

Simple Hückel theory

Concept

- 1 Simple Hückel theory only consider **planar conjugated hydrocarbons**
- 2 **σ orbitals** are neglected
- 3 Only **π electrons** are considered
- 4 This is a “**linear combination of atomic orbitals**” (LCAO) method
- 5 It gives **qualitative information** only!

Rules

- 1 Assume that all π orbitals are **orthogonal** $\Rightarrow \mathbf{S} = \mathbf{I} \Rightarrow \mathbf{F}\mathbf{C} = \mathbf{C}\mathbf{E}$
- 2 Diagonalize Fock matrix **\mathbf{F}** to find **molecular orbitals (MOs)** and their **energies**
- 3 **Diagonal elements** are assigned a value of α
- 4 **Off-diagonal elements** are either β if atoms A and B are neighbours or 0 otherwise
- 5 Note that $\beta < 0$

How to build the Fock matrix

For a molecule with n π electrons and n carbon atoms, the (orthogonal) basis set is

$$\{|p_z^{C_1}\rangle, |p_z^{C_2}\rangle, |p_z^{C_3}\rangle, \dots, |p_z^{C_{n-1}}\rangle, |p_z^{C_n}\rangle\} \equiv \{|1\rangle, |2\rangle, |3\rangle, \dots, |n-1\rangle, |n\rangle\}$$

From Hückel rules, we know that

$$\langle i|\mathbf{F}|i\rangle = \alpha \quad (i = 1, \dots, n) \quad \langle i|\mathbf{F}|j\rangle = \begin{cases} \beta & \text{if } i \text{ and } j \text{ neighbours} \\ 0 & \text{otherwise} \end{cases}$$

The Fock matrix is

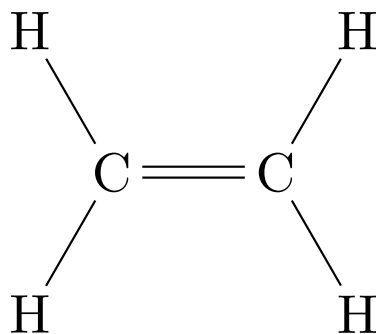
$$\mathbf{F} = \begin{array}{c|cccccc} & |1\rangle & |2\rangle & \dots & |n-1\rangle & |n\rangle \\ \hline \langle 1| & \langle 1|\mathbf{F}|1\rangle & \langle 1|\mathbf{F}|2\rangle & \dots & \langle 1|\mathbf{F}|n-1\rangle & \langle 1|\mathbf{F}|n\rangle \\ \langle 2| & \langle 2|\mathbf{F}|1\rangle & \langle 2|\mathbf{F}|2\rangle & \dots & \langle 2|\mathbf{F}|n-1\rangle & \langle 2|\mathbf{F}|n\rangle \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ \langle n-1| & \langle n-1|\mathbf{F}|1\rangle & \langle n-1|\mathbf{F}|2\rangle & \dots & \langle n-1|\mathbf{F}|n-1\rangle & \langle n-1|\mathbf{F}|n\rangle \\ \langle n| & \langle n|\mathbf{F}|1\rangle & \langle n|\mathbf{F}|2\rangle & \dots & \langle n|\mathbf{F}|n-1\rangle & \langle n|\mathbf{F}|n\rangle \end{array}$$

Ethene C₂H₄

The **Fock matrix** is

$$\mathbf{F} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

Molecule



To find the **MO energies**, we solve

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad \Leftrightarrow \quad \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

with $x = (\alpha - E)/\beta$. This yields

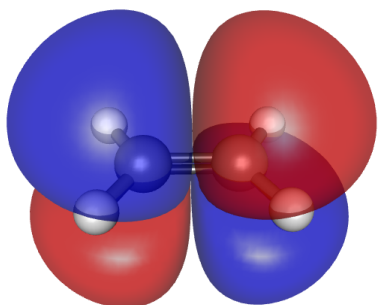
$$x^2 - 1 = 0 \quad \Leftrightarrow \quad (\alpha - E)^2 - \beta^2 = 0$$

Then

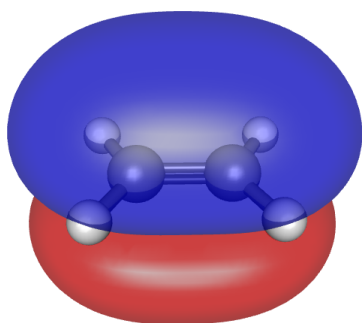
$$E_k = \alpha \pm \beta$$

Ethene C₂H₄ Take 2

Molecular orbitals



LUMO: $E_2 = \alpha - \beta$



HOMO: $E_1 = \alpha + \beta$

The MOs are

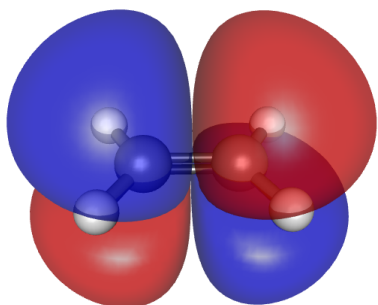
$$\psi_1 = \frac{\phi_1 + \phi_2}{\sqrt{2}} \quad \Leftrightarrow \quad E_1 = \alpha + \beta$$

$$\psi_2 = \frac{\phi_1 - \phi_2}{\sqrt{2}} \quad \Leftrightarrow \quad E_2 = \alpha - \beta$$

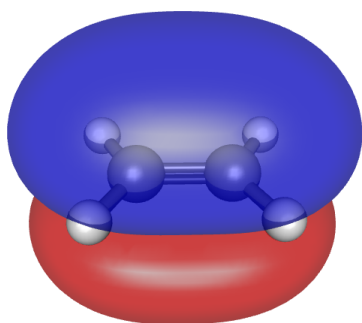
- ψ_1 is called the **HOMO**
= highest occupied MO
- ψ_2 is called the **LUMO**
= lowest unoccupied MO
- the HOMO and LUMO are the **frontier orbitals (FOs)**

Ethene C₂H₄ Take 3

Molecular orbitals



LUMO: $E_2 = \alpha - \beta$



HOMO: $E_1 = \alpha + \beta$

The **total energy** is

$$E_{\text{tot}} = 2 E_1 = 2(\alpha + \beta)$$

The **HOMO-LUMO energy gap**

$$\Delta E_{\text{HL}} = h\nu = E_{\text{LUMO}} - E_{\text{HOMO}} = -2\beta$$

correlates with **molecular electronic transitions** observed with UV/VIS spectroscopy

The **resonance energy** is

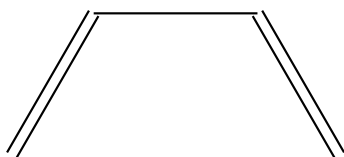
$$\Delta E_{\text{res}} = E_{\text{tot}} - 2\alpha = 2\beta$$

Butadiene C₄H₆

The **Fock matrix** is

$$\mathbf{F} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}$$

Molecule



To find the **MO energies**, we solve

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = (x^2 - x - 1)(x^2 + x - 1) = 0$$

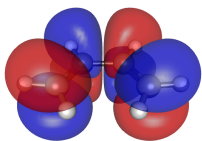
Then

$$E_k = x \pm \frac{1 \pm \sqrt{5}}{2}$$

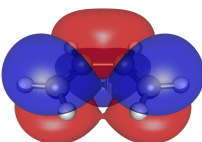
Butadiene C₄H₆ Take 2

The MOs are

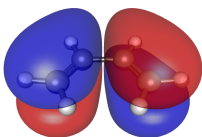
Molecular orbitals



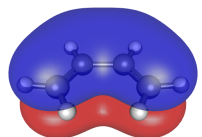
LUMO+1



LUMO



HOMO



HOMO-1

$$\psi_1 = \frac{\phi_1 + \phi_2 + \phi_3 + \phi_4}{2} \Rightarrow 0 \text{ node}$$

$$\psi_2 = \frac{\phi_1 + \phi_2 - \phi_3 - \phi_4}{2} \Rightarrow 1 \text{ node}$$

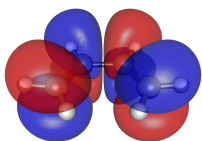
$$\psi_3 = \frac{\phi_1 - \phi_2 - \phi_3 + \phi_4}{2} \Rightarrow 2 \text{ nodes}$$

$$\psi_4 = \frac{\phi_1 - \phi_2 + \phi_3 - \phi_4}{2} \Rightarrow 3 \text{ nodes}$$

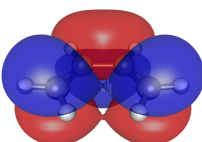
- ψ_1 is called the **HOMO-1** (bonding orbital)
- ψ_2 is called the **HOMO** (bonding orbital)
- ψ_3 is called the **LUMO** (anti-bonding orbital)
- ψ_4 is called the **LUMO+1** (anti-bonding orbital)

Butadiene C₄H₆ Take 3

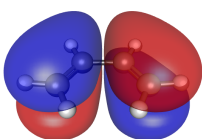
Molecular orbitals



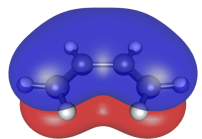
LUMO+1



LUMO



HOMO



HOMO-1

The **total energy** is

$$E_{\text{tot}} = 2 E_1 + 2 E_2 = 4\alpha + 2\sqrt{5}\beta$$

The **HOMO-LUMO energy gap** is

$$\Delta E_{\text{HL}} = (1 - \sqrt{5})\beta = -1.236\beta$$

The **resonance energy** is

$$\Delta E_{\text{res}} = E_{\text{tot}} - 4\alpha = 2\sqrt{5}\beta$$

The **delocalization energy**

$$\Delta E_{\text{deloc}} = 2(\sqrt{5} - 2)\beta = 0.472\beta$$

is defined as the difference between E_{tot} and a hypothetical energy in which all ethene units are assumed isolated

Butadiene C₄H₆ Take 5

Charge density

$$q_A = \sum_i^{\text{occ}} n_i (c_i^A)^2$$

- n_i is the **occupation number** of MO k (0, 1 or 2)
- $(c_i^A)^2$ is the square of the coefficient in the i th orbital on atom A

For butadiene, we have

$$q_{C_1} = 0.372 \times 2 + 0.602 \times 2 = 1$$

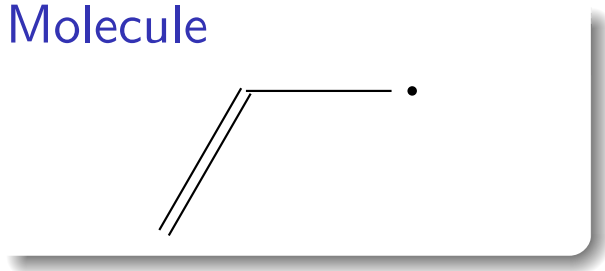
$$q_{C_2} = 0.602 \times 2 + 0.372 \times 2 = 1$$

Atomic charge

$$Q_{C_1} = 1 - q_{C_1} = 0 \quad Q_{C_2} = 1 - q_{C_2} = 0$$

@home: Allyl radical $C_3H_5^\bullet$

Molecule



The Fock matrix is

$$\mathbf{F} = ??$$

The MOs and their corresponding energies are

$$(1, \sqrt{2}, 1) \longrightarrow \alpha + \sqrt{2}\beta$$

$$(1, 0, 1) \longrightarrow \alpha$$

$$(1, -\sqrt{2}, 1) \longrightarrow \alpha - \sqrt{2}\beta$$

Can you find the total energy, the resonance energy, the HOMO-LUMO gap and the delocalization energy?

NB1: In the allyl radical, there is a so-called non-bonding MO of energy α

NB2: When the HOMO is singly occupied, we call it a SOMO

Linear Polyene C_nH_{n+2}

The **Fock matrix** is **tridiagonal** and reads

$$\mathbf{F} = \begin{pmatrix} \alpha & \beta & 0 & \cdots & 0 \\ \beta & \alpha & \beta & \ddots & \vdots \\ 0 & \beta & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & \alpha & \beta \\ 0 & \cdots & 0 & \beta & \alpha \end{pmatrix}$$

The **MO energies** are

$$E_k = \alpha + 2\beta \cos \frac{k\pi}{n+1}$$

Note that

$$\alpha + 2\beta \leq E_k \leq \alpha - 2\beta$$

The **total energy** is

$$\begin{aligned} E_{\text{tot}} &= 2 \sum_{k=1}^{n/2} \left\{ \alpha + 2\beta \cos \left(\frac{\pi}{n+1} \right) \right\} \\ &= n\alpha + 2\beta \left\{ \frac{1}{\sin \left[\frac{\pi}{2(n+1)} \right]} - 1 \right\} \end{aligned}$$

The **HOMO-LUMO gap** is

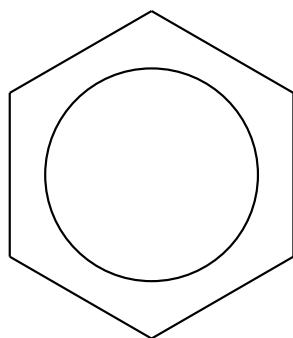
$$\Delta E = -4\beta \sin \left[\frac{\pi}{2(n+1)} \right]$$

The **delocalization energy** is

$$E_{\text{deloc}} = 2\beta \left\{ \frac{1}{\sin \left[\frac{\pi}{2(n+1)} \right]} - \frac{n}{2} - 1 \right\}$$

Benzene C₆H₆

Molecule



The **Fock matrix** is

$$\mathbf{F} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

and we need to solve

$$(x^2 - 4)(x^2 - 1)^2$$

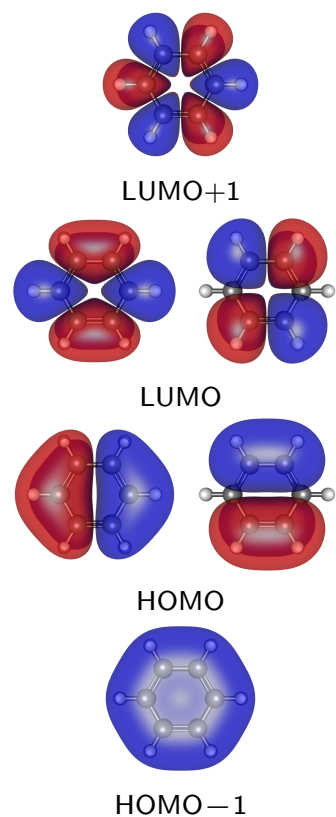
Therefore, the **MO energies** are

$$E_1 = \alpha + 2\beta \quad E_2 = E_3 = \alpha + \beta$$

$$E_4 = E_5 = \alpha - \beta \quad E_6 = \alpha - 2\beta$$

Benzene C₆H₆ Take 2

MOs



The MOs are

$$\psi_6 = \frac{\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6}{\sqrt{6}}$$

$$\psi_5 = \frac{2\phi_1 + \phi_2 - \phi_3 + 2\phi_4 + \phi_5 - \phi_6}{\sqrt{12}}$$

$$\psi_4 = \frac{\phi_2 - \phi_3 + \phi_4 - \phi_5}{\sqrt{4}}$$

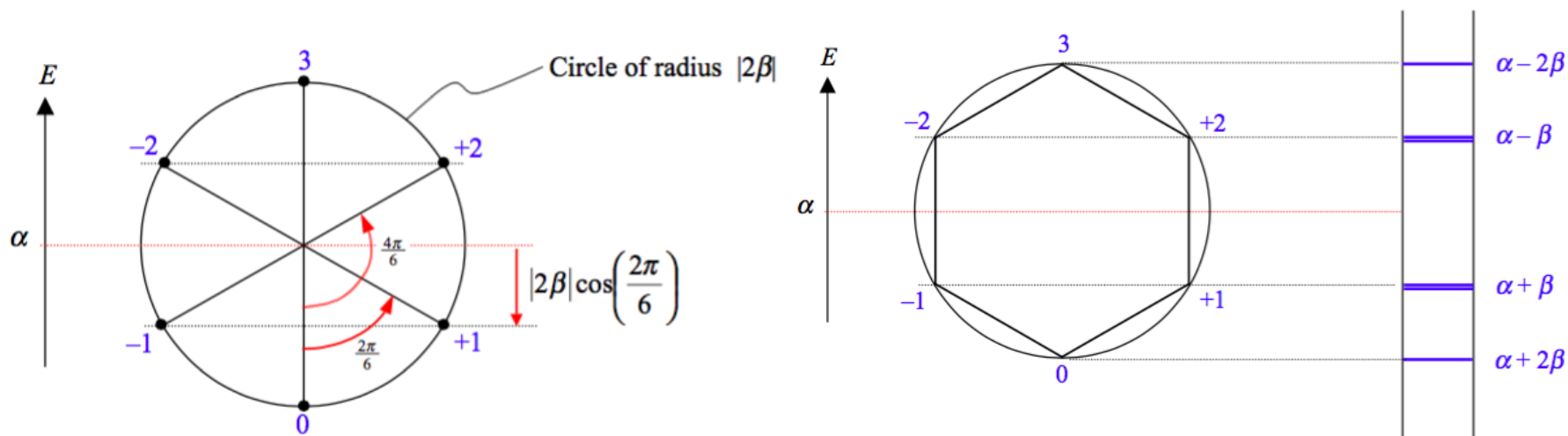
$$\psi_3 = \frac{2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6}{\sqrt{12}}$$

$$\psi_2 = \frac{\phi_2 + \phi_3 - \phi_4 - \phi_5}{\sqrt{4}}$$

$$\psi_1 = \frac{\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6}{\sqrt{6}}$$

Benzene C₆H₆ Take 3

Geometrical construction: Frost circle



$$E_k = \alpha + 2\beta \cos\left(\frac{2\pi k}{n}\right) \text{ for cyclic polyenes}$$

The delocalization energy in benzene is

$$E_{\text{deloc}} = 2\beta$$