical calculations use Gaussian-lobe orbitals (GLO) which are more convenient than Slater-type orbitals in solving the integrals.

The general form of a GTO is

$$X_{n,l,m}(r, \zeta) = N. e^{-\zeta r^2} \cdot Y_{l,m}(\theta, \phi) \quad 1.44$$

and GLO's are simply given by

$$X(r) = N. e^{-\zeta r^2} \quad 1.45$$

The angular part of a Gaussian-type orbital with $l > 0$ is simulated by the superposition of a number of symmetrically distributed spherical Gaussians. For example a p_z orbital is represented by the superposition of two functions, each representing a lobe

$$p_z(r) = \exp[-\zeta(x^2 + y^2 + (Z-R)^2)] - \exp[-\zeta(x^2 + y^2 + (Z+R)^2)] \quad 1.46$$

where, taking the nucleus as the origin, the Gaussians are centered at positions $(0, 0, \pm R)$. A p-type Gaussian lobe is therefore specified by the two parameters ζ and R .

In this work, we have used minimal basis sets of Gaussian-lobe orbitals (GLO) for ab initio calculations. Although the absolute

energy is quite poor, the relative energies are reasonable, as many works have proved (8,9). The main advantage of the GLO basis set is the decreased C.P.U. time .

By the LCAO-MO method the molecular orbitals will be constructed from these basis functions. To reach the HF limit, theoretically an infinite number of basis functions is needed, but in practice quite small basis sets have to be used because of the time of calculation. The sizes of basis sets which theoretical chemists always use are usually classified as:

1. Minimal basis sets.

This size of basis set will use only one basis function per orbital quantum number n, l, m , in each atom. For example, in HF the basis set will be $1s$ for hydrogen and $1s, 2s, 2p_x, 2p_y, 2p_z$ for Fluorine.

2. Extended basis sets.

Extended basis sets are larger than minimal basis sets and can include also polarization functions, for example p functions for hydrogen and d and f functions for higher atoms.

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