

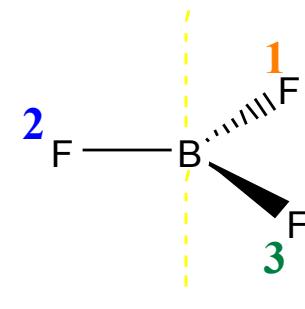
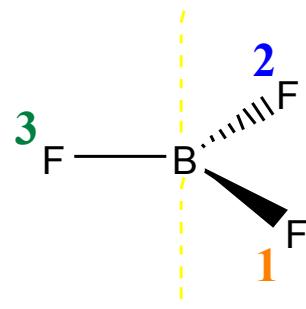
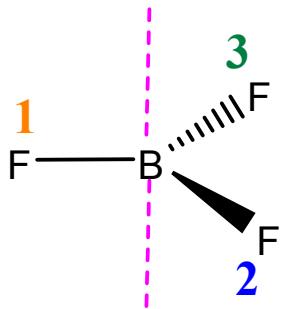
Huckel Theory Molecular Orbital Theory For Conjugated Systems

Symmetry of Objects

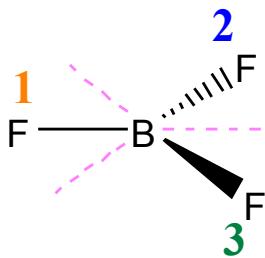


Symmetry

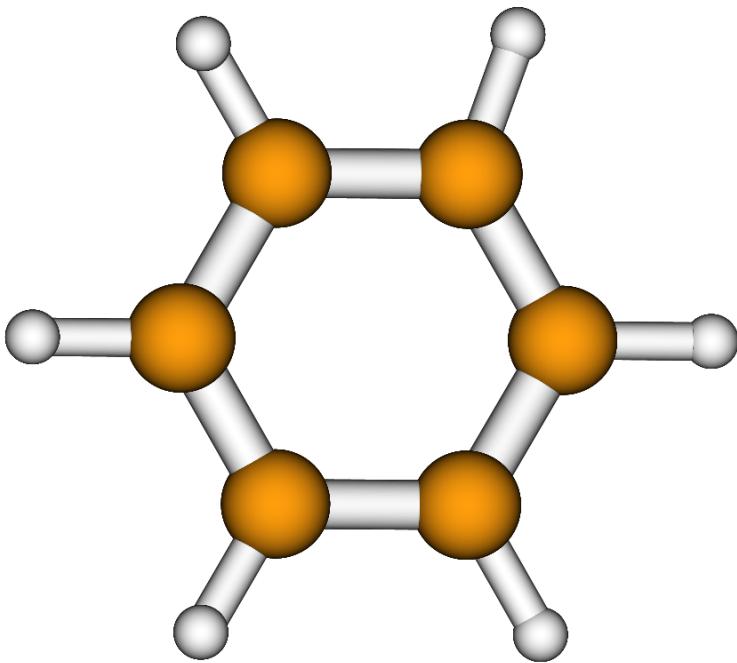
Rotation (C)



Reflection (σ)



Molecular Symmetry



One C_6 axis, Six C_2 axes

One σ_h , Six σ_v

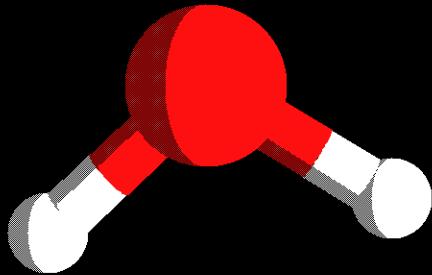
One i

Symmetry

Symmetry Elements

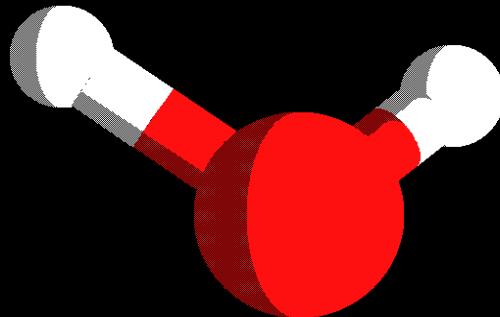
A geometrical entity such as **a line, a plane or a point**, with respect to which one or more symmetry operations may be carried out

1. Plane of symmetry
2. Center of symmetry or (inversion symmetry)
3. Axis of symmetry



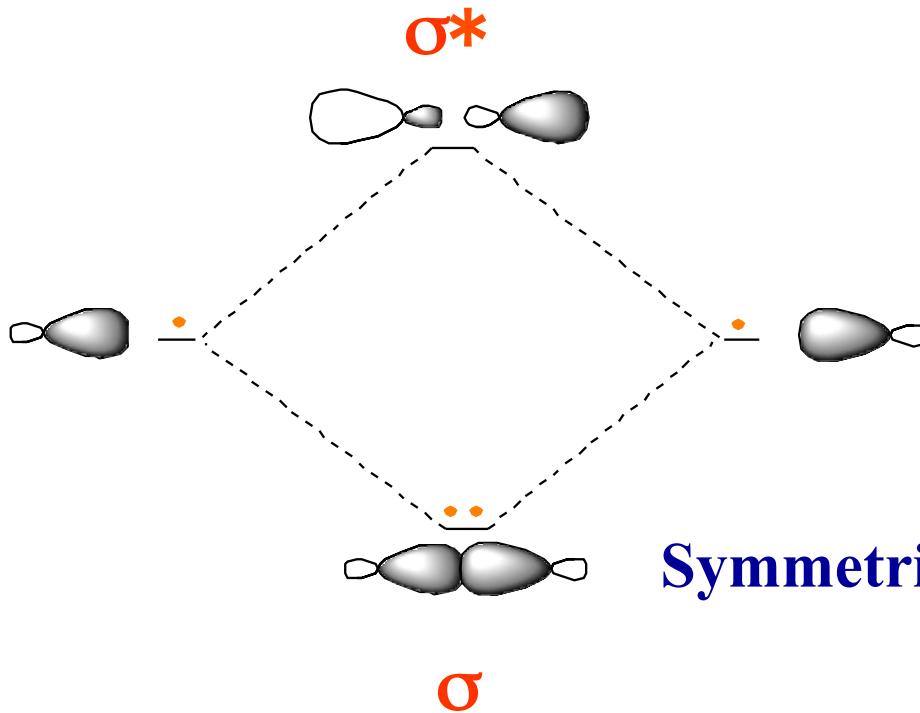
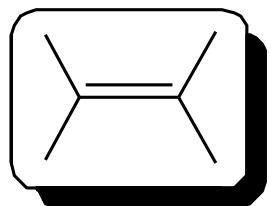
Symmetric
Stretch

Bending



Asymmetric Stretch

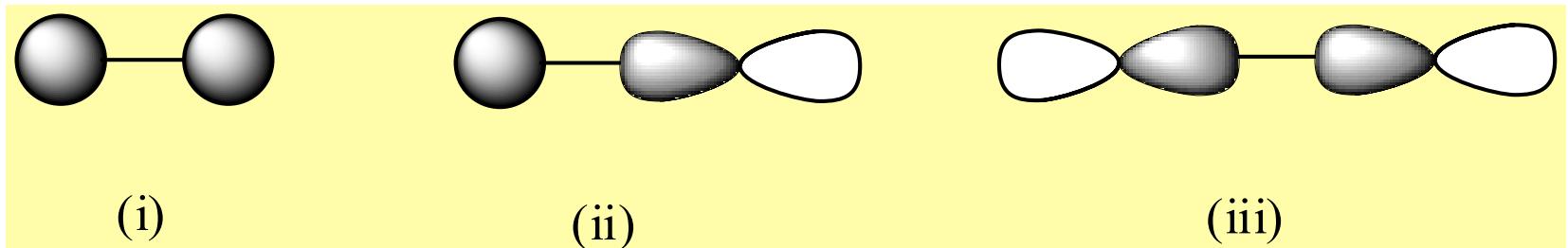
Orbital Symmetry



Symmetric along the axis

For any bonding molecular orbital (**BMO**) there should be a corresponding antibonding molecular orbital (**ABMO**)

More on sigma orbitals

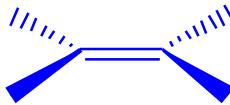
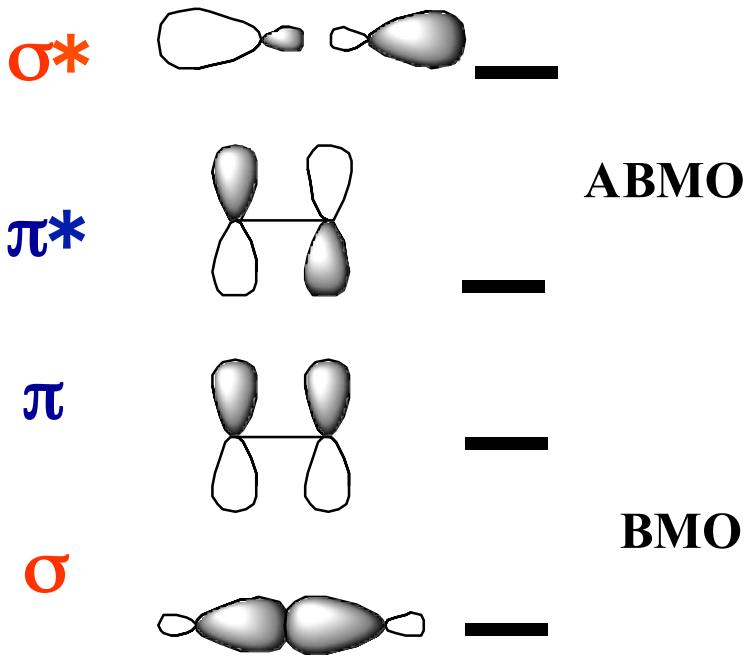
 σ

σ -type overlaps contain no nodes along the internuclear region/axis.

Symmetric along the axis

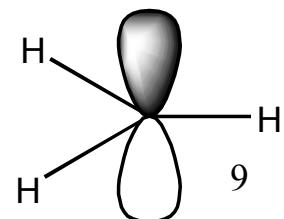
When a molecules is formed from the AOs of the constituent atoms, there are only molecular orbitals (MO) for the molecule. Nodes of MOs are only considered, not of that of the AOs

Types of Orbitals: Ethylene



Nonbonding orbital: e.g., p_z -orbital (AO) on BH₃

An orbital which is NOT Bonding (lone!)



Significance of Orbital Energies

Nucleophiles have higher energy filled nonbonding orbitals
(Ready to donate electrons to suitable electrophiles)

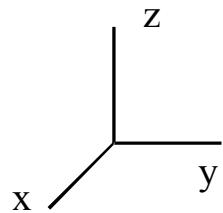
e.g., nonbonding MO in NH_3 , that contains the lone pair of electrons, is responsible for the nucleophilic character of the molecule

Electrophiles are characterized by lower energy unfilled nonbonding (or anti-bonding) orbitals

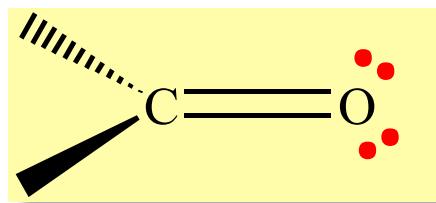
e.g., empty nonbonding MO in BF_3

electron rich to electron poor

Types of Orbitals: Formaldehyde

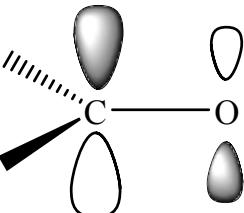


In xy-plane



Frontier MOs

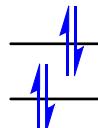
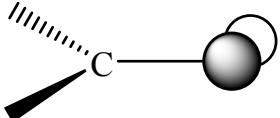
π_{CO}^*



—

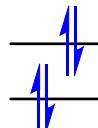
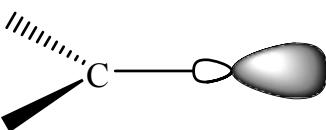
Empty levels

n_{O}

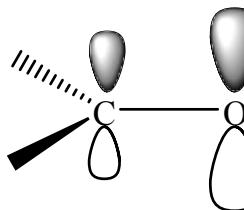


Filled levels

n'_{O}



π_{CO}

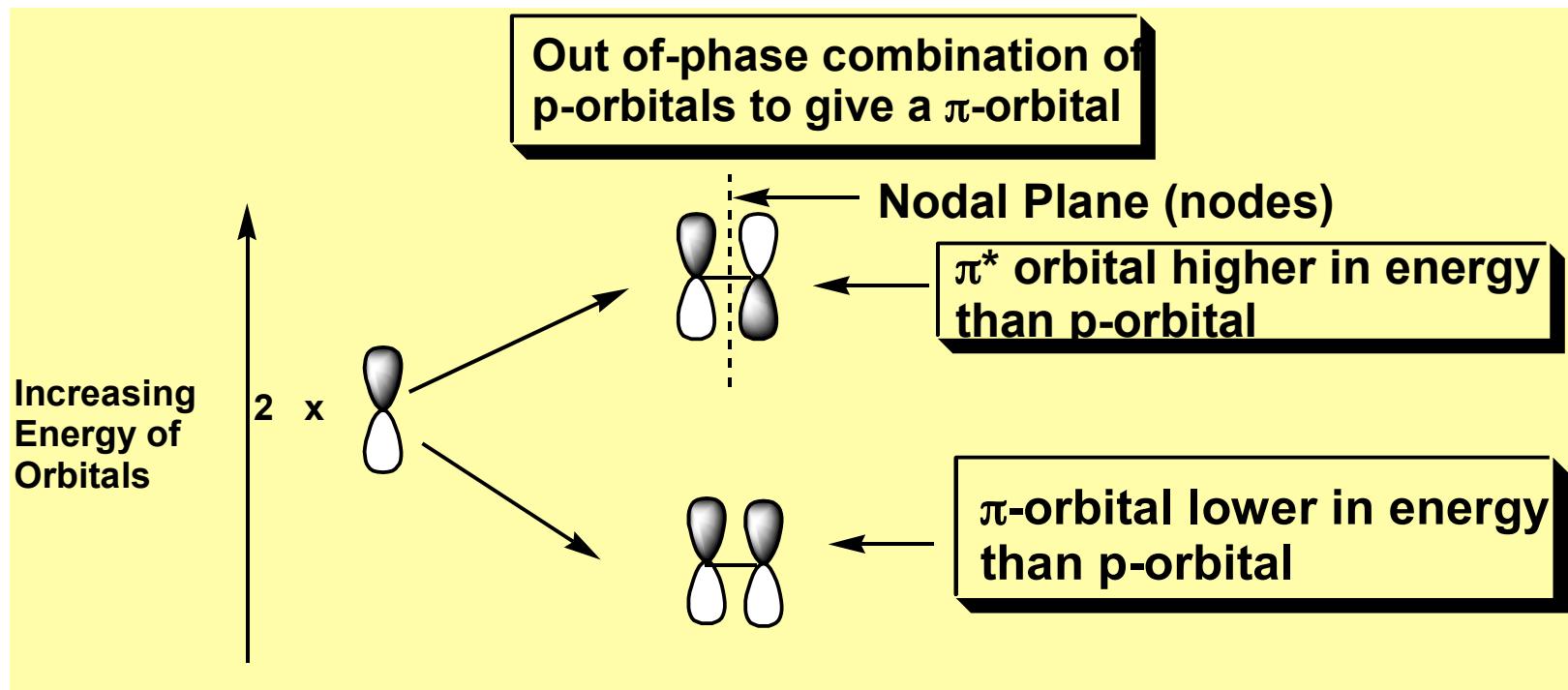


Ethylene MOs

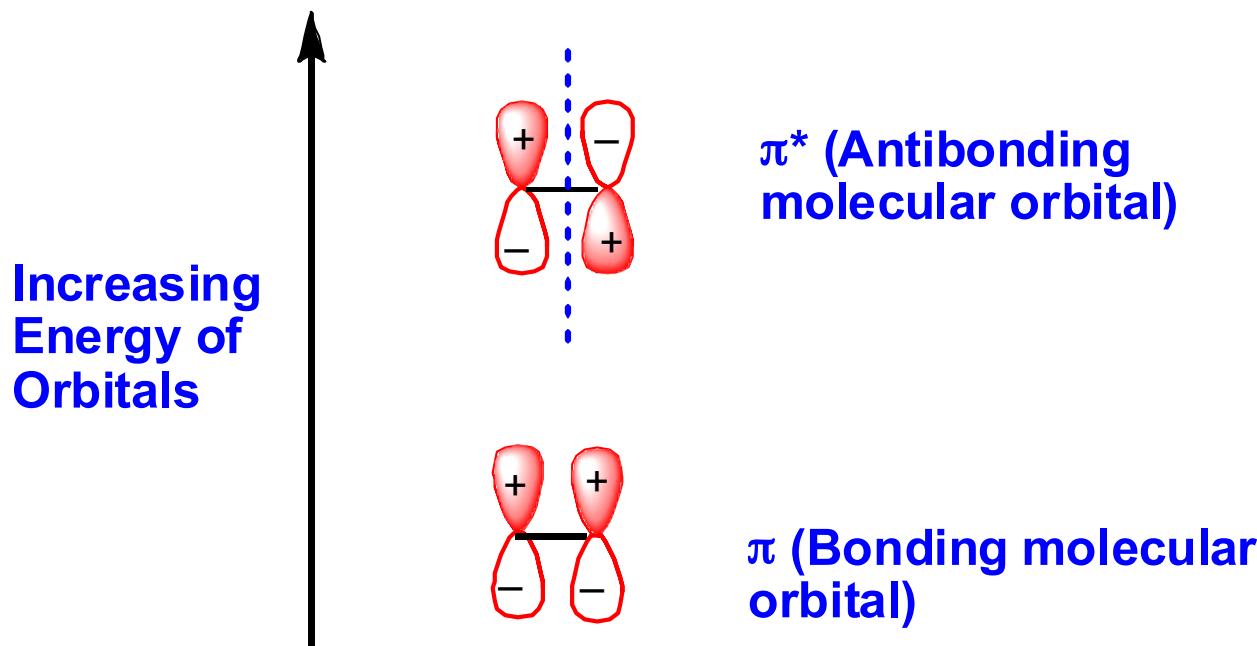
Ethylene shows interesting properties due to the presence of a π -bond

The C-C π -orbital is the **Highest Occupied Molecular Orbital (HOMO)** of the alkene

Linear Combination of p -orbitals, leading to C-C π -orbital can be represented as,



Ethylene MOs



Total Number of π -electrons = 2

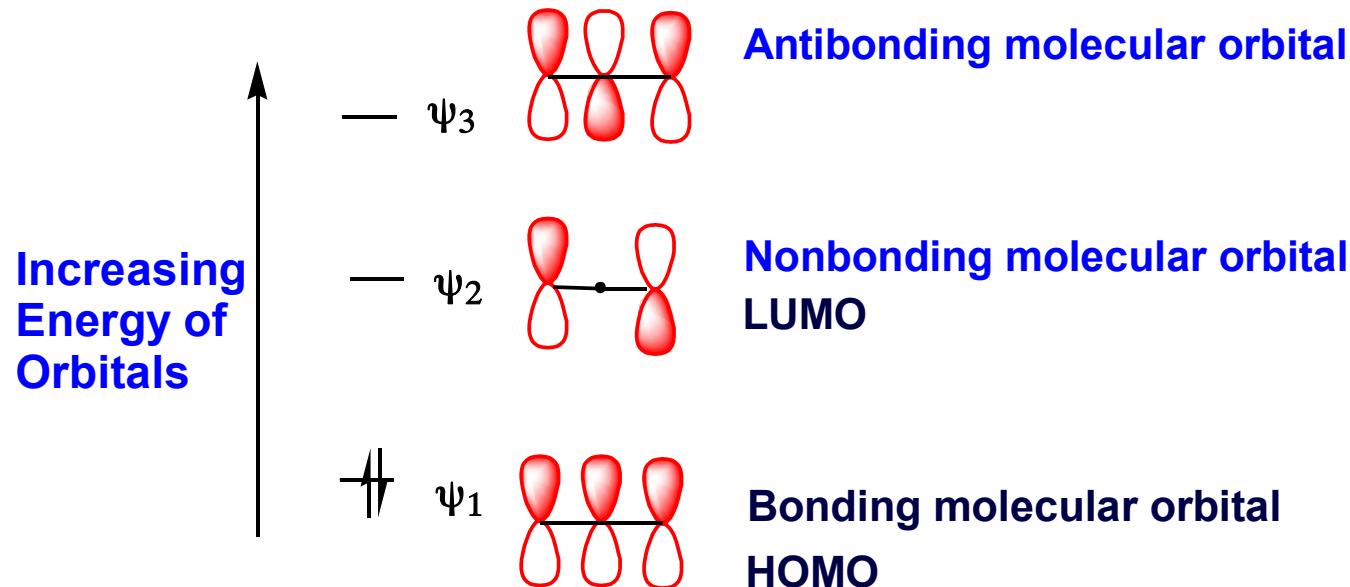
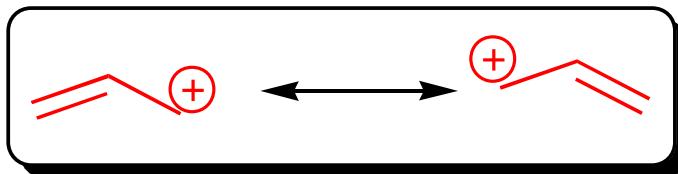
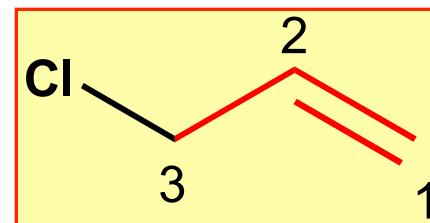
Total Number of π -orbitals = 2

Both electrons will occupy the lowest energy MO, i.e., BMO

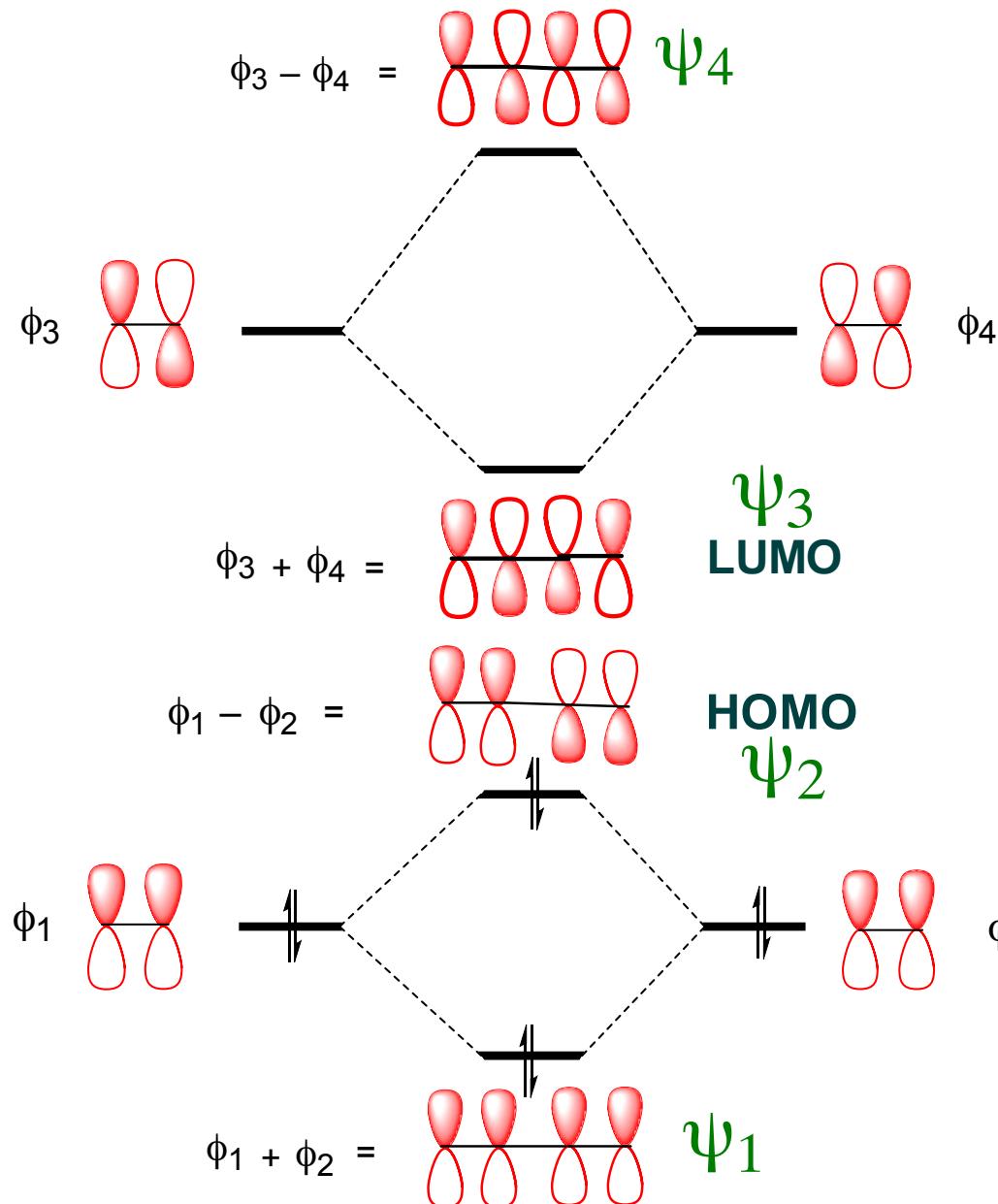
How about MOs for allyl system?

Allyl (three carbon conjugated system)

E.g., Allyl cation



Can we construct butadiene MOs?



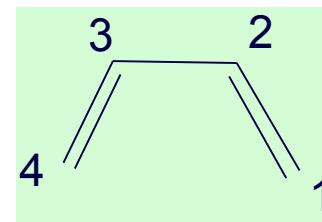
LUMO is lower in energy than the LUMO of ethylene

HOMO is higher in energy than the HOMO of ethylene

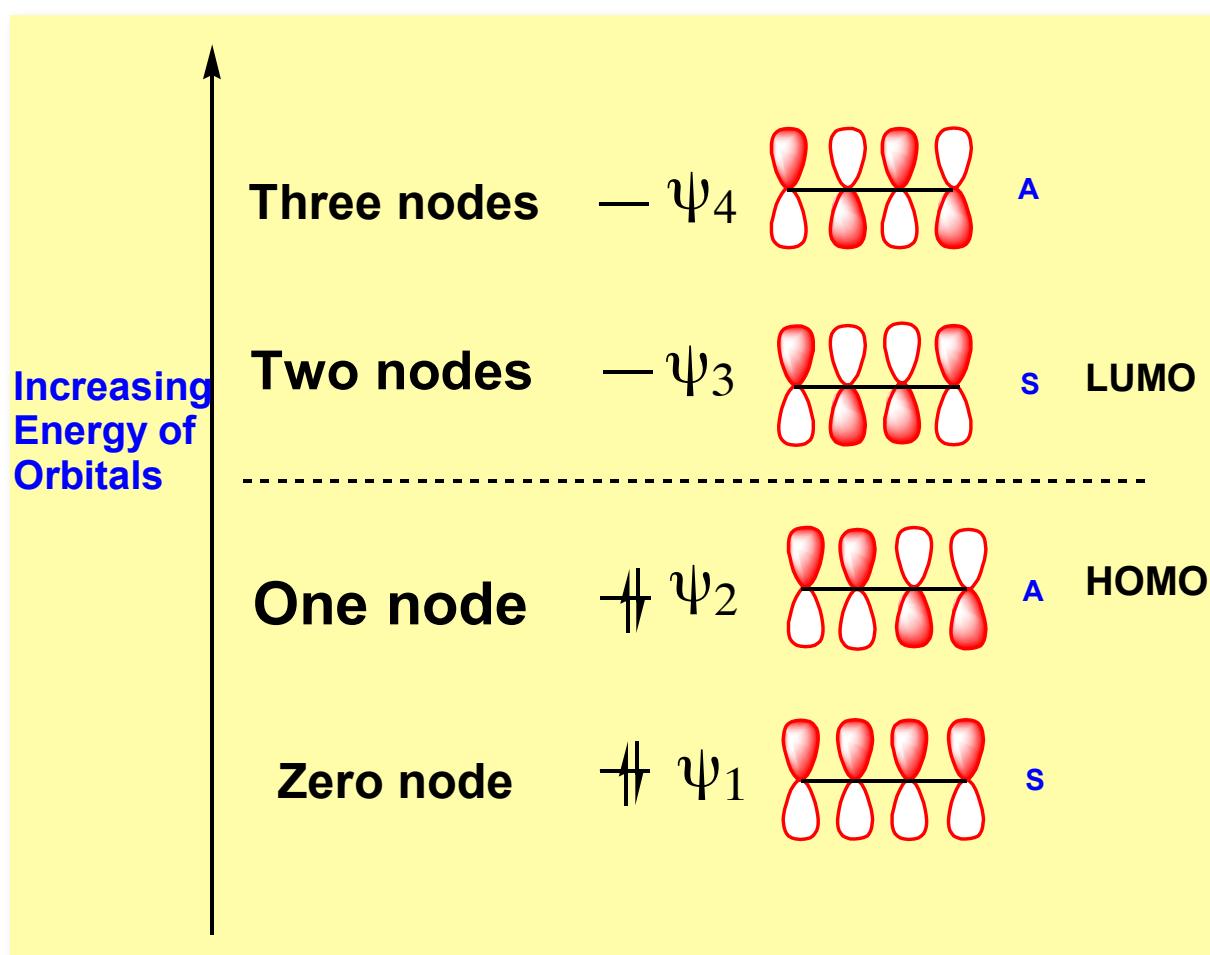
Butadiene MOs

Total number of π -orbitals = 4

Total number of π -electrons = 4

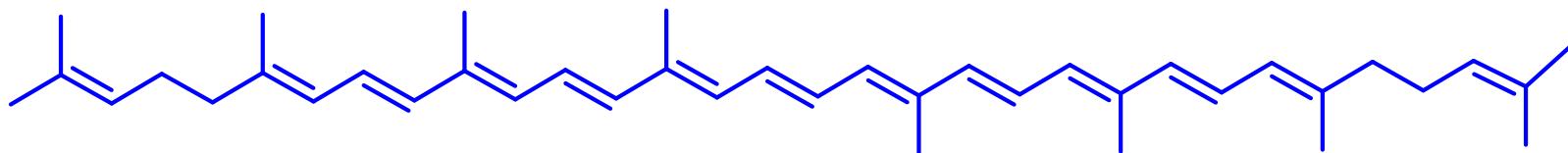


Butadiene is more reactive than ethylene

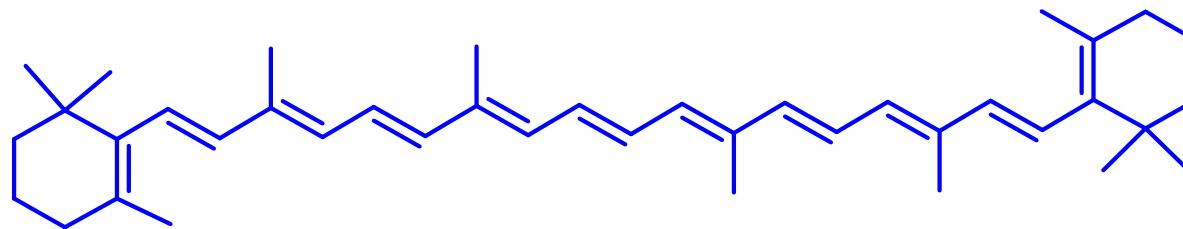


Extended Conjugation and Colour (E.g. 1)

If the conjugation is extended further, the gap between HOMO and LUMO will decrease to allow the compound to absorb visible light and hence would become COLOURED.



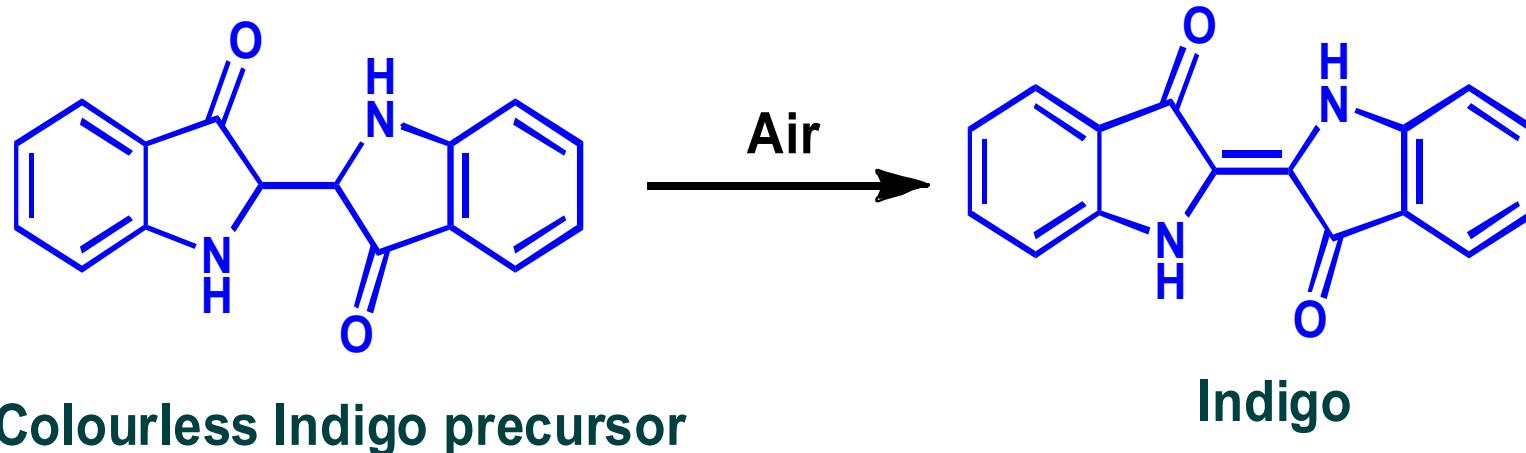
Lycopene, the red pigment present in tomatoes and other berries



β -carotene, the red pigment present in carrots and other vegetables

Extended Conjugation and Colour (E.g. 2)

The colour of the blue jeans come from the pigment indigo



Jeans are generally dyed by immersion in a vat of reduced indigo, which is colourless since there is no conjugation.

When the cloth is hung up to dry, the oxygen in the air oxidizes the pigment to indigo and the jeans turn blue.

Generalizations for acyclic polyenes

The lowest energy orbital is always symmetric with respect to the principal mirror plane

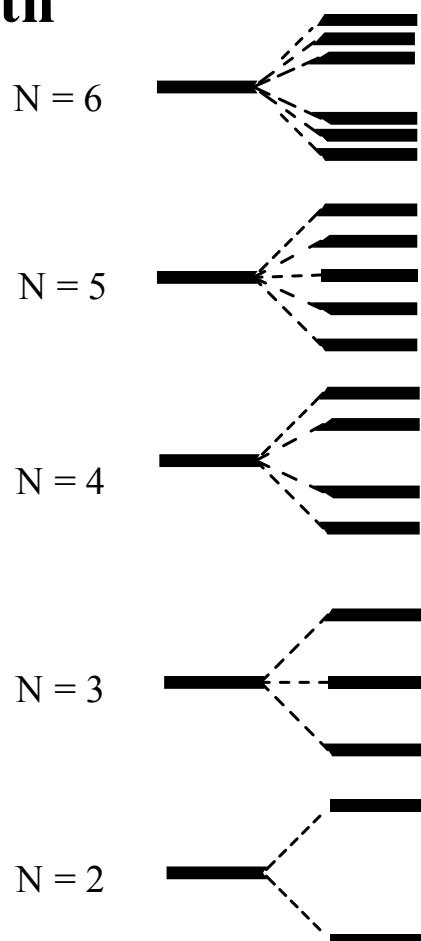
The number of nodes increases by ONE upon going from a lower energy orbital to the next higher energy orbital

Nodes must be symmetrically located with respect to the central mirror plane

In molecules with an odd number of atoms in the conjugated chain, the nodes can go through an atom

Polyenes to Solids

When Number of atoms (N) in a polyene become infinitely large, the difference between neighboring energy levels (MO-levels) will become progressively smaller. But the band has a finite width



Q.

Is it possible to calculate the '**width**' of the band, in an approximate fashion?

This will help us find '**overlap regions**' between *s* and *p* bands

Polyenes-to-Solids Analogies

Approximate Analogs Between Molecular and Solid-State Terminologies

Molecular Orbital

HOMO

LUMO

HOMO-LUMO gap

Band Orbital

Valence Band

Conduction Band

Band gap

Refer: Moore's law
(processor speed of cpus)

Advanced and Related Topics: Organic Semiconductors,
Organic LEDs, Conducting Polymers

Some questions of significance

Most of the reactivities of conjugated systems (say, butadiene, or a carbonyl compound) primarily arise due to the π -molecular orbitals.

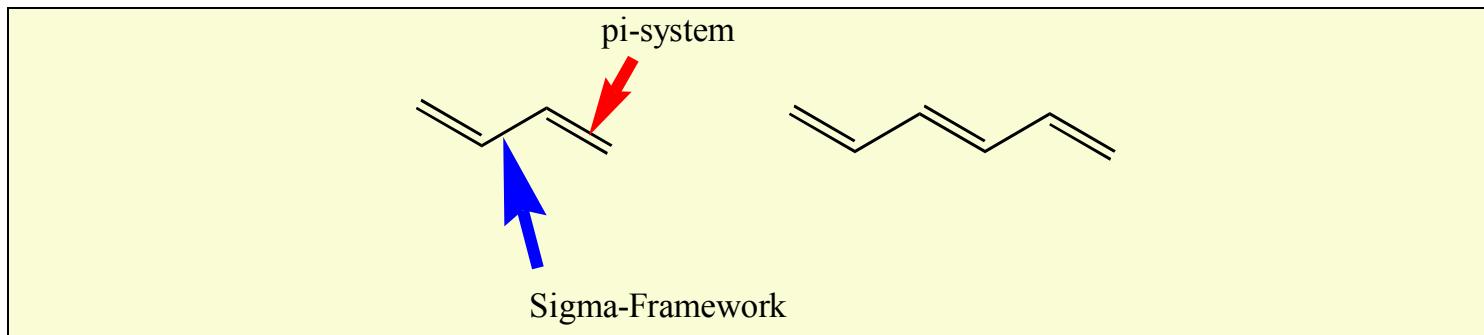
Is it possible to estimate the energies of the π -molecular orbitals?

Huckel MO Theory

Basic Approximations

- Used for the treatment of conjugated systems
- The π -system is treated independently of the σ -framework in planar conjugated molecules
- Or π -system do not interact with the σ -skeleton
- Interactions between $p\pi$ orbitals located on atoms which are not directly linked is zero.

π -electron approximation: π -electrons move in some fixed effective potential of σ framework



Energies of MOs in terms of Integrals

The energy of each p -orbital before interaction is set equal to α (**Coulomb integral**)

[refers to energy of an electron in the field of its own nucleus]



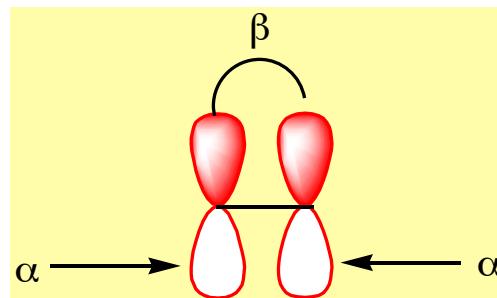
[can be taken as valence state ionization potential]

The interaction energy between two adjacent $p\pi$ orbitals equals to β (**Resonance integral**)

[refers to energy of i^{th} electron in the field of j^{th} nucleus]

[can be taken as the interaction between atomic orbitals i and j]

[energy of an electron in the field of two or more nuclei]



Energies of MOs

- The energy of the j^{th} MO for a linear unbranched conjugated polyene with N $p\pi$ orbitals (or N number of carbon atoms) is given by

$$e_j = \alpha + 2\beta \cos \frac{\pi}{N+1} j \quad j = 1, 2, \dots, N$$

- The energy of the j^{th} MO for a cyclic polyene with N $p\pi$ orbitals is given by

$$e_j = \alpha + 2\beta \cos \frac{2\pi}{N} j$$

$j = 0, \pm 1, \pm 2, \dots, \pm N/2$ (for even N)

$j = 0, \pm 1, \pm 2, \dots, \pm (N-1)/2$ (for odd N)

Note: α and β are negative (attractive !) by definition

The α and β are not calculated as numerical values, but the energies are expressed in terms of these quantities

Energies of MOs

- For Butadiene

$$\text{Energy of LUMO} = \alpha - 0.62\beta$$

$$\text{Energy of HOMO} = \alpha + 0.62\beta$$

Linear polyenes

- Linear polyenes

When the number of orbitals in the chain increases, the energies will be as,

For Highest energy MO = $\alpha - 2\beta$

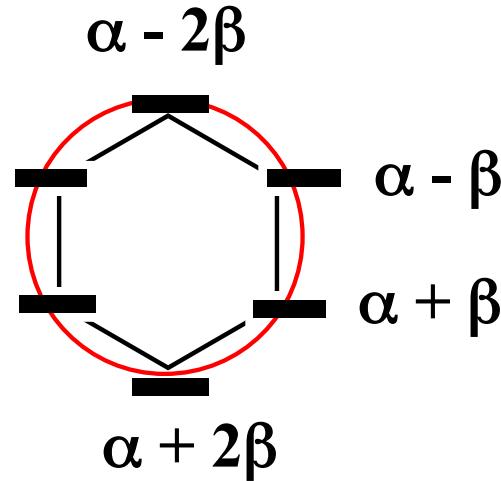
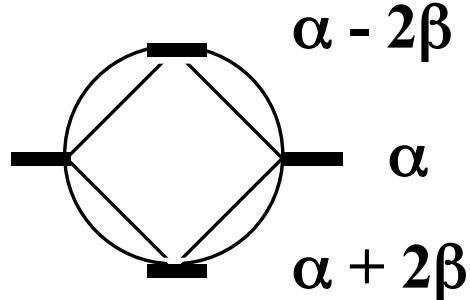
 Lowest energy MO = $\alpha + 2\beta$

Energies of MOs

Cyclic polyenes

Draw a circle of radius 2β and inscribe an N-vertex polygon such that two vertices are in the six o' clock position. The points of contact between the circle and the polygon defines the energy levels

Frost Diagram



The energy level α is at the same level as that of the center of the circle

Energies of MOs

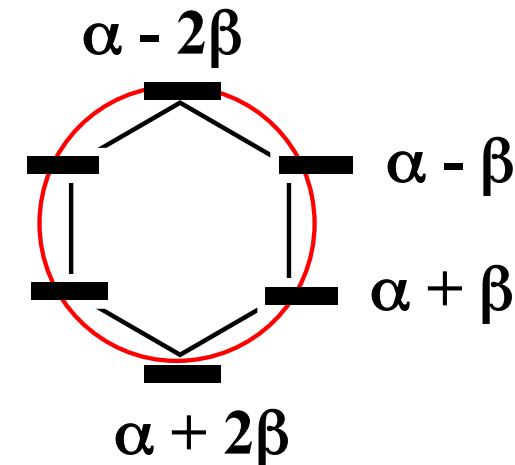
Calculate the total energy of π -electrons in benzene?

Total number of π -electrons = 6

$$\text{Total energy} = 2 * (\alpha + 2\beta) +$$

$$4 * (\alpha + \beta)$$

$$6\alpha + 8\beta$$



If the double bonds were localized (not conjugated)!

Equivalent to three ethylenes

$$\text{Total energy} = 6 * (\alpha + \beta)$$

Additional Stabilization in Benzene (fully delocalized) = 2β

$\beta \sim 18$ kcal/mol (experimental) [What is the resonance stabilization energy in benzene?]

Huckel's Rule of Aromaticity

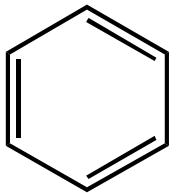
- Planar, fully conjugated, monocyclic systems with $(4n+2)\pi$ electrons having a closed shell of electrons all in bonding orbitals are exceptionally stable. Such compounds are said to be aromatic
- Analogous systems with $4n \pi$ electrons are described as **anti-aromatic**

i

Modern definition of aromaticity:

Compounds that possesses the ability to sustain induced ring current when subjected to magnetic field

Huckel's Rule of Aromaticity



Number of π electrons = 6

**Satisfies Huckel' rule,
where $n = 1$**

Aromatic



Number of π electrons = 4

Where $n = 1$

Anti-aromatic

Huckel's Rule and Aromaticity

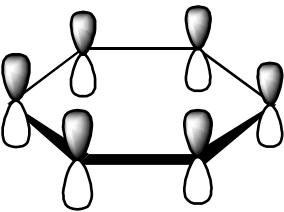
The compound must have an uninterrupted cyclic π -cloud of electrons

For the π -cloud to be cyclic, the molecule must be cyclic.

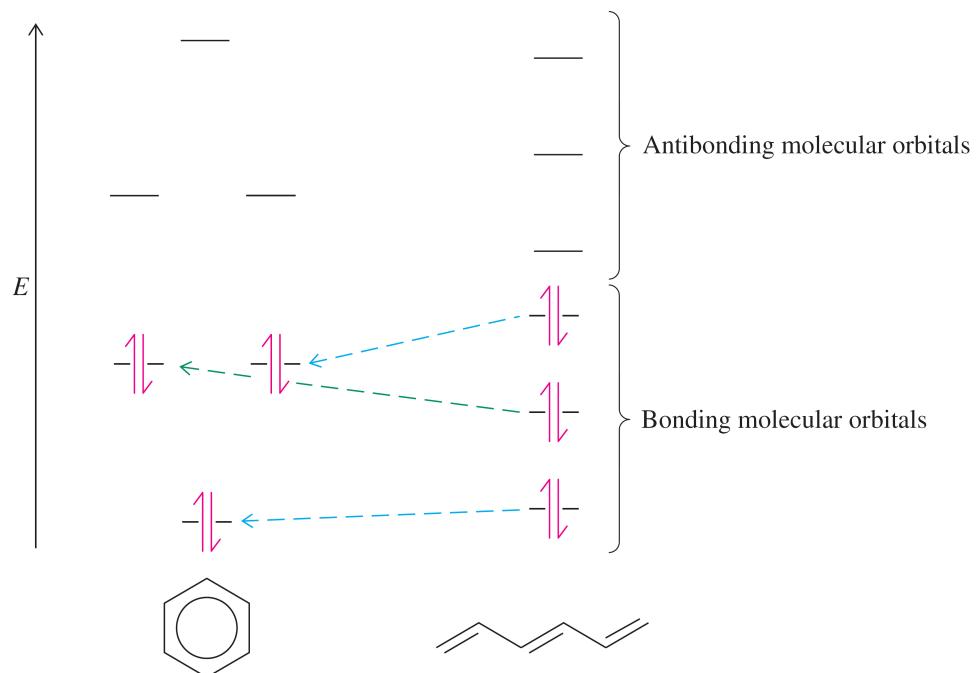
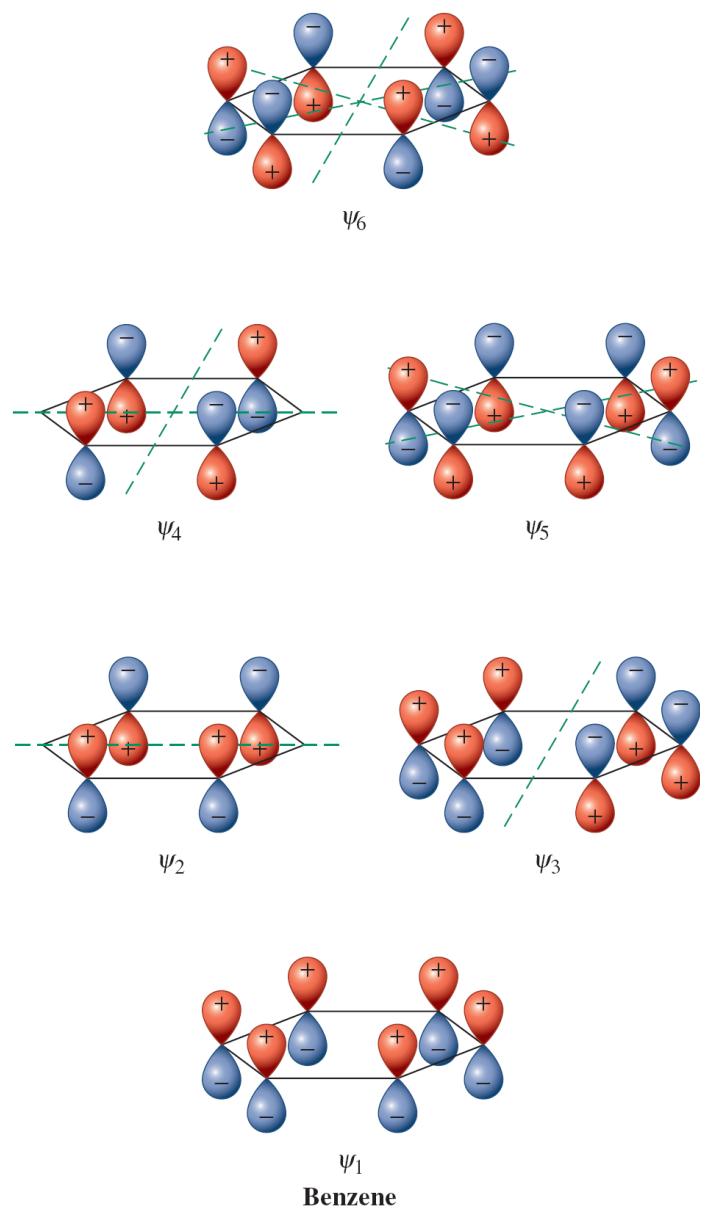
For the π -cloud to be uninterrupted, every atom in the ring must have a p-orbital

For the π -cloud to form, each p-orbital must be able to overlap with the p-orbitals on either side of it. This means that the molecule must be planar.

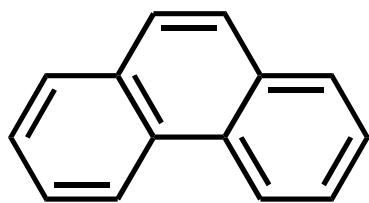
E.g., 1



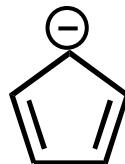
π Molecular Orbitals of Benzene



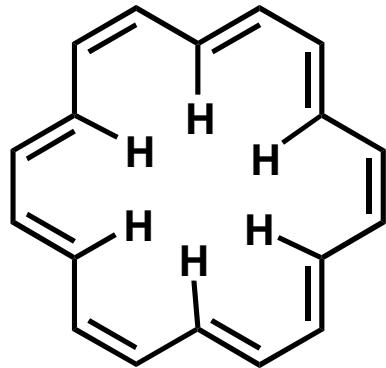
Examples for Aromatic Compounds



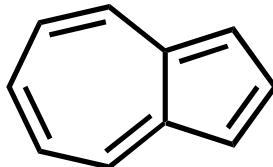
Phenathrene



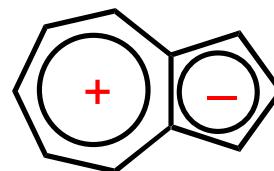
cyclopentadienyl anion



[18]-annulene

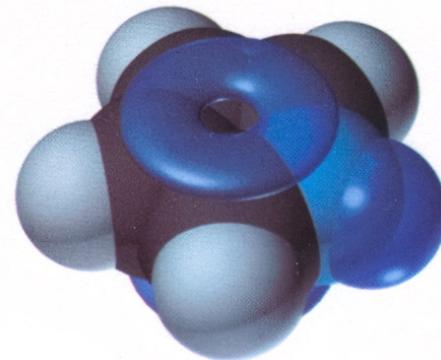
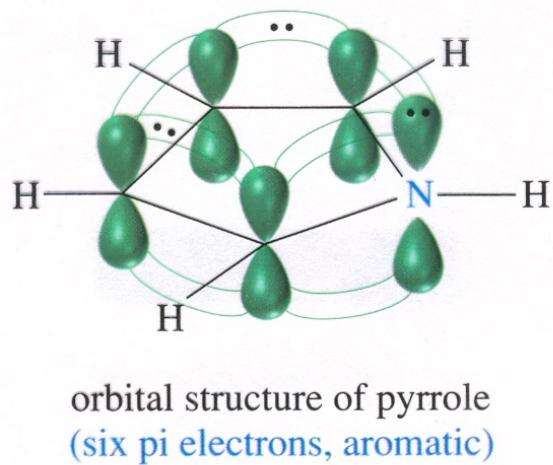
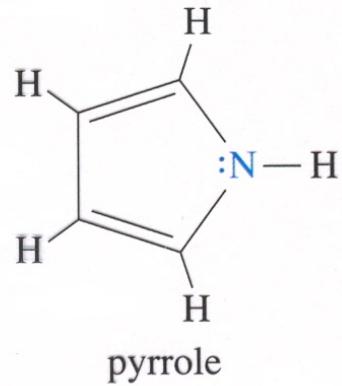
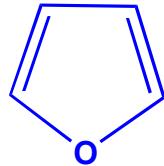
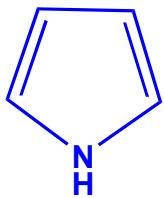


Azulene



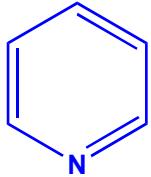
Aromatic Heterocyclic Compounds

Lone pair is part of the aromatic system



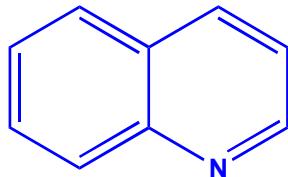
Aromatic Heterocyclic Compounds

Lone pair not involved in aromatic system



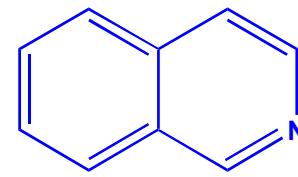
6π electrons

$$4n + 2 = 6, \text{ with } n=1$$



10π electrons

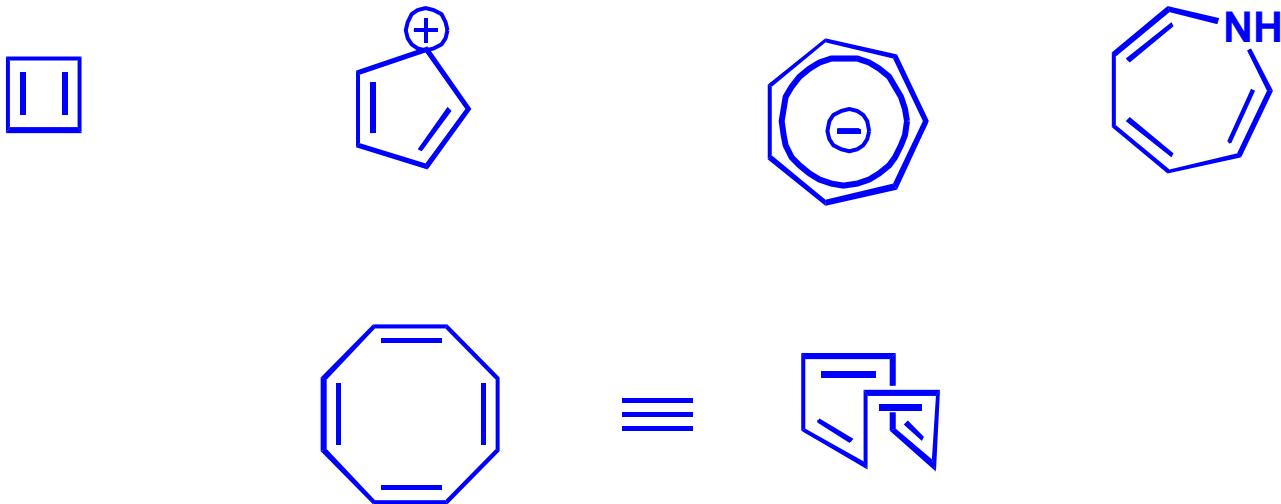
$$4n + 2 = 10, \text{ with } n=2$$



Antiaromatic Compounds

Cyclic planar molecules with conjugated $4n \pi$ -electrons (where n is an integer) are antiaromatic

Antiaromatic compounds are less stable than the open chain counterpart



A cyclic compound that does not have a continuous conjugated p orbitals are known as **nonaromatic**

e.g., 1,2-cyclohexadiene or 1,3-cyclohexadiene

Additional Slides

**For only those who are
interested in knowing
additional details**

The Secular Determinant

Start with a trial wave function

$$\phi = C_1 f_1 + C_2 f_2 \quad \text{--- (1)}$$

Solve variational integral,

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = E \phi \quad \text{--- (2)}$$

$$\begin{aligned} \int \phi^* \hat{H} \phi dz &= \int (C_1 f_1 + C_2 f_2) \hat{H} (C_1 f_1 + C_2 f_2) dz \\ &= C_1^2 \hat{H}_{11} + 2C_1 C_2 \hat{H}_{12} + C_2^2 \hat{H}_{22} \quad \text{--- (3)} \end{aligned}$$

where $\int f_i \hat{H} f_j = \hat{H}_{ij}$ and $H_{ij} = H_{ji}$

$$\int \phi^* \phi dz = C_1^2 S_{11} + 2C_1 C_2 S_{12} + C_2^2 S_{22} \quad \text{--- (4)}$$

where $\int f_i f_j = S_{ij}$ and $S_{ij} = S_{ji}$

Minimizing energy E with respect
 c_1 and c_2

$$E(c_1, c_2) = \frac{c_1^2 \hat{H}_{11} + 2c_1 c_2 \hat{H}_{12} + c_2^2 \hat{H}_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$c_1^2 \hat{H}_{11} + 2c_1 c_2 \hat{H}_{12} + c_2^2 \hat{H}_{22} = E(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22})$$

— (5)

Maximum contribution from
 f_1 to the total function ϕ will happen
 if

$$\frac{\partial E}{\partial c_1} = 0$$

Differentiate (5) with respect to c_1

$$c_1 \hat{H}_{11} + c_2 \hat{H}_{12} = E(c_1 S_{11} + c_2 S_{12})$$

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0$$

Similarly, differentiating w.r.t c_2

$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 = 0$$

Two linear simultaneous equations in C_1 and C_2 can exist only if the following determinant is equal to zero,

i.e

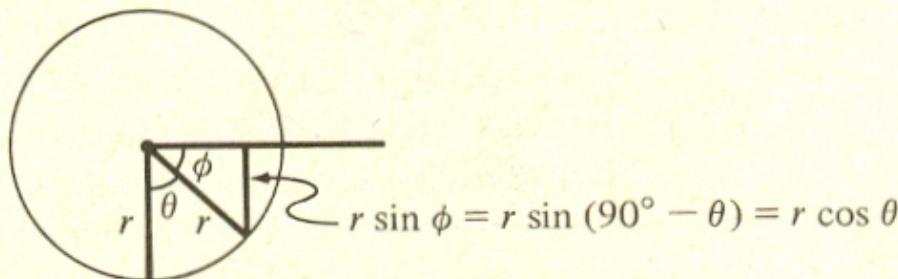
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (6)$$

Secular Determinant

Substituting

$H_{ii} = \alpha$
$H_{ij} = \beta$





The projection method for finding π orbital energies of monocyclic conjugated rings. The ring is inscribed point downward in a circle of radius 2β . Projection horizontally of each vertex generates an energy-level diagram with energy α at the level of the center of the circle. The circle at the bottom of the figure demonstrates that the vertical distance below the horizontal of a point on the circle of radius r is $r \cos \theta$, where θ is the angle measured from the vertical line. The polygon vertices (numbered by the index J , counting counterclockwise starting at the bottom with $J = 0$) are at angles $2\pi J/N$, where N is the number of vertices. The energy at the level of the center of the circles is α and the radii are 2β ; therefore the energies are given by the formula

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

Note that the orbital numbering starts at $J = 0$ and is cyclic around the ring, as illustrated for the cyclooctatetraene model. The method originates with Frost, A. A.; Musulin, B. *J. Chem. Phys.*, **1953**, 21, 572.