Lecture # 2

Bonding Theories (continued)

TODAY: (1) Hückel Molecular Orbital Theory
(2) Frontier Molecular Orbital Theory
(3) Arrow-Pushing Mechanisms

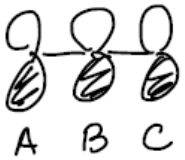
Hückel Theory

- only for π-systems
- generates MO's for conjugated polyenes

Assumptions / Simplifications

(1) valence e⁻s only

(2) Only nearest neighbor interactions



A ⇔ B B ⇔ C ✓

A ⇔ C ignored

(3) Orbital overlap = ∅

(4) e⁻ - e⁻ repulsion neglected.

Setting up Hückel MOs:

1) Basis set

of sp^2 atoms = # of AO's = # of MOs.

↑ p on each atom.

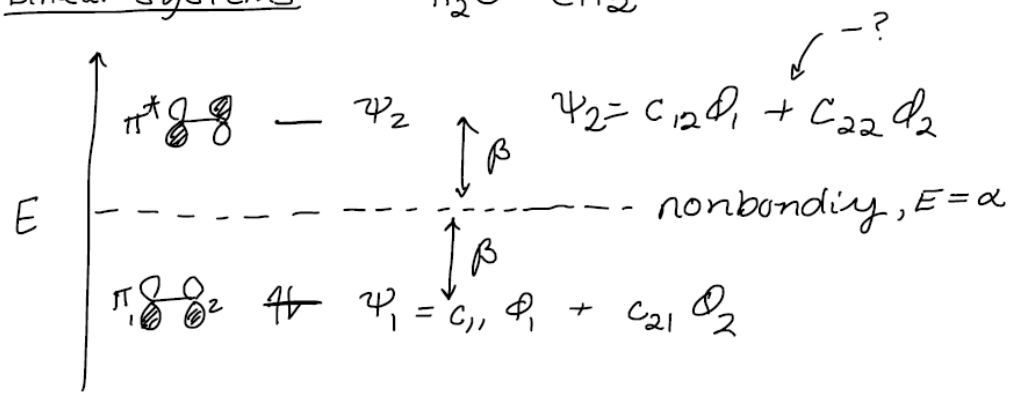
2) ψ (MO's) ≈ symmetrically disposed about nonbonding level.

3) Nodes: ψ_1 = Ø nodes
ψ_2 = 1 nodes
ψ_3 = 2 nodes ...

4) Symmetry of MO's must reflect symmetry of molecule.

(5) Odd linear polyenes have MO @ nonbonding level.

Linear systems $H_2C=CH_2$



$E_j = \alpha + m_j\beta$

$m_j = 2\cos\left(\frac{j\pi}{n+1}\right)$ $\quad j$ = orbital # ; 1, 2, 3, ...
n = # of MO's / C's

ψ_1: $E_1 = \alpha + m_j\beta$, $j=1$

$$m_1 = 2\cos\left(\frac{1\cdot\pi}{2+1}\right) = 2\cdot\frac{1}{2} = 1$$

$$E_1 = \alpha + \beta$$

r = AO #

$$C_{rj} = \left(\frac{2}{n+1}\right)^{1/2} \sin\left(\frac{rj\pi}{n+1}\right)$$

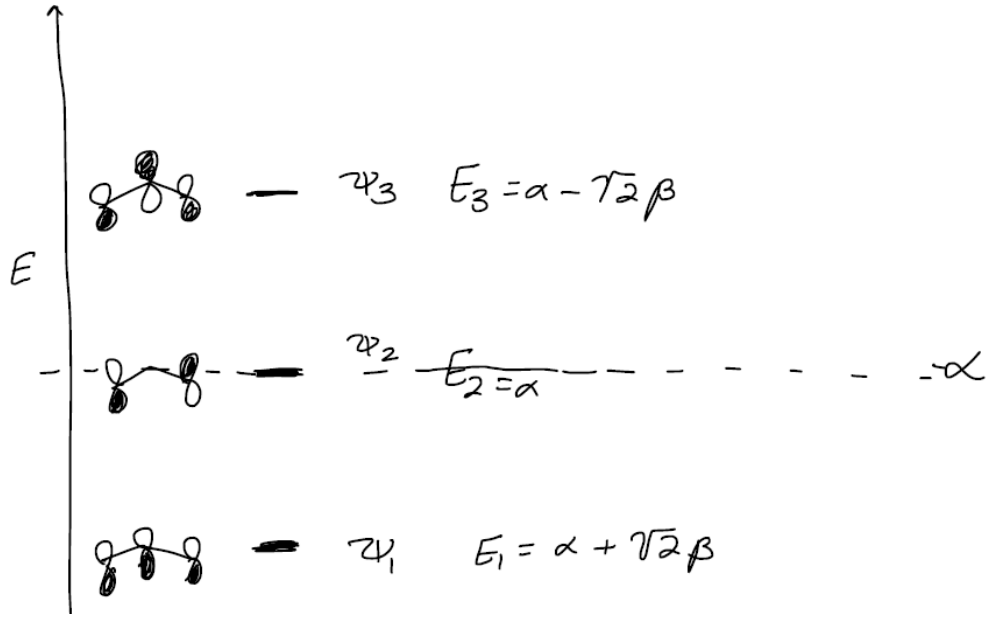
α = Coulomb integral = Energy of e- in lone p orbital

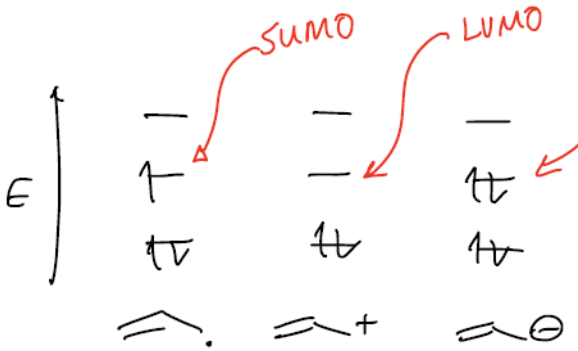
β = Resonance integral = Energy of sharing e- in covalent bond

Allyl

$$E_1 = \alpha + \underbrace{2\cos\left(\frac{1\pi}{4}\right)}_{\sqrt{2}}\beta$$

$$2\cdot\frac{\sqrt{2}}{2}$$

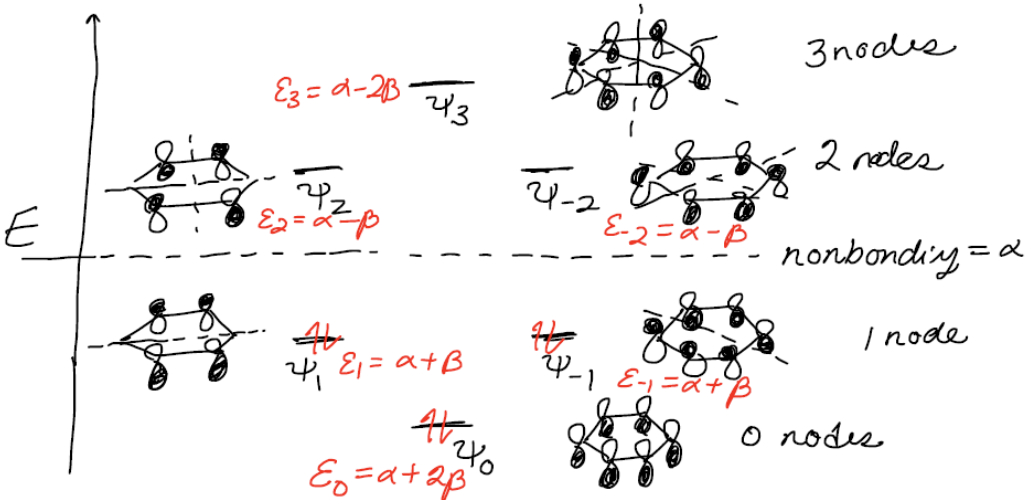




Allyl radical, cation & anion all form bonds to C1 & C3, not C2.

Cyclic Systems

- Degenerate orbitals possible.



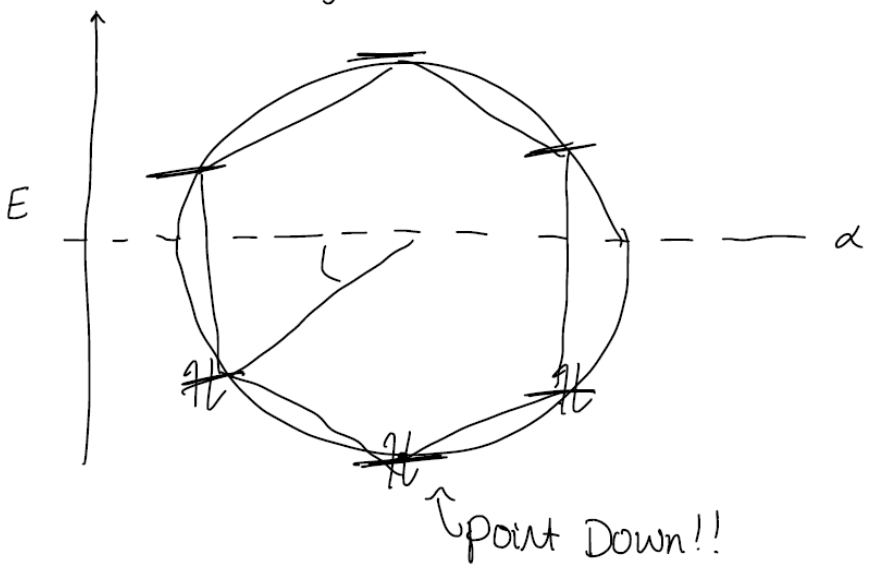
$$\varepsilon_i = \alpha + 2\beta\cos\left(\frac{2i\pi}{N}\right)$$

$i = 0, \pm 1, \pm 2, \ldots \pm \frac{N}{2}$ ← for N = even

or $\ldots \pm \left(\frac{N-1}{2}\right)$ ← for N = odd

N = total # of orbitals

Trick: Frost Magic Circle



PREDICTIONS:

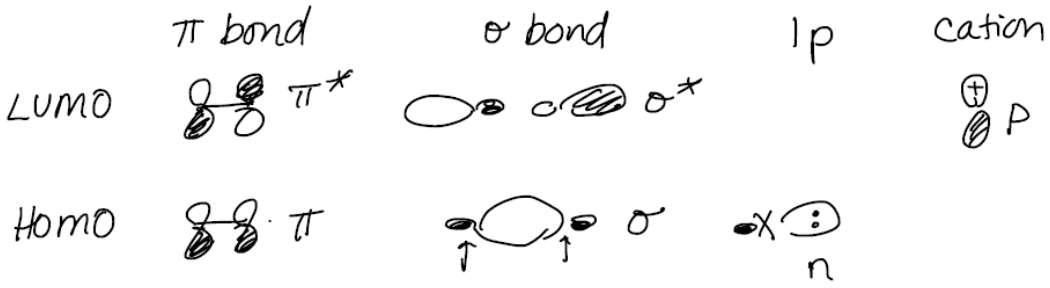
1) Closed shell configuration will have
   2, 6, 10, ... e-s $(4n+2)$

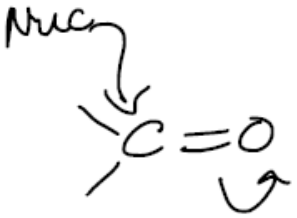
2) 4n e-s will have open shell (diradical) character.

⇒ Hückel Rule of Aromaticity

Frontier Molecular Orbital Theory (FMO)

* Consider only FMO's (HOMO, LUMO, SOMO)
  - SOMO: singly occupied MO

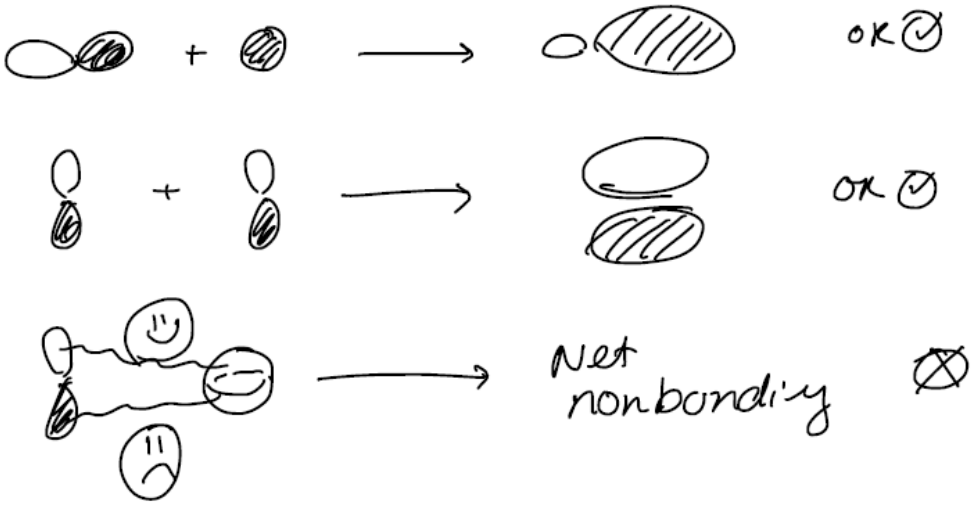




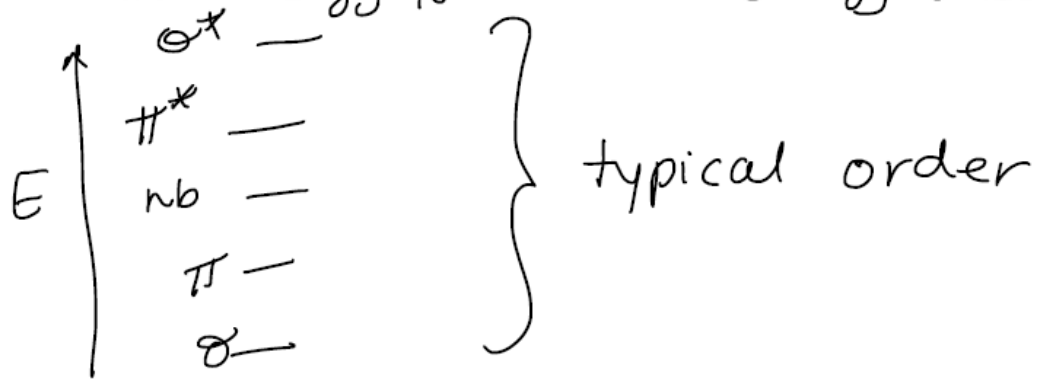
Addition to π*

Guidelines for FMO

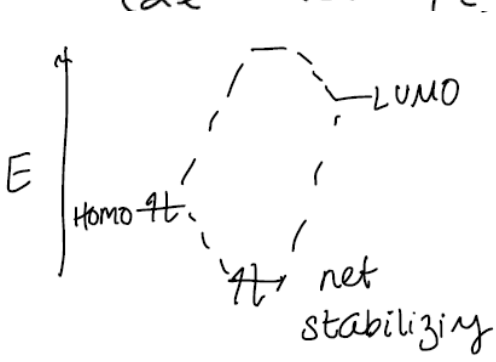
① Only orbitals of "like symmetry" can interact.

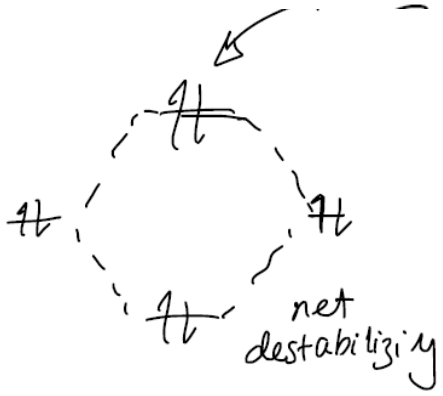
ex 

② Interacting orbitals must be close enough in energy to obtain energy overlap.

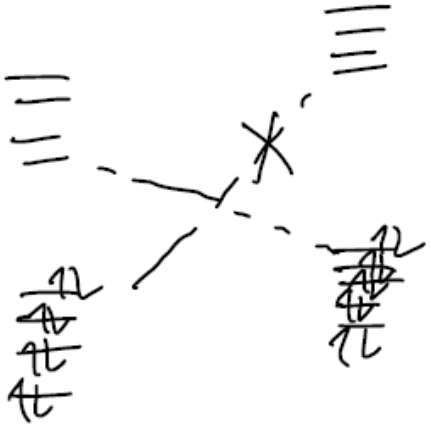


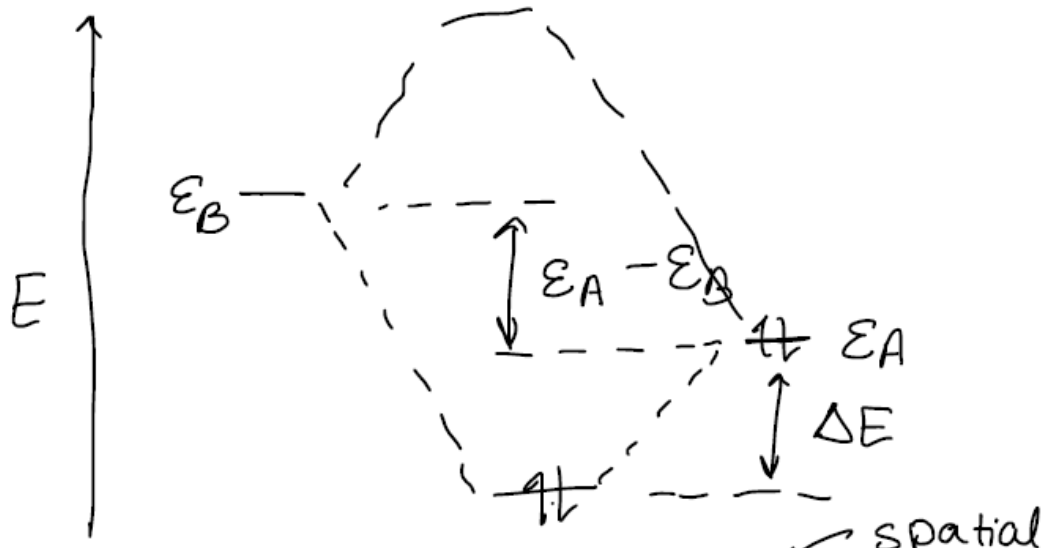
③ Must result in otabilization (2e- vs. 4e-)





④ Choose closest Homo/Lumo gap





$\Delta E \propto \frac{\text{orbital overlap}}{\varepsilon_A - \varepsilon_B}$ ← spatial

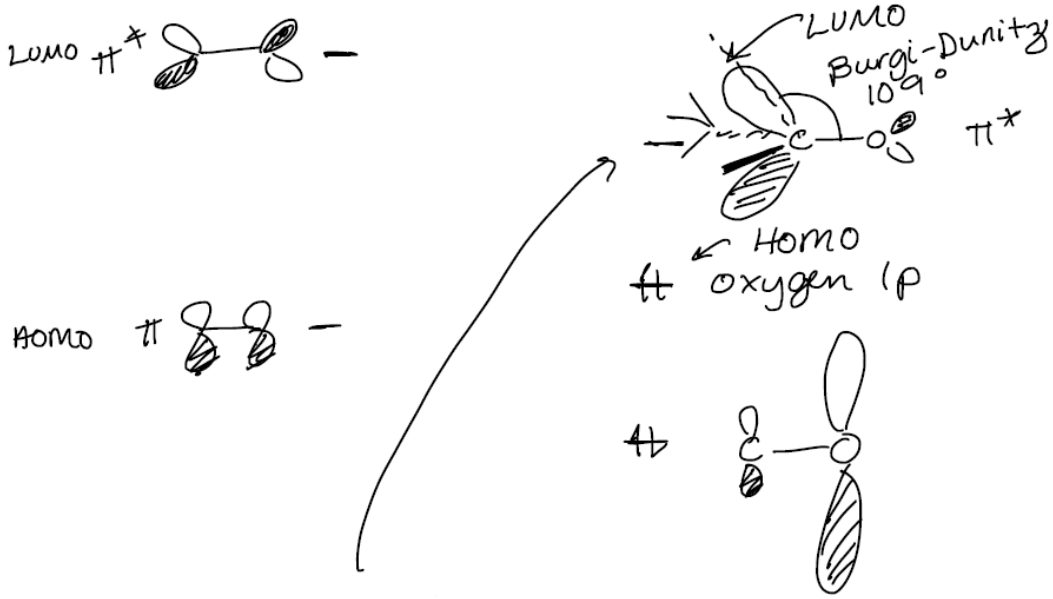
← closer in energy

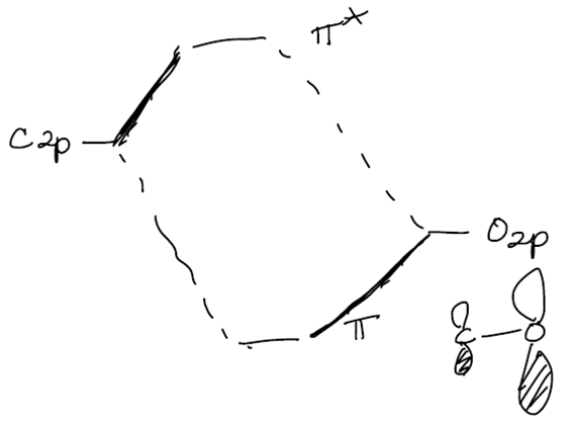
↓

more stabilization

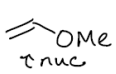
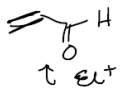
What about heteroatoms?

$CH_2=CH_2$ vs $H_2C=O$





Substituent Effects

Perturbation (vs)	HOMO	LUMO
=	–	–
	↑	↓
EDG 	↑	↑
EWG 	↓	↓