SEMESTER-IH-ORGANIC CHEMISTRY:

Basics of Organic Chemistry Bonding and Physical Properties

MO theory:

MOLECULAR ORBITAL THEORY:

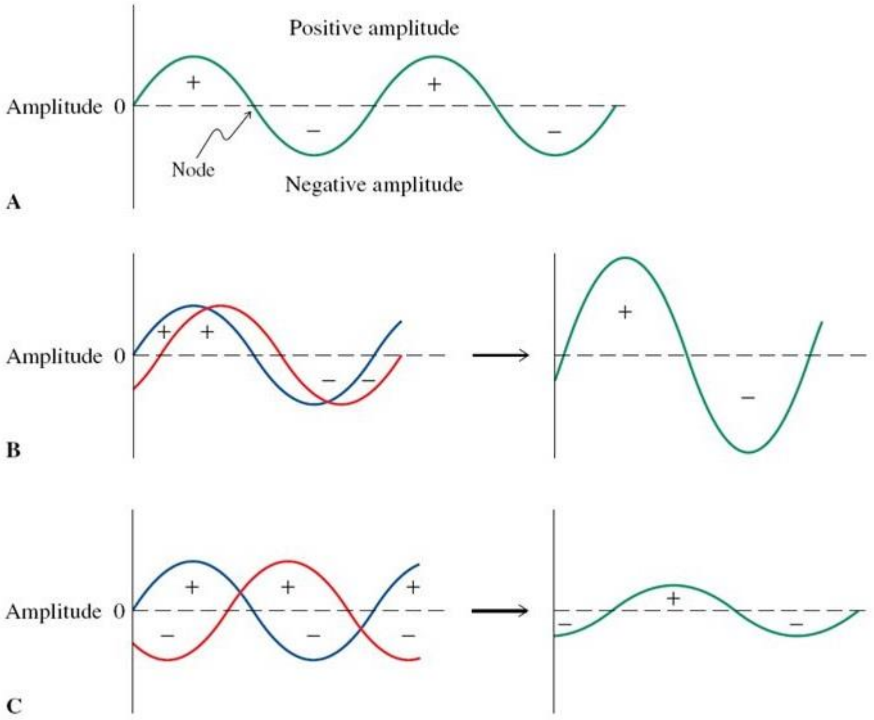
In this approach electrons are not assigned to individual bonds between atoms but are treated as moving under the influence of the nuclei in the whole molecule. Main differences with VBT where the orbitals are considered to be concentrated between two specific atoms, molecular orbital are extended over the entire molecule.

In order to construct the MOs is to combine Atomic Orbitals of the atoms that make up the molecules.

Linear Combination of Atomic Orbitals (LCAO) where n numbers of atomic orbitals are linearly combined to generate n numbers of Molecular Orbitas.

To understand this MOT, we have to be clear about the concept of orbital. According to wave-particle duality electrons can also be considered as wave. To construct MO, combining wave is important. We can superpose one wave over other either constructively (in-phase) or either destructively (out of phase). This is called interference of wave in Physics.

The electron waves contain nodes, where the amplitude of the wave changes sign, and can interact with each other, producing either constructive or destructive interference:



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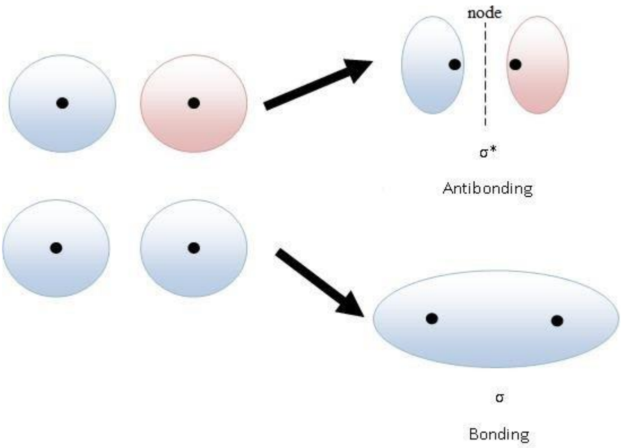
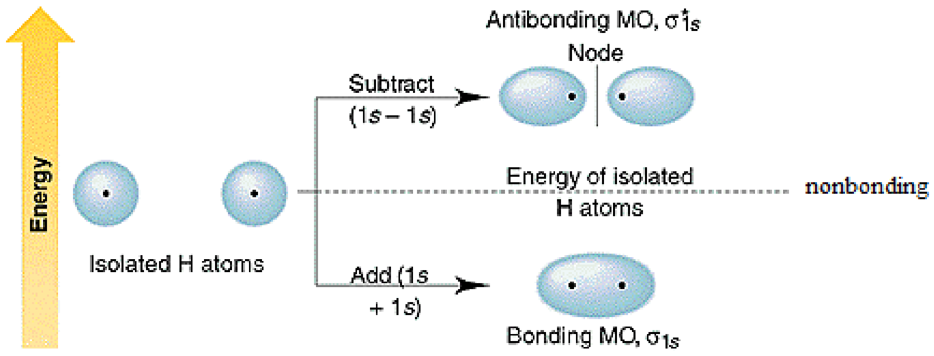
CONCEPT OF BONDING AND ANTIBONDING:

σ- σ* of s orbitls:

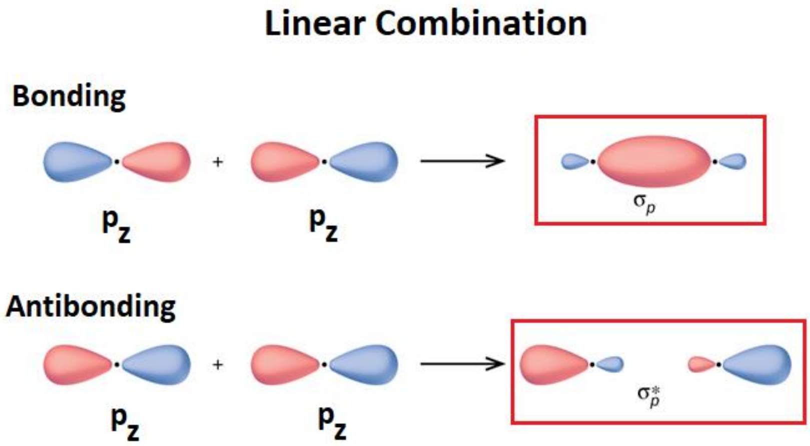


Destructive Interference

Constructive Interference



σ- σ* of p orbitls:



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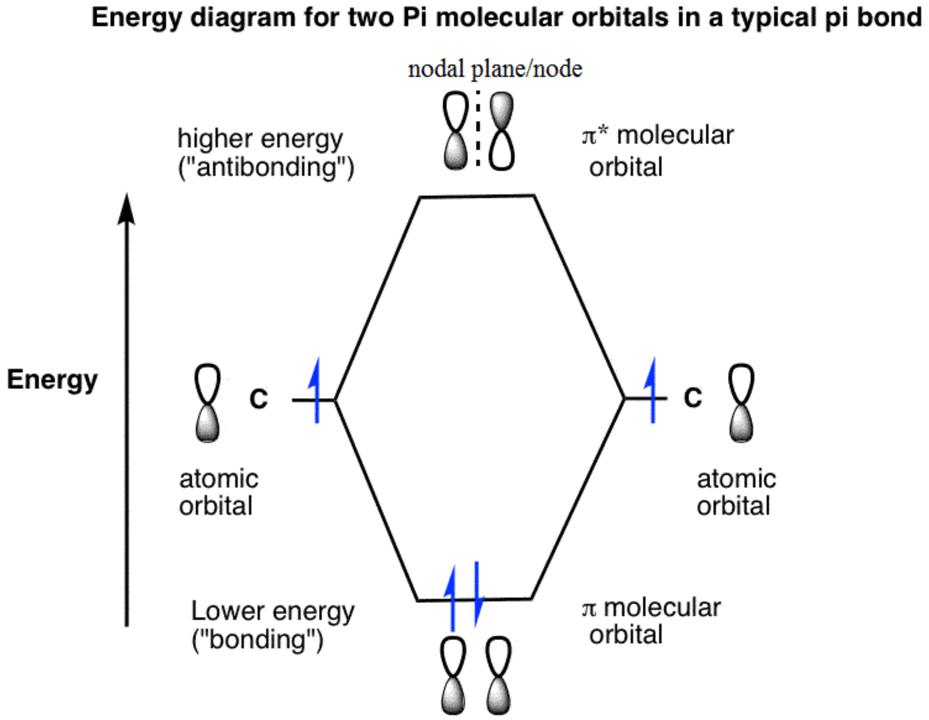
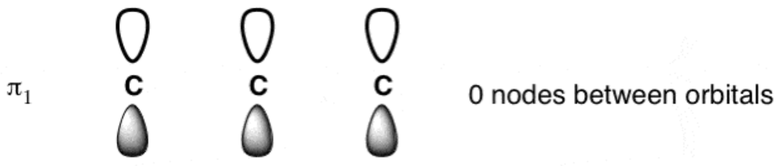
π- π * of p orbitls:



To draw π- MO:

1. The number of molecular orbitals (n) for a pi-system is equal to the number of contributing p orbitals. For the allyl system, n=3. We had three contributing p orbitals and thus three pi molecular orbitals.

2. The lowest-energy orbital always has zero nodes between the p-orbitals (note that we say “no nodes between the p-orbitals” because we’re not counting the node between the individual lobes, which is inherent to all p-orbitals). That is, in the lowest-energy orbital, all phases of the contributing p-orbitals are aligned the same way.



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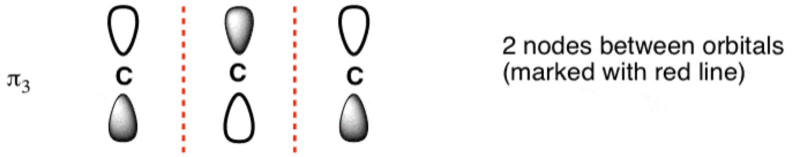
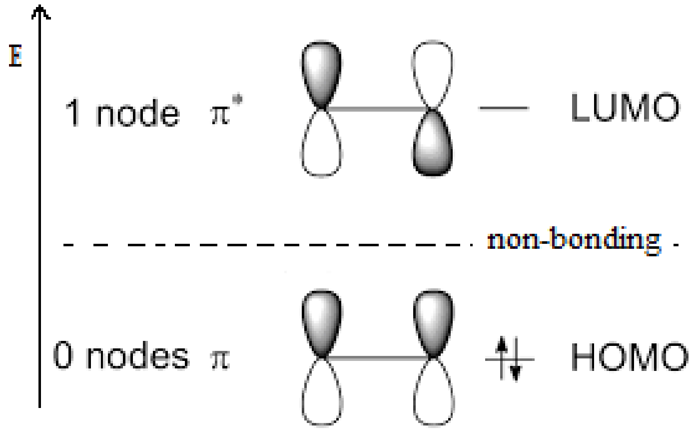
3. The number of nodes between p-orbitals increases by 1 for each successive energy level, such that the highest-energy orbital has (n-1) nodes (all phases of contributing p-orbitals alternate).

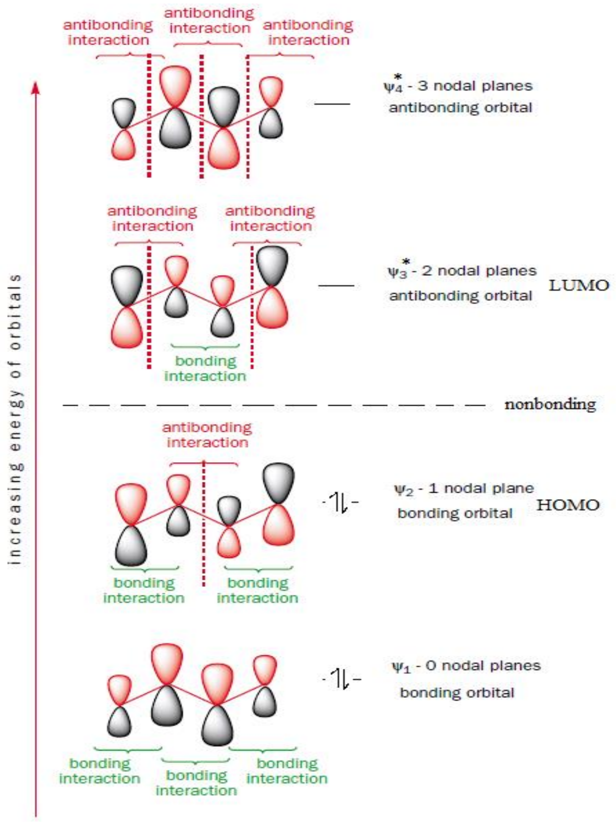


4. Two sets of orbitals are distributed each side of horizontal non-bonding line; below non-bonding level there are bonding M.O. and above it antibonding M.O.

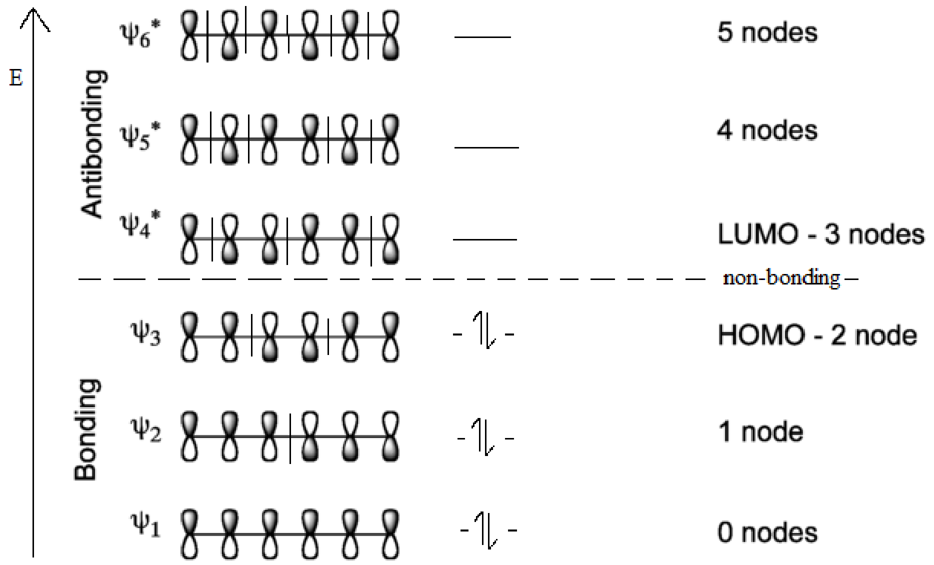
I. π- MO of Ethylene:



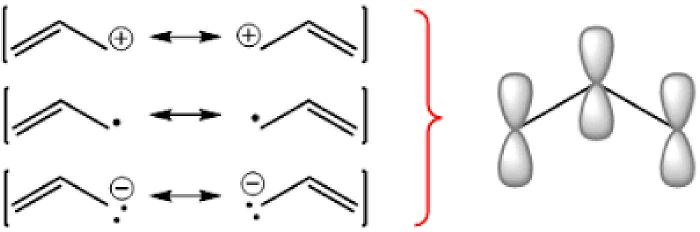
II. π- MO of conjugated diene (1,3 butadiene):

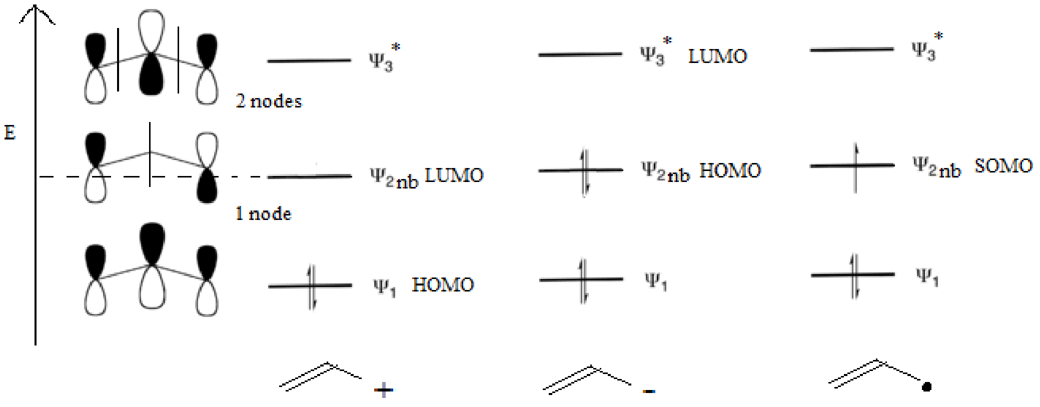


III. π- MO of 1,3,5 hexatriene:

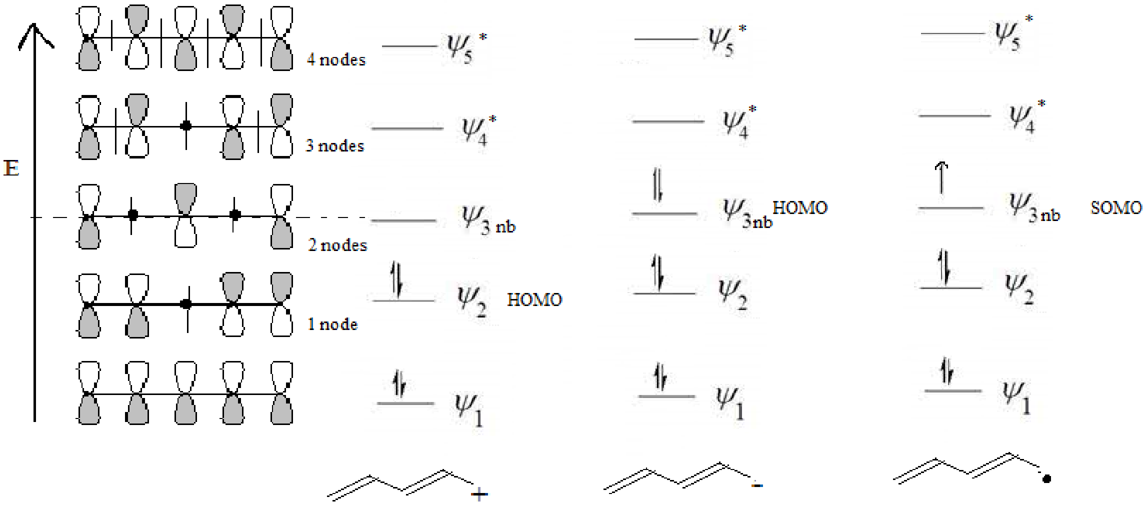


IV. π- MO of Allyl systems:





V. π- MO of Pentadienyl systems:



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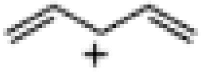
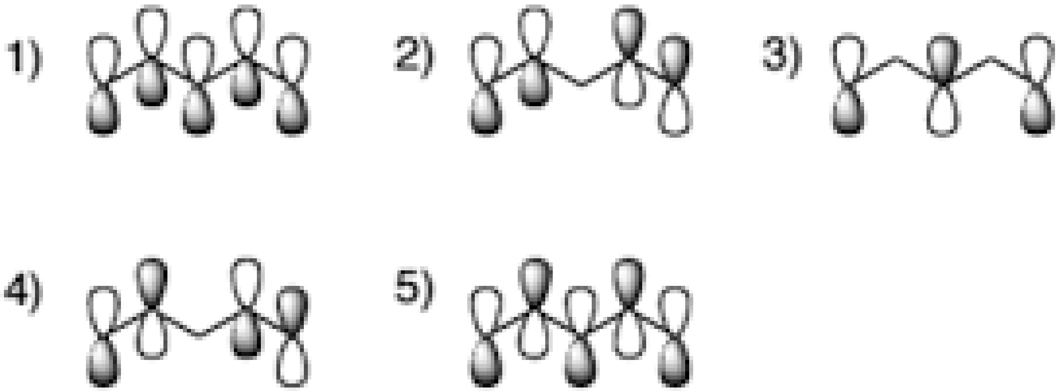
OR

Orbital picture can be drawn in zigzag way.

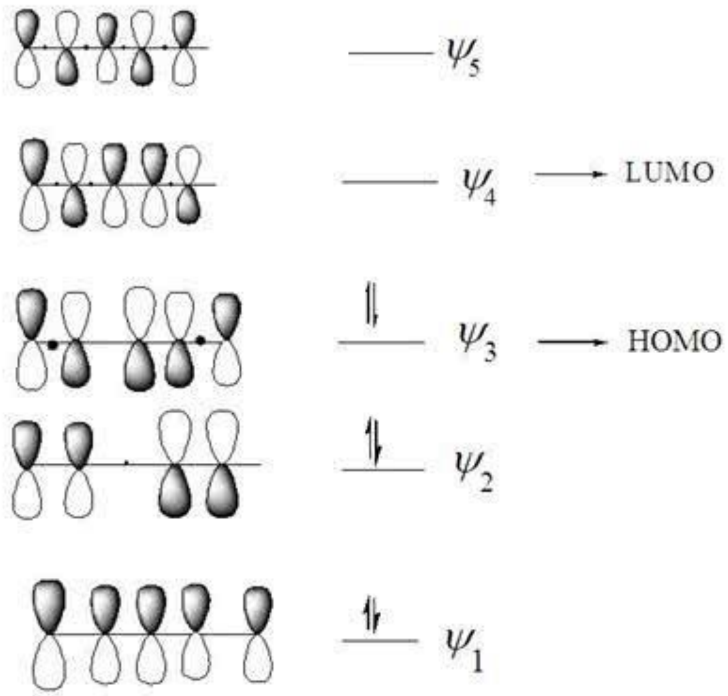




OR

Pentadienyl anion resonance structures

Pi molecular orbitals of pentadienyl anion is,



This is having six pi electrons.Si-3 is HOMO and HOMO has two nodes.

SEMIH-ORGANIC CHEMISTRY _LECTURE 7_APS

Frost Diagram: A learning technique for determining the number and relative energies for the π-molecular orbitals of cyclically conjugated systems.

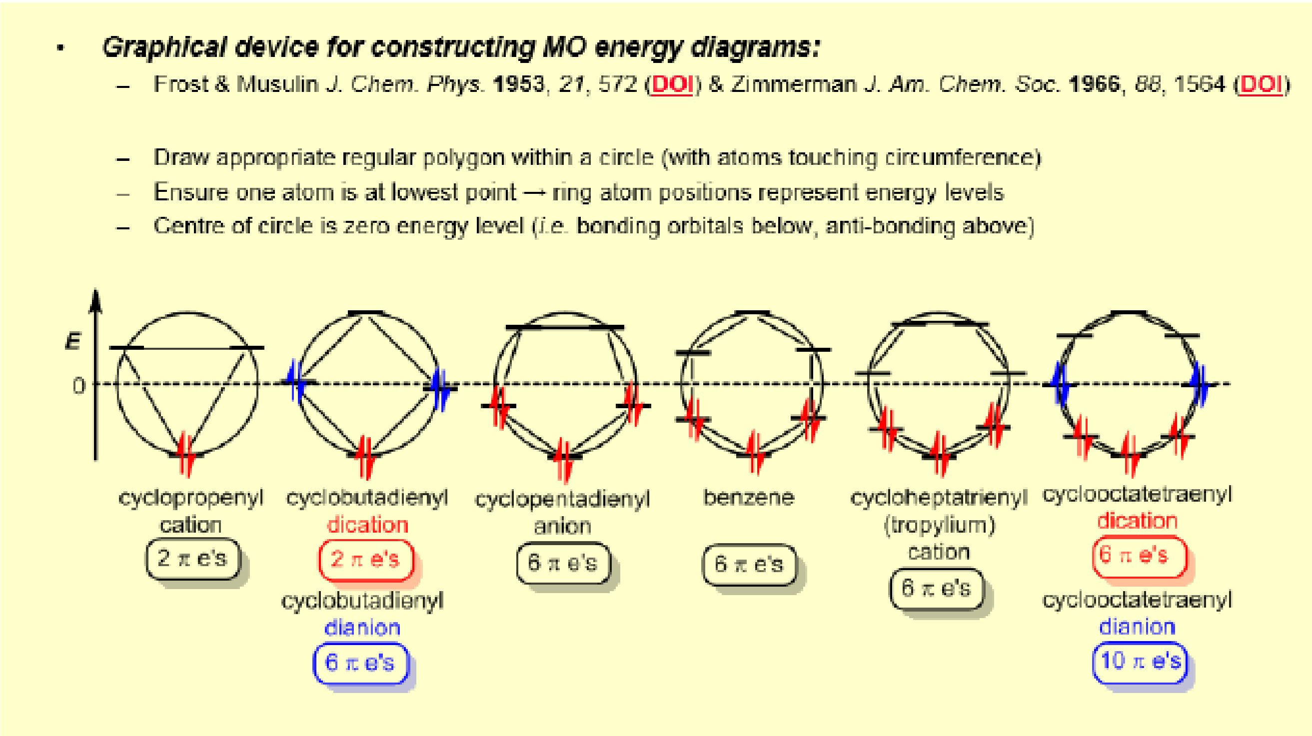
Steps:

1. Draw a circle.

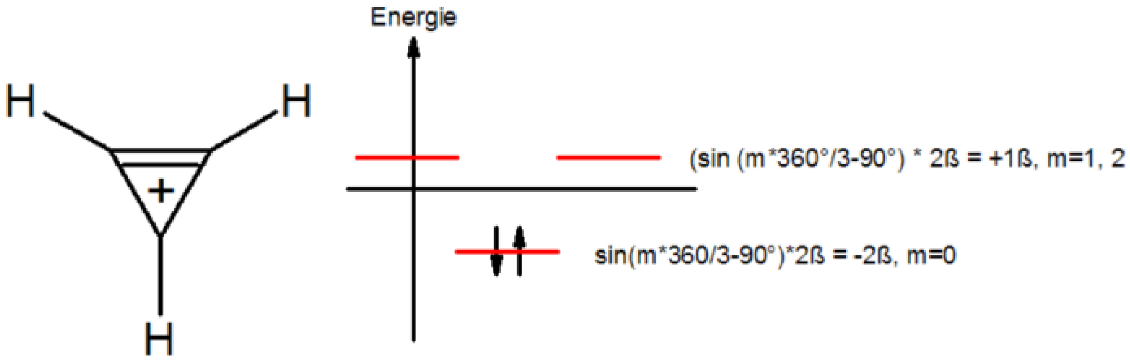
2. Inscribe a regular polygon inside the circle so that one of the corners is at the bottom.

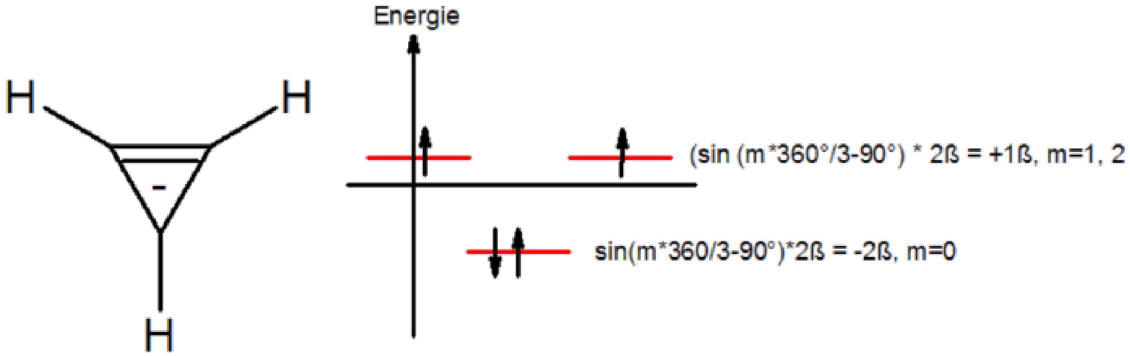
3. Draw a horizontal line at each vertex intersecting the circle. These are the energy levels of the MOs.

4. Draw a dotted-line through the center of the circle. This represents the boundary between bonding and antibonding orbitals. Orbitals coinciding with this line are nonbonding.



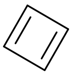
- ***Graphical device for constructing MO energy diagrams:***
  - Frost & Musulin *J. Chem. Phys.* **1953**, *21*, 572 (DOI) & Zimmerman *J. Am. Chem. Soc.* **1966**, *88*, 1564 (DOI)
  - Draw appropriate regular polygon within a circle (with atoms touching circumference)
  - Ensure one atom is at lowest point → ring atom positions represent energy levels
  - Centre of circle is zero energy level (*i.e.* bonding orbitals below, anti-bonding above)



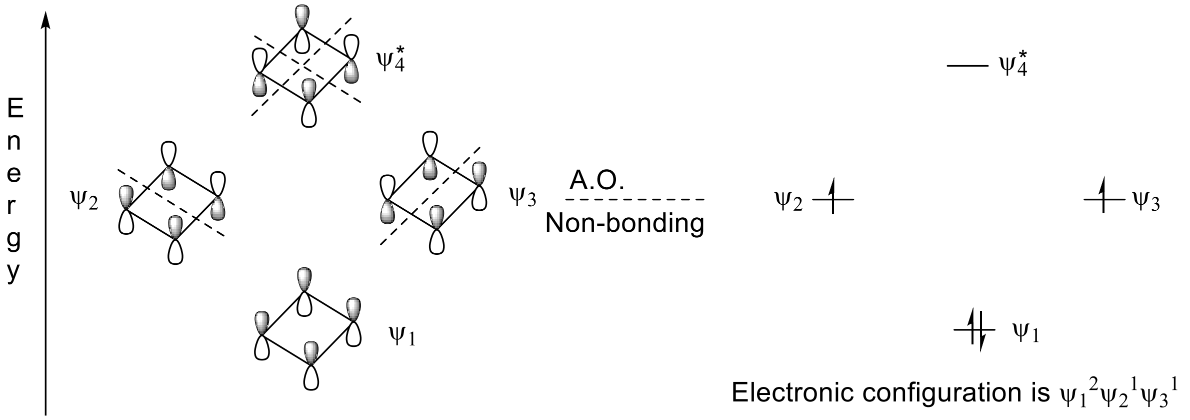


1. **π- MO of cyclic system:**

i) Cyclobutadiene:



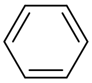
cyclobutadiene



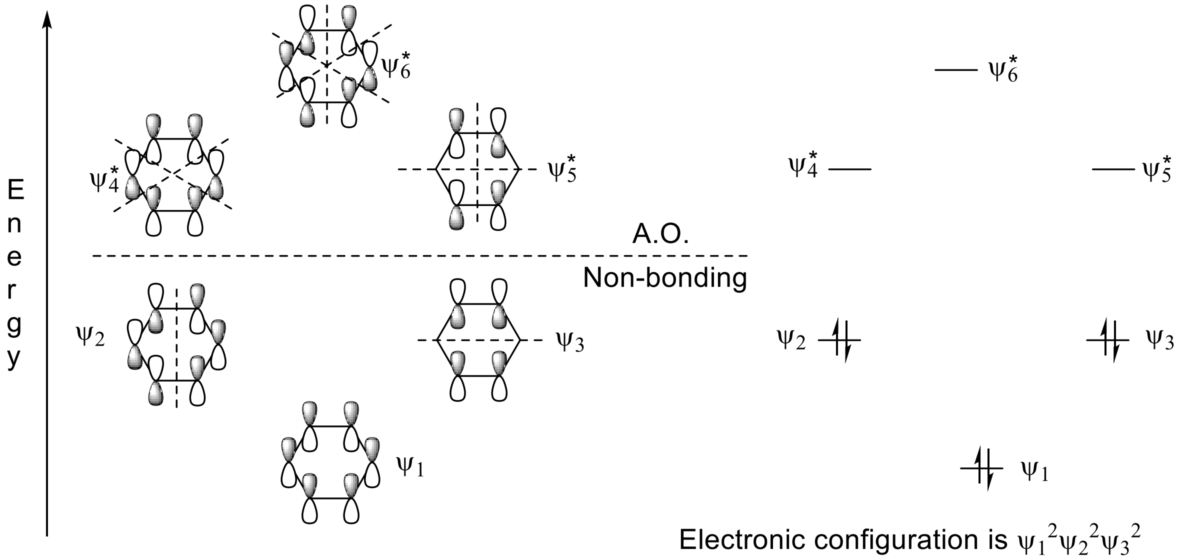
Electronic configuration is $\psi_1^2\psi_2^1\psi_3^1$

Here, ψ_1 is bonding and ψ_4 antibonding orbital. ψ_2 and ψ_3 are non-bonding orbital since they both have 2 bonding and 2 antibonding interaction between the p orbitals i.e., no net bonding and antibonding interaction.

ii) Benzene:



Benzene



Electronic configuration is $\psi_1^2\psi_2^2\psi_3^2$

Here, ψ_2 and ψ_3 have same energy and both are completely filled. Thus, ψ_2 and ψ_3 both are HOMO. Similarly, ψ_4^* and ψ_5^* both have same energy and hence both are LUMO.

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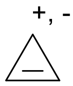
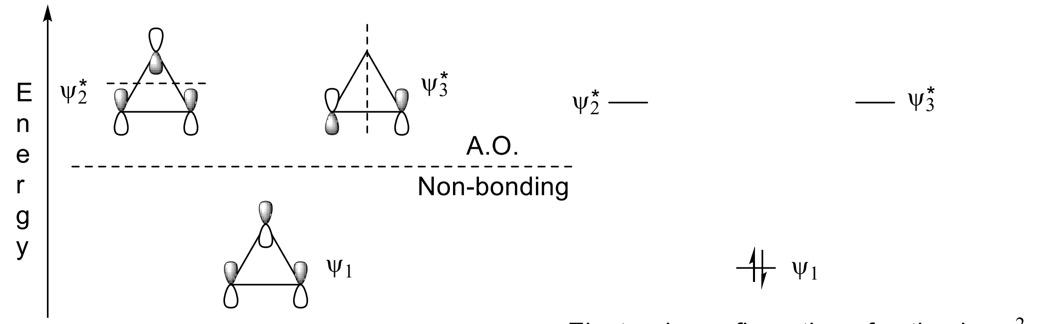
iii) Cyclopropenyl cation, anion and radical:



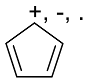
cyclopropenyl system



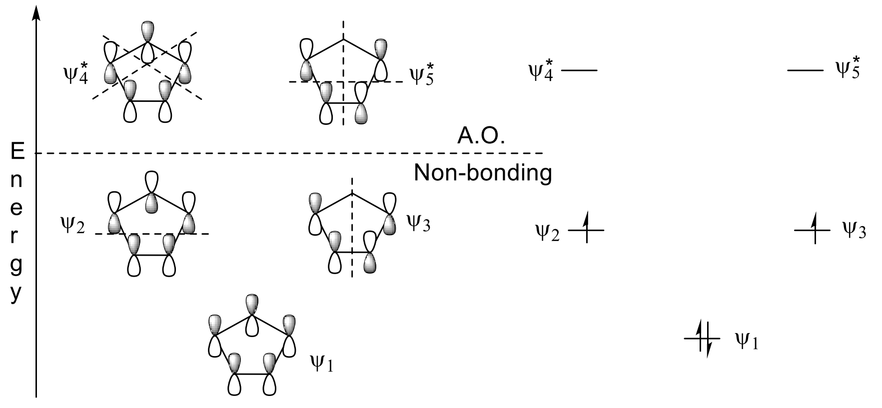
Electronic configuration of cation is ψ_1^2

Similarly, the electronic configuration of cyclopropenyl anion is $\psi_1^2\psi_2^{*1}\psi_3^{*1}$
and the electronic configuration of cyclopropenyl radical is $\psi_1^2\psi_2^{*1}$

iv) Cyclopentadienyl cation, anion and radical:



cyclopentadienyl system



Electronic configuration of cation is $\psi_1^2\psi_2^1\psi_3^1$

Similarly, the electronic configuration of cyclopropenyl anion is $\psi_1^2\psi_2^2\psi_3^2$
and the electronic configuration of cyclopropenyl radical is $\psi_1^2\psi_2^2\psi_3^1$

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Hückel's Rule:

" Planar, monocyclic, completely conjugated system in which each ring element contains a p-orbital will be aromatic only when the ring contains (4n+2)π electrons.[n=0,1,2,3....].

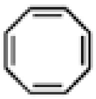
<u>AROMATIC:</u> Compounds those posses extra stability as a result of cyclically delocalized π-systems compared to corresponding open chain analogue.

<u>ANTIAROMATIC:</u> Compounds that are destabilized as a result of cyclically delocalized π-systems compared to corresponding open chain analogue. In this case the ring contains 4nπ electrons.[n=0,1,2,3....].

<u>NONAROMATIC:</u>

Non aromatic compounds, as the name implies, are not aromatic due to reasons such as lack of planarity or disruption of delocalization. They may contain 4n or 4n+2 π electrons.

Delocalization is possible only if atoms sharing the electrons lie in or close to the same plane so that their p orbitals can overlap efficiently. For example, cyclooctatetraene is 8 π electron system; If completely planar, this molecule will become antiaromatic but the molecule is actually boat shaped and nonaromatic. Nonaromatic form is more stable than an antiaromatic form.

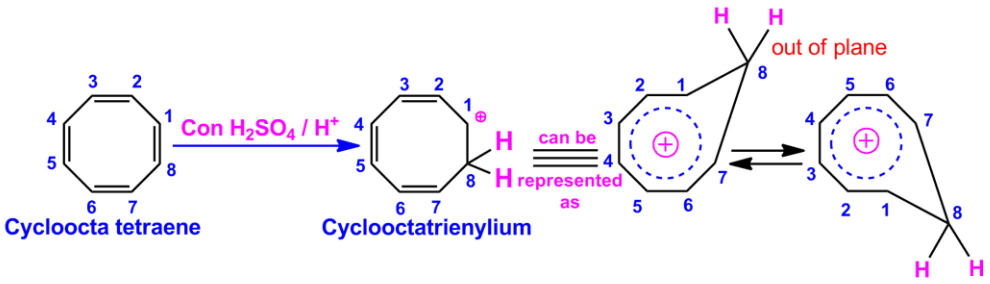


Cyclooctatetraene "escapes"
from anti-aromaticity by twisting
into a "tub" shape
more stable than the
flat, anti-aromatic form)

<u>HOMOAROMATIC</u>

If a stabilized cyclic conjugated system (4n+2 e s) can be formed by bypassing one saturated atom, that lead to homoaromaticity. Compared to true aromatic systems, the net stabilization here may be low due to poorer overlap of orbitals.

Cyclooctatrienyl cation (homotropylium ion) formed when cyclooctatetraene is dissolved in concentrated sulfuric acid is the best example to demonstrate homoaromaticity. Here, six electrons are spread over seven carbon atoms as in Tropylium cation. Electron delocalization in this case is pictorially represented below



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