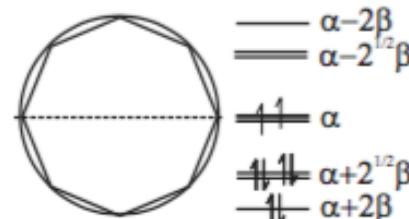
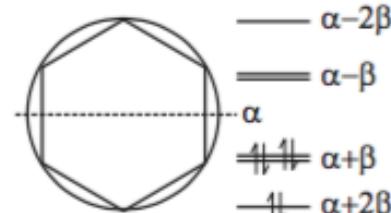
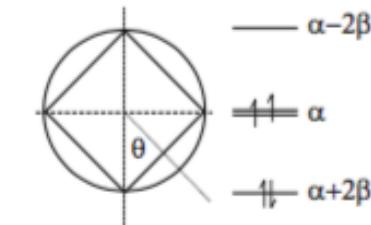


$4n + 2$ Hückel rule

"In organic chemistry, the term **aromaticity** is used to describe a **cyclic**, **planar** molecule with a ring of **resonance** bonds that exhibits more stability than other geometric or connective arrangements with the same set of atoms"

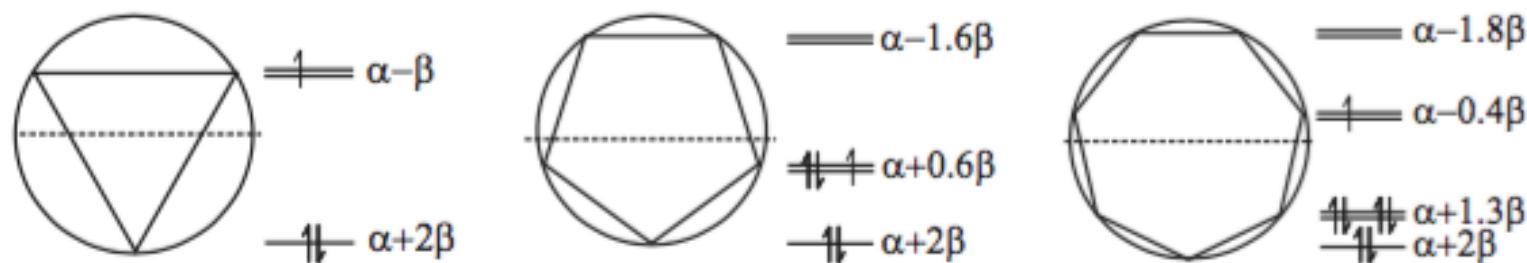
Aromatic or not?



- C₆H₆ has 6 π electrons ($n = 1$)
- C₈H₈²⁻ has 10 π electrons ($n = 2$) and is planar
- Planar ring molecules with **$4n \pi$ electrons do not obey Hückel's rule**
 - they are less stable
 - they have **triplet ground states** with two unpaired electrons
 - they distort from planar regular polygons
- C₄H₄ is **rectangular** rather than square
- C₄H₄ is said to be **anti-aromatic** ($4n$ rule)
- C₈H₈ has a nonplanar "tub" structure

$4n + 2$ Hückel rule (Take 2)

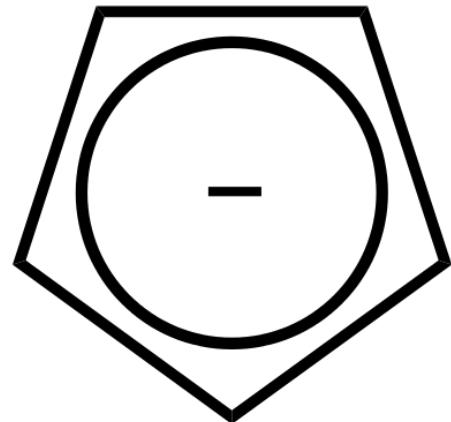
Aromatic or not?



- $C_3H_3^+$ is an example of aromatic molecule for $n = 0$
- $C_5H_5^-$ is considerably more stable than C_5H_5 and $C_5H_5^+$
- $C_5H_5^-$ is planar
- $C_7H_7^+$ is more stable than C_7H_7

@home: Cyclopentadienyl anion $C_5H_5^-$

Molecule



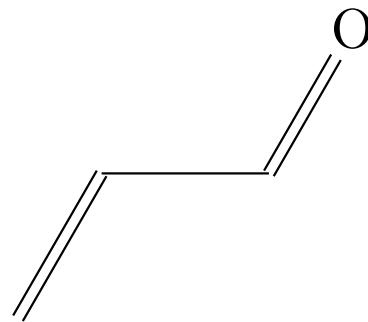
The Fock matrix is

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

Let's try with HuLiS!

How to deal with heteroatoms?

Acrolein as an example



Secular determinant

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1.06 \\ 0 & 0 & 1.06 & x + 0.97 \end{vmatrix}$$

What should I do?

- you must modify the diagonal element for heteroatoms:

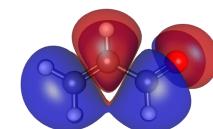
$$\alpha_O = \alpha + 0.97\beta$$

- you must modify the off-diagonal elements between heteroatoms and others:

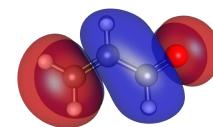
$$\beta_{CO} = 1.06\beta$$

- The heteroatom might bring more than one π electron
 - O brings one π electron
 - F brings two π electrons
- It can be a group instead of a heteroatom
(-CH₃, -OR, -NR₂, =NR, etc)

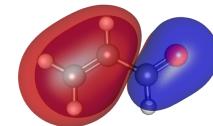
MOs



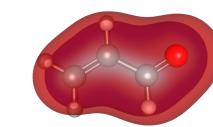
LUMO+1



LUMO



HOMO



HOMO-1

How to deal with heteroatoms? (Take 2)

Molecular Orbitals

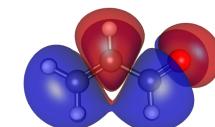
E_i	$\alpha + 1.91\beta$	$\alpha + 0.99\beta$	$\alpha - 0.38\beta$	$\alpha - 1.55\beta$
C ₁	0.22	-0.59	-0.66	-0.42
C ₂	0.42	-0.58	0.25	0.65
C ₃	0.58	0.01	0.56	-0.59
O ₄	0.66	0.56	-0.44	0.25

$$E_{\text{tot}} = 4\alpha + 5.81\beta$$

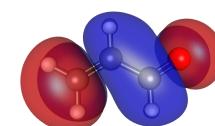
Atomic charges

Atom	Charge
C ₁	0.21
C ₂	-0.03
C ₃	0.32
O ₄	-0.49

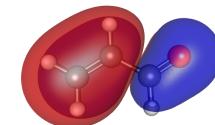
MOs



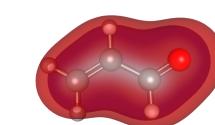
LUMO+1



LUMO



HOMO



HOMO-1

Going beyond simple Hückel...

Extended Hückel Theory (EHT)

- Created by Roald Hoffmann in the 60's
- Consider **valence** electrons (π and σ)
- **Core electrons** are still ignored
- The basis is not assumed to be orthonormal anymore: we must calculate the **overlap matrix S**
- The **atomic basis functions** are **Slater functions**
- It uses **Koopmans' theorem** for the diagonal elements

$$F_{ii} = -I_i \quad \text{where } I_i \text{ is the atomic ionization potential of the atom}$$

- Off-diagonal are

$$F_{ij} = -\frac{K}{2}(I_i + I_j)S_{ij} \quad \text{where } K = 1.75 \text{ is an empirical constant}$$

Generalized eigenvalue problem

How to solve a generalized eigenvalue problem $\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$?

This is simple: let's transform $\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$ into $\mathbf{F}'\mathbf{C}' = \mathbf{C}'\mathbf{E}$

- ① Calculate the **orthogonalization matrix \mathbf{X}** such as $\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{I}$
- ② Compute the Fock matrix in the **orthogonal basis $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$**
- ③ Compute the **eigenvectors \mathbf{C}' and eigenvalues \mathbf{E} of \mathbf{F}'**
- ④ Back-transform the MOs in original basis: $\mathbf{C} = \mathbf{X} \mathbf{C}'$

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E} \Rightarrow \mathbf{F}\mathbf{X}\mathbf{C}' = \mathbf{S}\mathbf{X}\mathbf{C}'\mathbf{E} \Rightarrow \underbrace{\mathbf{X}^\dagger \mathbf{F} \mathbf{X}}_{\mathbf{F}'} \mathbf{C}' = \underbrace{\mathbf{X}^\dagger \mathbf{S} \mathbf{X}}_{\mathbf{I}} \mathbf{C}'\mathbf{E} \Rightarrow \mathbf{F}'\mathbf{C}' = \mathbf{C}'\mathbf{E}$$

Different orthogonalizations

- ① **Symmetric orthogonalization** $\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U} \mathbf{s}^{-1/2} \mathbf{U}^\dagger$
- ② **Canonical orthogonalization** (when you have linear dependencies) $\mathbf{X} = \mathbf{U} \mathbf{s}^{-1/2}$
- ③ **Gram-Schmidt orthogonalization** (numerically not super stable)