

MOLECULAR ORBITAL APPROXIMATION

(a) Many Electron Wavefunction

For a molecule with more than one electron, an exact solution of the Schrödinger equation cannot be obtained. A common approximation, is to write the electronic wavefunction Ψ as a sum of products of one-electron molecular orbitals $\{\psi_i\}$. Since the Pauli principle demands that the wavefunction must change sign when the coordinates of any two electrons are interchanged, Ψ can be written as a Slater determinant. For example, with a two-electron system we have

$$\Psi = \frac{1}{2^{1/2}} \begin{vmatrix} \psi_a(1) & \psi_b(1) \\ \psi_a(2) & \psi_b(2) \end{vmatrix} \quad (1.1)$$

It can be shown that the $\{\psi_i\}$ satisfy the Fock equation

$$\hat{F} \psi_i = \epsilon_i \psi_i \quad (1.2)$$

where \hat{F} is an effective one-electron hamiltonian which contains the kinetic energy operator and nuclear attraction potential energy of one-electron, together with an average potential of interaction with the other electrons.

(b) Linear Combination of Atomic Orbitals

A common form for the molecular orbitals is to expand them as a Linear Combination of Atomic Orbitals (LCAO):

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_n \phi_n = \sum_{j=1}^n c_j \phi_j \quad (1.3)$$

The $\{\phi_j\}$ are basis functions which are normally atomic orbitals (s, p, d etc.) centred on the atoms in the molecule.

here we look at a simple method for determining the molecular orbital coefficients $\{c_j\}$.

(c) Secular Equations

The variational principle can be used to obtain the best molecular orbital coefficients. For the operator \hat{F} of equation (1.2) and the LCAO expansion for ψ of equation (1.3), we have

$$\epsilon = \frac{\langle \psi | \hat{F} | \psi \rangle}{\langle \psi | \psi \rangle} \geq \epsilon_0 \tag{1.4}$$

where ϵ_0 is the lowest eigenvalue of \hat{F} .

Minimization of ϵ with respect to the molecular orbital coefficients $\{c_j\}$ gives the secular equations

$$\sum_{j=1}^n (F_{ij} - \epsilon S_{ij}) c_j = 0 \tag{1.5}$$

where $i = 1, 2, \dots, n$.

In equation (1.5) we have

$$F_{ij} = \langle \phi_i | \hat{F} | \phi_j \rangle \tag{1.6}$$

and

$$S_{ij} = \langle \phi_i | \phi_j \rangle \tag{1.7}$$

The n eigenvalues are obtained by solving the secular determinant equation

$$\det (F_{ij} - \epsilon S_{ij}) = 0 \tag{1.8}$$

This yields an n 'th order polynomial in ϵ . For each eigenvalue ϵ , the linear simultaneous equations (1.5) are then solved to obtain the corresponding molecular orbital coefficients $\{c_j\}$.

It is common to normalize the molecular orbitals. If the basis functions $\{\phi_i\}$ themselves are normalised and orthogonal such that

$$S_{ij} = 1, i = j \tag{1.9}$$

$$= 0, i \neq j \tag{1.10}$$

then we have

$$\sum_{j=1}^n c_j^2 = 1. \quad (1.11)$$

(d) Hückel's Approximation

If the matrix elements F_{ij} and S_{ij} can be calculated, then the secular equations can be solved. Nowadays it is possible to determine the molecular orbitals for quite large molecules using the computer, but these ab initio techniques are outside the scope of this course.

A very simple approximation was introduced by Hückel. He approximated the matrix elements by

$$F_{ij} = \alpha_i, \quad i = j \text{ ("Coulomb Integral")} \quad (1.12)$$

$$= \beta_{ij}, \quad i \neq j \text{ ("Resonance Integral")}. \quad (1.13)$$

It is often assumed that the basis functions are orthogonal and normalised such that (1.9) and (1.10) hold. The α_i and β_{ij} are parameters which can be obtained by comparing results such as molecular orbital energies with experimental data. α_i is identified with the energy in atomic orbital ϕ_i , while β_{ij} is associated with the energy of interaction of the two atomic orbitals ϕ_i and ϕ_j . Normally, α_i and β_{ij} are negative.

(e) Example: The two-level problem

For the two basis functions ϕ_1 and ϕ_2 we have

$$\psi = c_1 \phi_1 + c_2 \phi_2. \quad (1.14)$$

The secular equations in the Huckel approximation are then

$$\begin{aligned} (\alpha_1 - \epsilon S_{11})c_1 + (\beta_{12} - \epsilon S_{12})c_2 &= 0 \\ (\beta_{12} - \epsilon S_{12})c_1 + (\alpha_2 - \epsilon S_{22})c_2 &= 0. \end{aligned} \quad (1.15)$$

(i) Zero Overlap

If overlap is neglected such that $S_{12}=0$, $S_{11}=S_{22}=1$, the solutions for the molecular orbital energies are

$$\epsilon = \frac{1}{2}(\alpha_1 + \alpha_2) \pm \left[\frac{1}{4}(\alpha_1 - \alpha_2)^2 + \beta^2 \right]^{\frac{1}{2}} \quad (1.16)$$

If $|\beta|$ is very small compared to $|\alpha_1 - \alpha_2|/2$, then the solutions are close to $\epsilon=\alpha_1$ with $c_1=1$ and $c_2=0$, and $\epsilon=\alpha_2$ with $c_1=0$ and $c_2=1$.

If $\alpha = \alpha_1 = \alpha_2$, we have

$$\epsilon = \alpha \pm \beta \quad (1.17)$$

and, for the solution $\epsilon=\alpha+\beta$, the secular equations become

$$\begin{aligned} -\beta c_1 + \beta c_2 &= 0 \\ \beta c_1 - \beta c_2 &= 0 \end{aligned} \quad (1.18)$$

Thus $c_1 = c_2$ and, since $c_1^2 + c_2^2 = 1$, we have

$$\psi = \frac{1}{\sqrt{2}} \phi_1 + \frac{1}{\sqrt{2}} \phi_2 \quad (1.19)$$

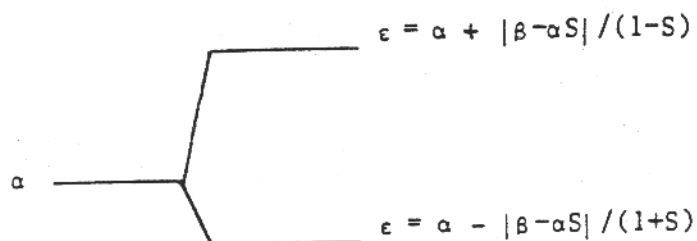
Similarly, for $\epsilon=\alpha-\beta$, we get

$$\psi = \frac{1}{\sqrt{2}} \phi_1 - \frac{1}{\sqrt{2}} \phi_2 \quad (1.20)$$

(ii) Non-Zero Overlap

Here S_{11} and $S_{22} = 1$, $S_{12} \neq 0$.

We have



and the antibonding orbital is moved up higher than the bonding orbital is moved down.