Lecture 22

Hückel MO Theory

Study Goal of This Lecture

- Hückel model

- Hückel Hamiltonian

- Example, Hückel rule

22.1 Preface

So far we have demonstrated the Hartree-Fock LCAO-MO-SCF method and computational chemistry through webMO program. You should be able to carry out a computational experiment and get "numbers"/"molecular orbital" to interpret. Yet very often we only need a qualitative description $\rightarrow$ Hückel theory.

22.2 Hückel Molecular Orbital Theory

The HF method is called an "ab-initio" or first principle method, because only elementary physical contents are required to calculate physical properties of molecular systems. There are, however, other sets of methods which simplified the calculations by using experimentally determined parameters or by chopping them in the full HF equation. These are semiempirical methods. One such method specifically designed to treat π-conjugated systems is the so called Hückel molecular orbital theory. The Hückel theory considers only π-electrons, which is justified by:

1. π-MOs have higher energies.

2. Different symmetry of the σ and π orbitals.

3. Greater polarizability of the π-electrons.

By focusing on the π electrons, the Hückel theory can explain many chemical phenomena qualitatively.

The basic assumption of the Hückel theory is

- independent electrons

- only π-orbitals are important

therefore, the Hamiltonian is

$$\hat{H}_\pi = \sum_{i=1}^{n_\pi} \hat{h}_i. \tag{22.1}$$

We want to solve

$$\hat{h}_i \psi_i = E_i \psi_i, \tag{22.2}$$

with

$$\psi_i = \sum_{r=1}^{n_c} C_r^{(i)} \phi_r, \tag{22.3}$$

n_c is the number of carbon atoms in the π-systems, ϕ_r is p_z orbital on the r-th carbon and the $\hat{h}_i$ is single electron Hamiltonian for all π-electrons. (It is the same for all electrons.)

The coefficient $C_r^{(i)}$ are determined "variationally", thus, the energies are determined by the secular equation:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n_\pi - ES_{1n_\pi}} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2n_\pi - ES_{2n_\pi}} \\ \vdots & & & \vdots \\ H_{n_\pi 1} - ES_{n_\pi 1} & H_{n_\pi 2} - ES_{n_\pi 2} & \cdots & H_{n_\pi n_\pi - ES_{in_\pi}} \end{vmatrix}. \tag{22.4}$$

We further approximate:

1. $H_{rr} = \langle \phi_r | \hat{h}_i | \phi_r \rangle = \alpha$, the Coulomb integral term.

2. $H_{rs} = \langle \phi_r | \hat{h}_i | \phi_s \rangle = \beta < 0$ if r & s are connected by a π-bond.

3. $H_{rs} = 0$ if not π-bonded.

4. $S_{rs} = \delta_{rs}$ (neglect the overlap)

Actually, this can be cast into a eigenvalue problems. $\langle \phi_i | \phi_j \rangle = 0$, form orthornormal basis. Therefore,

$$|\psi_i\rangle = \sum_j C_r |\phi_r\rangle = \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_{n_\pi} \end{pmatrix} \qquad (22.5)$$

and

$$\hat{H} = \begin{pmatrix} h_{11} & h_{12} & \cdots & h_{1n} \\ h_{21} & h_{22} & \ddots & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \alpha & \beta & 0 & \cdots \\ \beta & \alpha & \beta & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \qquad (22.6)$$

α: diagonal, site energy,

β: nearest neighbor coupling.

To find eigenfunctions, we solve

$$\underbrace{(H - I \cdot E)}_{\substack{\text{determinant} \\ |H - IE| = 0 \\ \Rightarrow \text{seqular eq.}}} |\psi_i\rangle = 0. \qquad (22.7)$$

The more simple rule will be:

1. All C-atoms in the conjugated system as the basis.

2. $\alpha - E$ in diagonal.

3. β if connected.

For example, the 1,3-butadiene:

Figure 22.1: 1,3-butadiene.

then the seqular equation:

$$
\begin{array}{cccc}
C_1 & C_2 & C_3 & C_4
\end{array}
$$

$$
\begin{vmatrix}
\alpha - E & \beta & 0 & 0 \\
\beta & \alpha - E & \beta & 0 \\
0 & \beta & \alpha - E & \beta \\
0 & 0 & \beta & \alpha - E
\end{vmatrix} = 0, \tag{22.8}
$$

use $x = \frac{\alpha - E}{\beta}$, we have

$$
\begin{vmatrix}
x & 1 & 0 & 0 \\
1 & x & 1 & 0 \\
0 & 1 & x & 1 \\
0 & 0 & 1 & x
\end{vmatrix} = 0. \tag{22.9}
$$

Thus, we obtain

$$
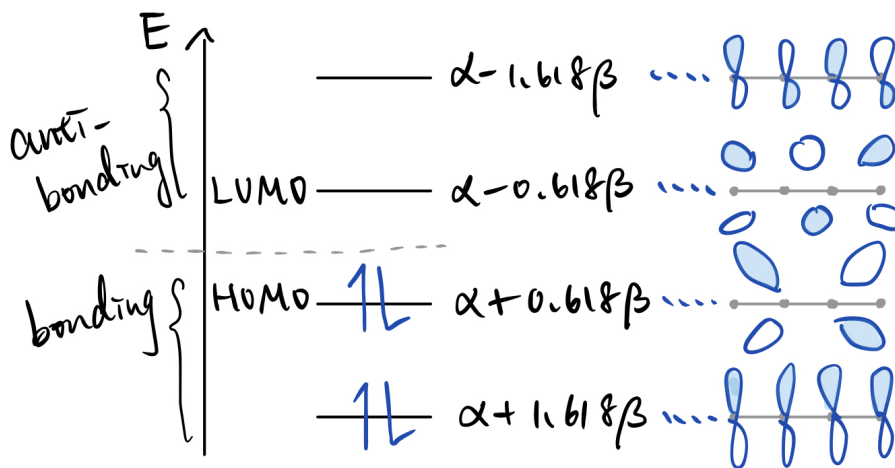x^4 - 3x^2 + 1 = 0, \ x = \pm 0.618, \ \pm 1.618. \tag{22.10}
$$

Figure 22.2: MO of 1,3-butadiene.

Acutally, it looks like the wavefunction of particle in a box.

In general, the energy for polyene system solved via Hückel's theory:

$$
\text{Linear: } E_k = \alpha + 2\beta \cos\left(\frac{k\pi}{n+1}\right) \tag{22.11}
$$

$$\text{Cyclic: } E_k = \alpha + 2\beta \cos\left(\frac{2k\pi}{n}\right) \tag{22.12}$$

We can then fill in the electrons according to the Pauli exclusion principle and obtain useful information of 1,3-butadiene. Such as:

- The total energy $E_{tot} = 2E_1 + 2E_2$.

- The lowest transition energy $\simeq$ HOMO $\to$ LUMO $\Rightarrow$ $2 \times 0.618|\beta|$.

With each E, the wavefunction can be determined. Note that the secular equation is determined by the following equation:

Define

$$\hat{h} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}, \tag{22.13}$$

$$\hat{h}\,|\psi\rangle = E\,|\psi\rangle. \tag{22.14}$$

It is a eigenvalue problem for $\hat{h}$. It can be seen that the Hückel Hamiltonian is determined by the "Hückel" rule. Extending this to treat rings allows us to understand the $4n + 2$ rule for aromatic systems $\Leftarrow$ See Silbey. It can't be emphasized enough that the advantage of Hückel's theory is that one can obtain qualitative properties of π-conjugated system via using the matrix diagonalization routine in many mathematical program.

22.3   More Example of Using Huckel's Theory
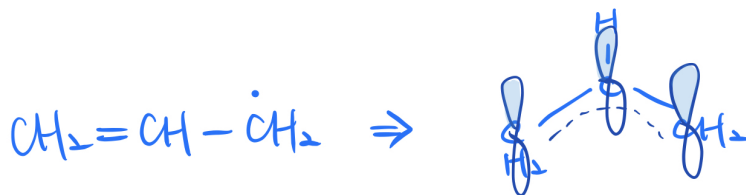
22.3.1   Allyl radical

Figure 22.3: Allyl radical

The Hückel interaction Hamiltonian:

$$\hat{h} = \begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix}, \tag{22.15}$$

solving $\hat{h}\psi = E\psi \Rightarrow (\hat{h} - EI)\psi = 0$ secular equation:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0, \tag{22.16}$$

define $x = \frac{\alpha - E}{\beta} \Rightarrow$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{22.17}$$

$\Rightarrow$

$$x^3 - 2x = 0 \Rightarrow x = 0, \pm\sqrt{2}. \tag{22.18}$$

Thus,

$$E = \alpha + \sqrt{2}\beta, \alpha, \alpha - \sqrt{2}\beta. \tag{22.19}$$

To find out eigenfunctions:

$$\begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} \tag{22.20}$$

$$\Rightarrow \begin{pmatrix} \alpha C_1 + \beta C_2 \\ \beta C_1 + \alpha C_2 + \beta C_3 \\ \beta C_2 + \alpha C_3 \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} \Rightarrow \begin{cases} \alpha C_1 + \beta C_2 = EC_1 \\ \beta C_1 + \alpha C_2 + \beta C_3 = EC_2 \\ \beta C_2 + \alpha C_3 = EC_3 \end{cases} \tag{22.21}$$

then for $E_1 = (\alpha + \sqrt{2}\beta)$

$$\Rightarrow \begin{cases} \cancel{\alpha C_1} + \beta C_2 = \cancel{\alpha C_1} + \sqrt{2}\beta C_1 \\ \beta C_1 + \alpha C_2 + \beta C_3 = \alpha C_2 + \sqrt{2}\beta C_2 \\ \beta C_2 + \cancel{\alpha C_3} = \cancel{\alpha C_3} + \sqrt{2}\beta C_3 \end{cases} \Rightarrow \begin{array}{l} C_2 = \sqrt{2}C_1 \\ C_3 = \dfrac{1}{\sqrt{2}}C_2 = C_1 \end{array} \tag{22.22}$$

also, by normalizaiton condition,

$$C_1^2 + C_2^2 + C_3^2 = 1 \tag{22.23}$$

$$C_1 = \frac{1}{2}, \ C_2 = -\frac{1}{\sqrt{2}}, \ C_3 = \frac{1}{2}. \tag{22.24}$$

We can further solve the eigenfunction for $E = \alpha$ & $E = \alpha + \sqrt{2}\beta$

$$E = \alpha + \sqrt{2}\beta, \ \psi = \begin{pmatrix} \frac{1}{2} \\ +\frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix},$$

$$E = \alpha, \ \psi = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \tag{22.25}$$

$$E = \alpha - \sqrt{2}\beta, \ \psi = \begin{pmatrix} \frac{1}{2} \\ -\frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix}.$$
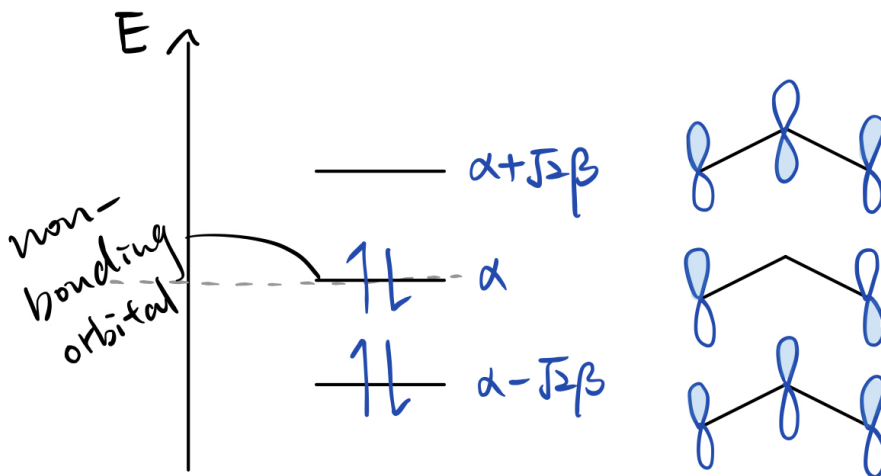

Figure 22.4: Allyl radical MO

Note how we obtain the coefficient and how the number of nodes is correlated to the energy and MO.

Another important class of conjugated systems includes monocyclic conjugated polyenes such as C_4H_4, C_5H_5, C_6H_6. For example the benzene, the Hamiltonian is:

$$\hat{h} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}, \tag{22.26}$$

and the seqular equation is:

$$\begin{vmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{vmatrix} = 0. \tag{22.27}$$

The solution is:

$$\begin{aligned} E = & \alpha + 2\beta, \ \alpha + \beta, \ \alpha + \beta, \\ & \alpha - 2\beta, \ \alpha - \beta, \ \alpha - 2\beta. \end{aligned} \tag{22.28}$$
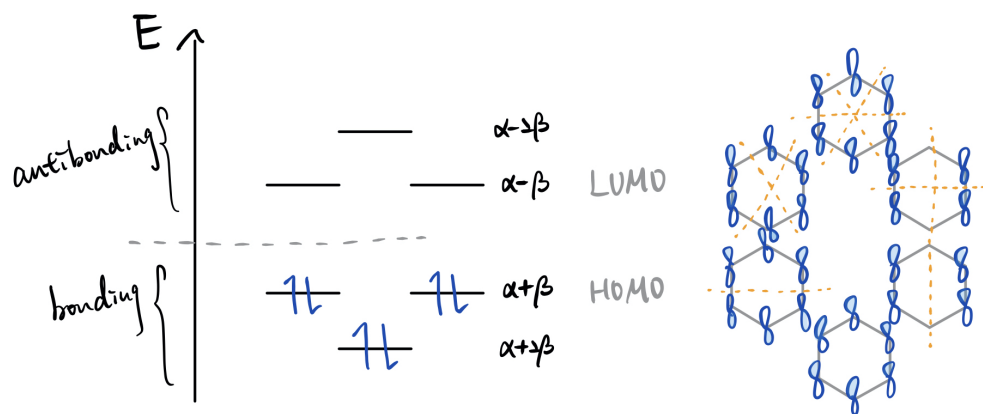

Figure 22.5: Benzene energy levels.

Note that the doubly degeneracy for the middle-level MOs is general for all monocyclic conjugated systems. Thus, to have a stable filled-shell π-electron configuration, the number of electron must satisfy: $N_\pi = 4N + 2$, $n = 0, 1, 2, \cdots$. This is the famous $4N + 2$ rule. These systems are said to be aromatic. A good example is the cyclopentadienyl system:

cyclopentadienyl radical: $\cdot C_5 H_5$ $N_\pi = 5$, not stable.

cyclopentadienyl anion: $C_5 H_5^-$ $N_\pi = 6$, very stable.

22.4   Summary

The semiempirical treatment of Hückel concludes the MO description, which consists of using LCAO of delocalized MOs to describe the behavior of a single electron in a complex molecular system.