Chapter 5 Structures of Polyatomic Molecules (I)

Introduction

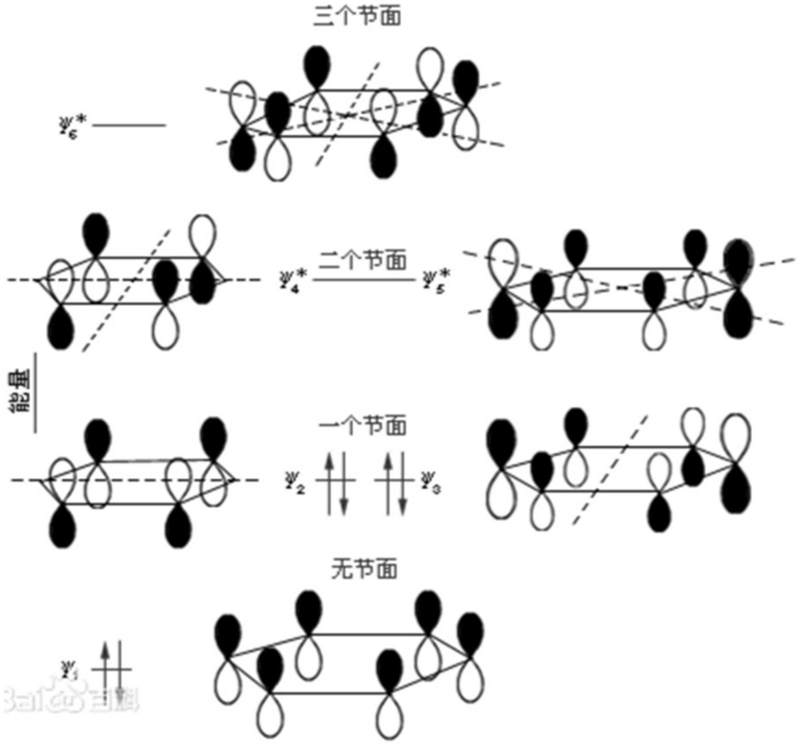
Molecular Orbital Theory vs. Valence Bond Theory

- **VB theory**: focusing on the (***localized***) bonds formed between valence electrons/atomic orbitals of neighboring atom(s)***, easier to visualize/imagine VB model of a molecule***, i.e., "of ***chemical intuition***!". e.g., CH_4
- **MO theory**: more powerful and more sophisticated than **VB theory** in many aspects, e.g., description of electron delocalization in Benzene, but sometimes not so easy to visualize/imagine a MO model e.g., for CH_4!

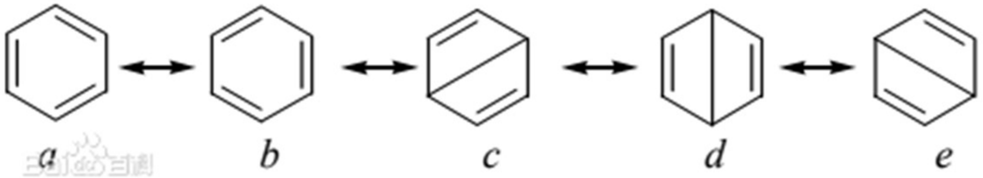
Comparison of MO and VB theories

VB Theory	Molecular orbital theory
The electrons pair to ***localize*** in a bond. $\psi^{bond} \approx AO_1 \cdot AO_2$	MOs are formed by the overlap of AOs. $\Psi^{MO} \approx \Sigma c_i AO_i$
Demands hybridization of AO	Electrons are "***delocalized***" within MOs consisting of AOs.
Basis of Lewis structures, resonance, and hybridization.	Electrons fill up the MOs according to the *aufbau* principle.
Good theory for predicting molecular structure.	Give accurate bond dissociation energies, IP, EA, and spectral data.
Easier to visualize/imagine VB model for a molecule, i.e., "of *chemical intuition*!".	Sometimes *not so easy to visualize/imagine* a MO model for a molecule!

Electron Delocalization in Benzene



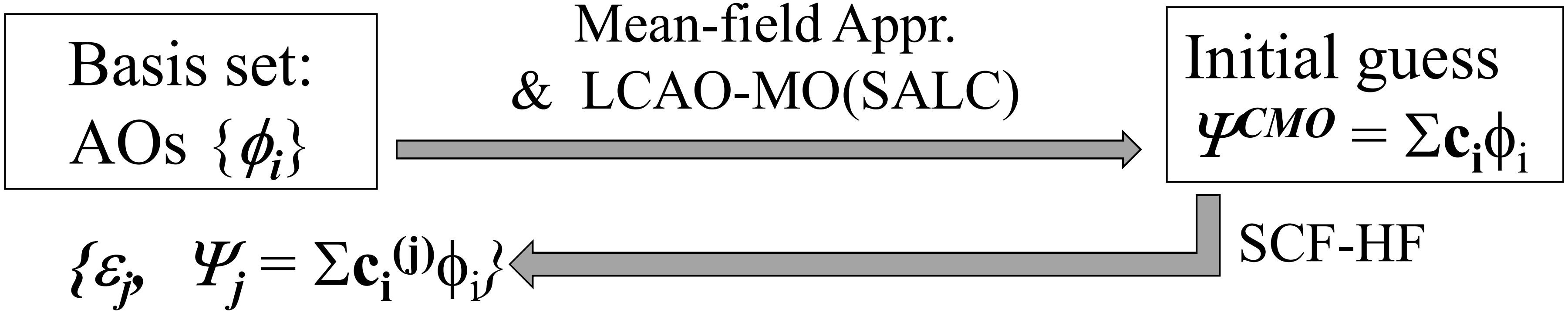
MO description：
inherently describing
electron delocalization!



VB description:
have to introduce resonance of
localized VB structures

Molecular Orbital (MO) Theory Treatment of Polyatomic Molecules

- LCAO-MO & group Theory (in part B of ***Chapter 3***)



Basis set: AOs $\{\phi_i\}$

Mean-field Appr. & LCAO-MO(SALC)

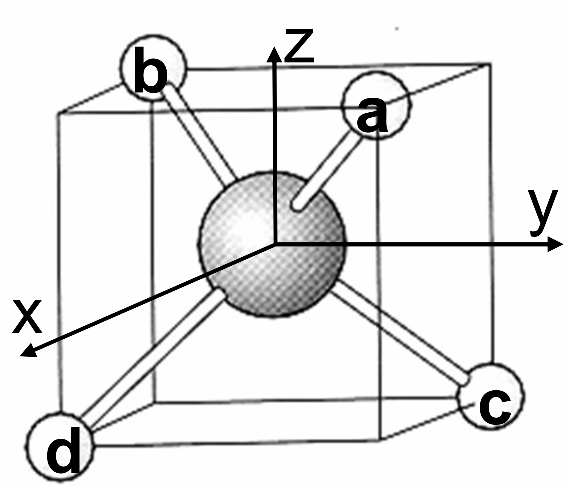
Initial guess $\Psi^{CMO} = \Sigma \mathbf{c_i} \phi_i$

SCF-HF

$\{\varepsilon_j, \ \Psi_j = \Sigma \mathbf{c_i}^{(j)} \phi_i\}$

Canonical molecular orbitals of CH_4 (valence electrons only!)

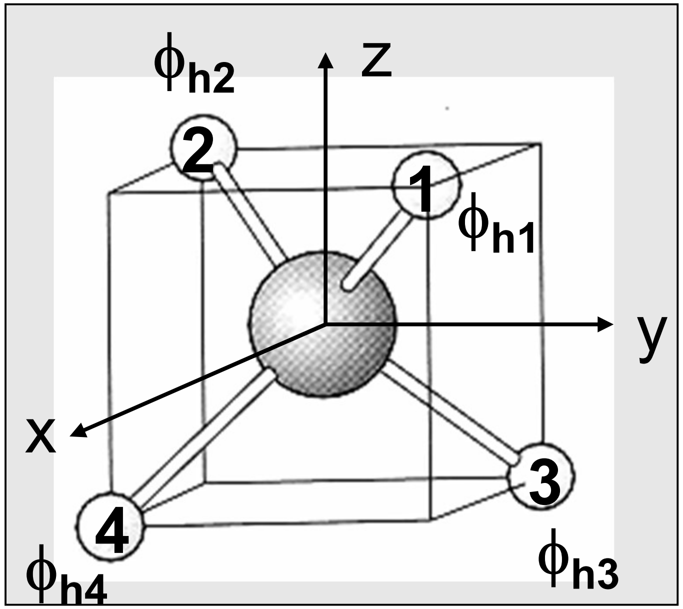
CMO	H 1s AOs	C AOs
$\psi(A_1)_{\pm}$	$= c_a(\phi_1 + \phi_2 + \phi_3 + \phi_4)/2$	$\pm\, c_b C2s$
$\psi(T_2)_{x\pm}$	$= c_c(\phi_1 - \phi_2 - \phi_3 + \phi_4)/2$	$\pm\, c_d C2p_x$
$\psi(T_2)_{y\pm}$	$= c_c(\phi_1 - \phi_2 + \phi_3 - \phi_4)/2$	$\pm\, c_d C2p_y$
$\psi(T_2)_{z\pm}$	$= c_c(\phi_1 + \phi_2 - \phi_3 - \phi_4)/2$	$\pm\, c_d C2p_z$



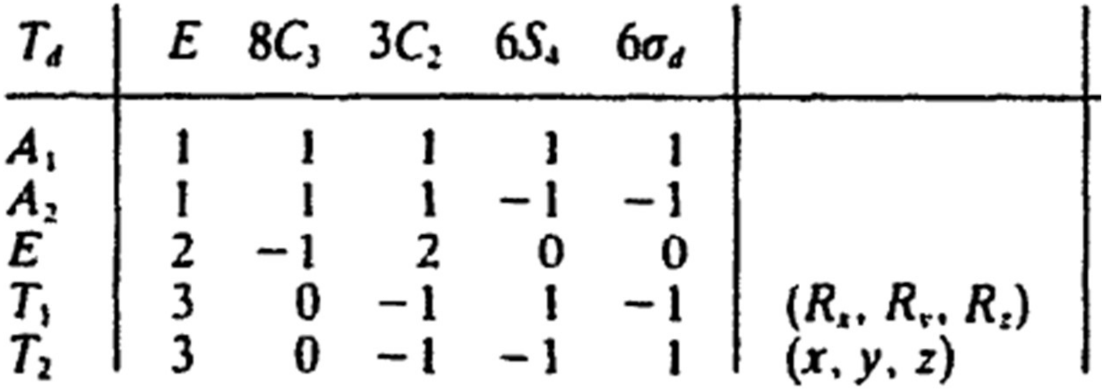
All delocalized!

How to get the CMOs of a molecule?

- **Group theory treatment– SALCs:** ***CH_4, T_d***



C: 2s (A_1), (T_2) $2p_x$, $2p_y$, $2p_z$ 4 H: 1s



T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)
T_2	3	0	−1	−1	1	(x, y, z)

$\Gamma(4H_{1s})$ 4 1 0 0 2

$$\boxed{a_i = \frac{1}{h}\sum_R g(R)\chi(R)\chi_i(R)} \Rightarrow \boxed{\Gamma(4H) = A_1 + T_2} \Rightarrow \boxed{\Psi^j_{SALC} = \hat{P}^j\phi_i = \frac{l_j}{h}\sum_R \chi_j(R)\hat{R}\phi_i} \Rightarrow$$

$\theta_a = (\phi_1+\phi_2+\phi_3+\phi_4)/2 \sim A_1$

$\theta_b = (\phi_1-\phi_2-\phi_3+\phi_4)/2 \sim$ x-like T_2

$\theta_c = (\phi_1-\phi_2+\phi_3-\phi_4)/2 \sim$ y-like T_2

$\theta_d = (\phi_1+\phi_2-\phi_3-\phi_4)/2 \sim$ z-like T_2

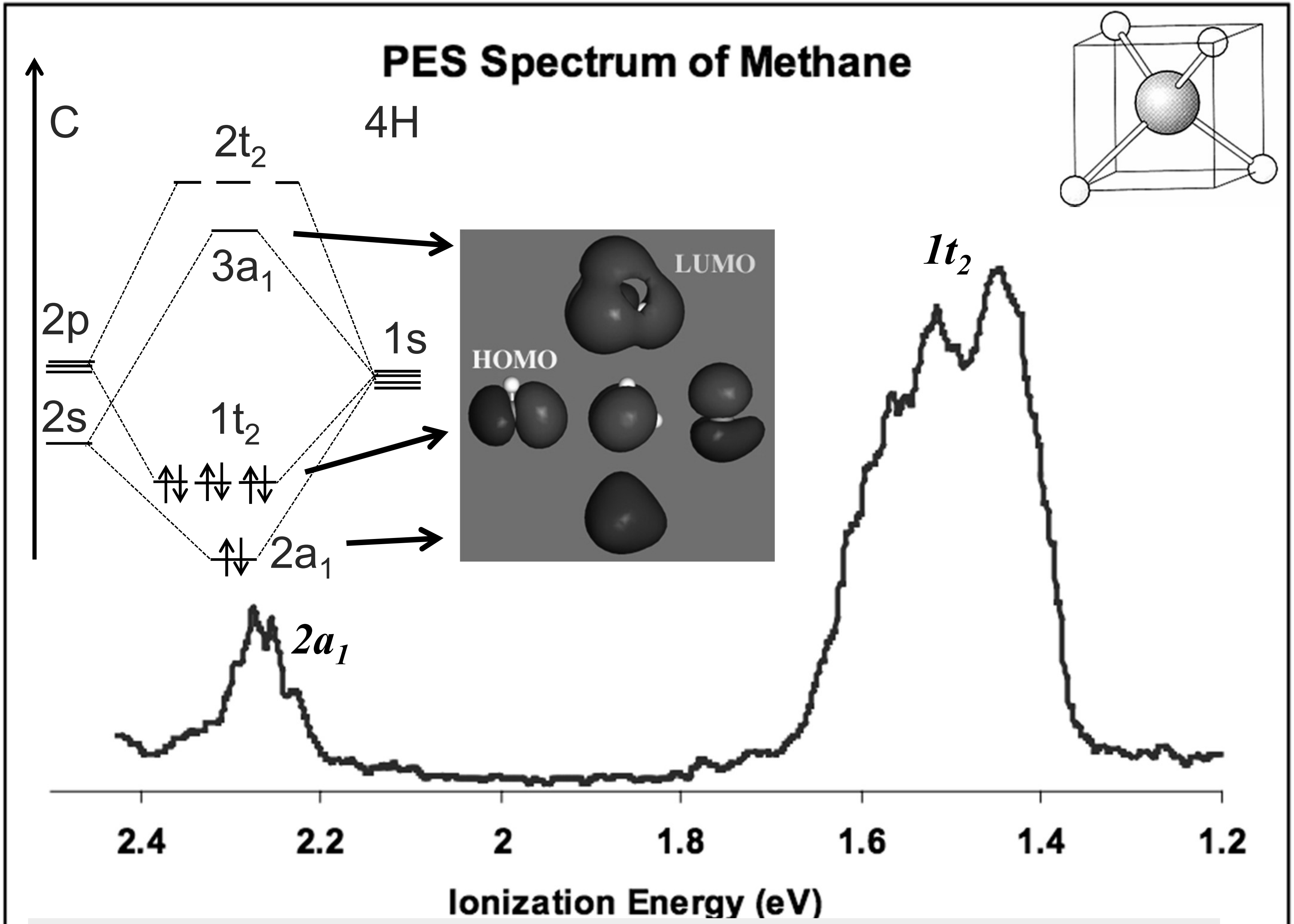
$\psi_{s\pm} = c_a(\phi_1+\phi_2+\phi_3+\phi_4)/2 \pm c_b C2s$

$\psi_{x\pm} = c_c(\phi_1-\phi_2-\phi_3+\phi_4)/2 \pm c_d C2p_x$

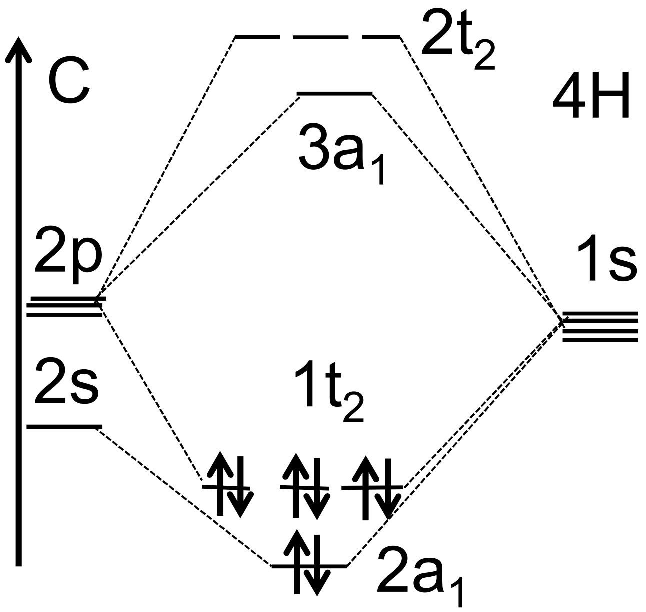
$\psi_{y\pm} = c_c(\phi_1-\phi_2+\phi_3-\phi_4)/2 \pm c_d C2p_y$

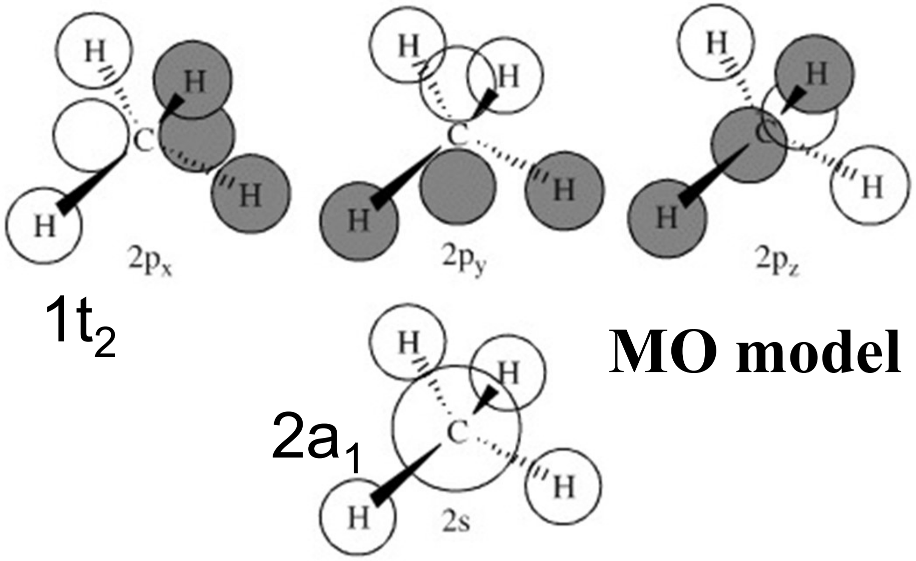
$\psi_{z\pm} = c_c(\phi_1+\phi_2-\phi_3-\phi_4)/2 \pm c_d C2p_z$

PES Spectrum of Methane

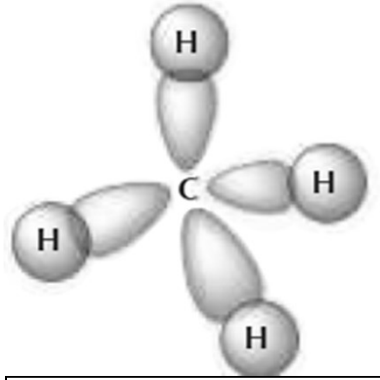


MO Theory explains the PES quite well!





MO model



VB model

sigma bonds between *s* and *sp*^{3} orbitals

$$\boxed{\Psi^{VB}_{\mathrm{CH_i}} = HO_i(1)\cdot\phi_i(2) + HO_i(2)\cdot\phi_i(1)}$$

The MO model of CH_4 does not explicitly reflect the 4 equivalent C-H σ-bonds of “*chemical intuition*” as the VB model does !

How can the MO model become *chemically intuitive* as the VB model does ?

http://www.science.oregonstate.edu/~gablek/CH334/Chapter1/methane_MOs.htm

Now consider the linear combinations of the four CMOs,

$\Psi_1 = (\psi_s + \psi_x + \psi_y + \psi_z)/2$ $\Psi_2 = (\psi_s + \psi_x - \psi_y - \psi_z)/2$

$\Psi_3 = (\psi_s - \psi_x - \psi_y + \psi_z)/2$ $\Psi_4 = (\psi_s - \psi_x + \psi_y - \psi_z)/2$

Let $c_b = c_d$ & $c_a = c_c$

$\Psi_1 = [(c_b C2s + c_d(C2p_x + C2p_y + C2p_z) + (c_a + 3c_c)\phi_1 + (c_a - c_c)(\phi_2 + \phi_3 + \phi_4)]/2$

$\Psi_1 = c_b(C2s + C2p_x + C2p_y + C2p_z)/2 + c_a'\phi_1$

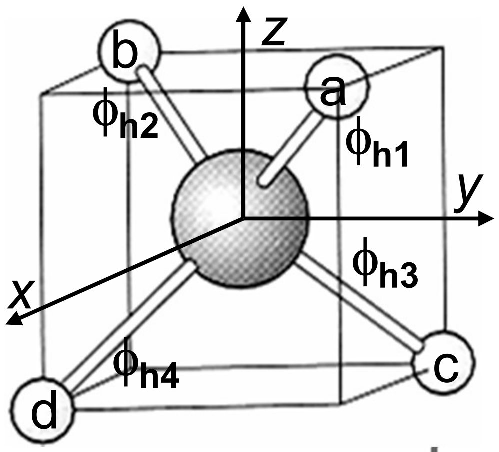
$\Psi_2 = c_b(C2s - C2p_x - C2p_y + C2p_z)/2 + c_a'\phi_2$

$\Psi_3 = c_b(C2s - C2p_x + C2p_y - C2p_z)/2 + c_a'\phi_3$

$\Psi_4 = c_b(C2s + C2p_x - C2p_y - C2p_z)/2 + c_a'\phi_4$

Localized molecular orbitals (LMOs) describing C-H bonds

4 sp3-hybridized orbitals on C



The 4LMOs are in effect similar to those 4 covalent C-H bonds described in VB theory.

主观题 10分

设置

Are the four LMOs of CH_4 equal in energy?

If so, please prove that after class!

Q1: Note that hybrid orbitals are used in both the VB and LMO descriptions of a covalent bond (e.g., in CH_4). What is the difference in the two models?

Q2: How to construct hybridized atomic orbitals for further construction of LMOs of a molecule ?

作答

Content of this chapter

1. Hybrid Orbital Theory

2. VSEPR Model (after-class)

→ σ-bonds/σ-framework of a molecule (Qualitative, MO&VB theory)

3. Delocalized π-conjugation and Delocalized MO Theory

→ π-bonds of a molecule (VB & MO theories, Qualitative)

4. Hückel MO Theory and Conjugated Systems

→ (Semi-Quantitative/ Semiempirical MO)

5. Symmetry Rules for Molecular Reactions

→ Molecular reactions (Qualitative)

§ 5.1 Hybrid Orbital Theory and Atomic Orbital Hybridization

1. Hybrid orbital theory – first proposed by Pauling in 1928.

- Hybridization was introduced to explain molecular geometry when valence bond theory failed to correctly predict them.

VALENCE BOND THEORY

- Valence electrons are localized between two atoms (or as lone pairs).
- Half-filled atomic orbitals overlap to form bonds.
- VB theory demands ***orbital hybridization*** if necessary!

MO THEORY

- Sometimes ***Atomic orbital hybridization*** is naturally taken into account!

Please refer to Webtext:
http://www.chem1.com/acad/webtext/chembond/cb06.html

http://www.chem1.com/acad/webtext/chembond/cb07.html

Linus Pauling (1901-1994) was the most famous American chemist of the 20th century and the author of the classic book ***The Nature of the Chemical Bond***. He won the Nobel Prize in Chemistry in 1954 and the Nobel Peace Prize in 1962.

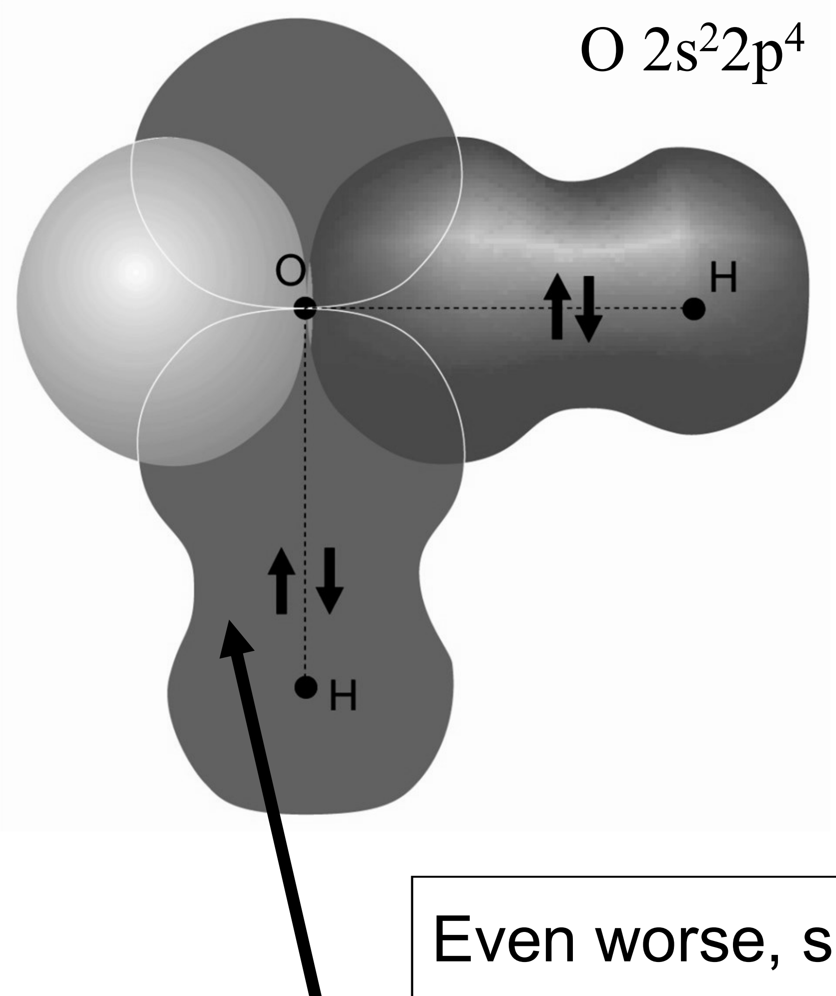
a. Central Themes of Valence Bond Theory

***Basic Principle of Valence Bond Theory**:* **a covalent bond forms when the orbitals from two atoms overlap and a pair of electrons occupies the region between the nuclei.**

1) Opposing spins of the electron pair.
2) Maximum overlap of bonding orbitals.
3) Hybridization of atomic orbitals, if required.

Pauling proposed that ***the valence atomic orbitals in a molecule are different from those in the isolated atoms.*** We call this ***Hybridization*!**

b. Why do atomic orbitals need hybridization? e.g., H_2O

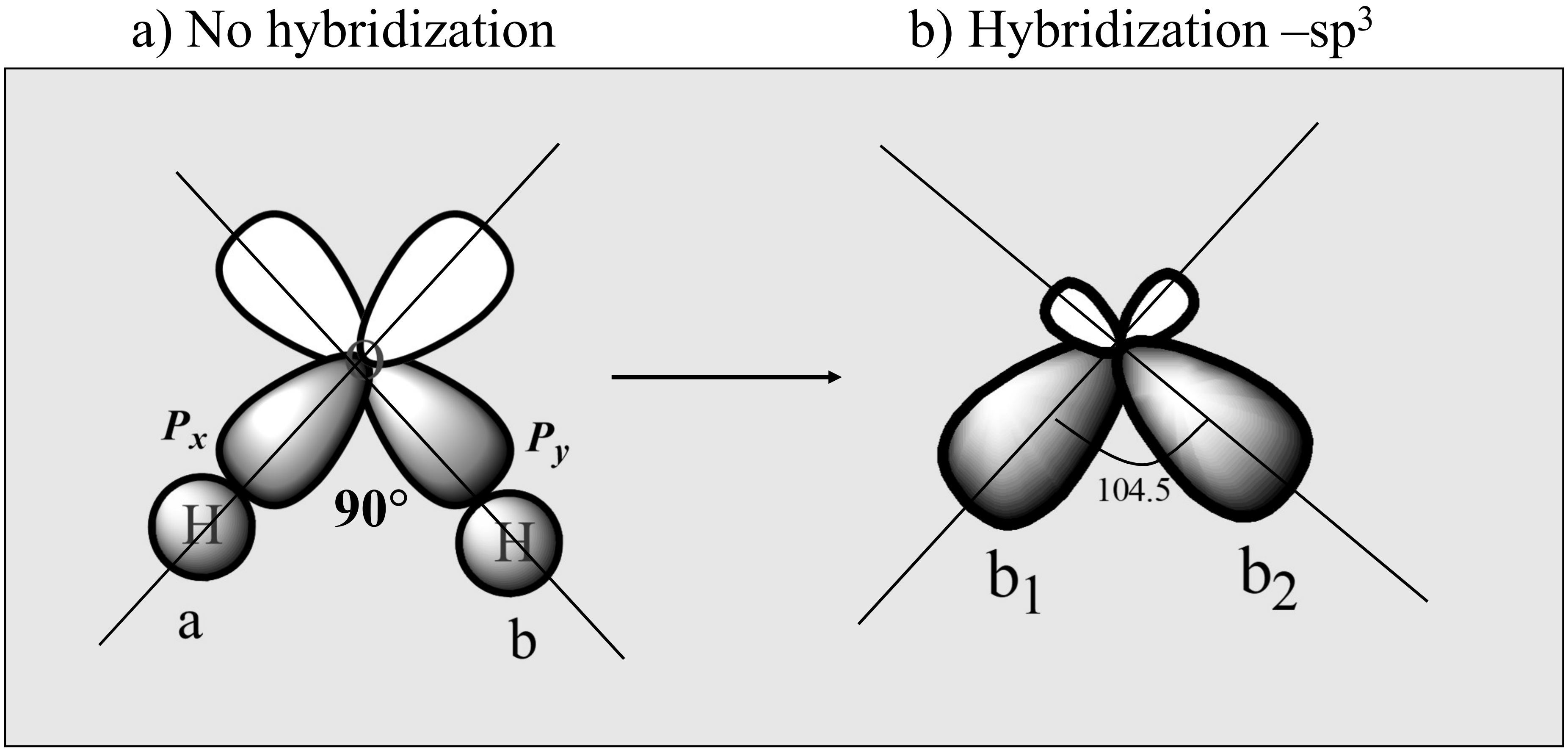


O $2s^2 2p^4$

- Suppose each σ bond arises from the overlap of an H_{1s} AO with one of the O_{2p} AO.
- This model suggests that the H-O-H bond angle should be 90°, much smaller than the observed one (104.5 °).

Use of O p - orbitals

Even worse, such a bonding motif would ***pose very strong repulsion*** among the occupied 2s (O) AO and the two O-H bonds!



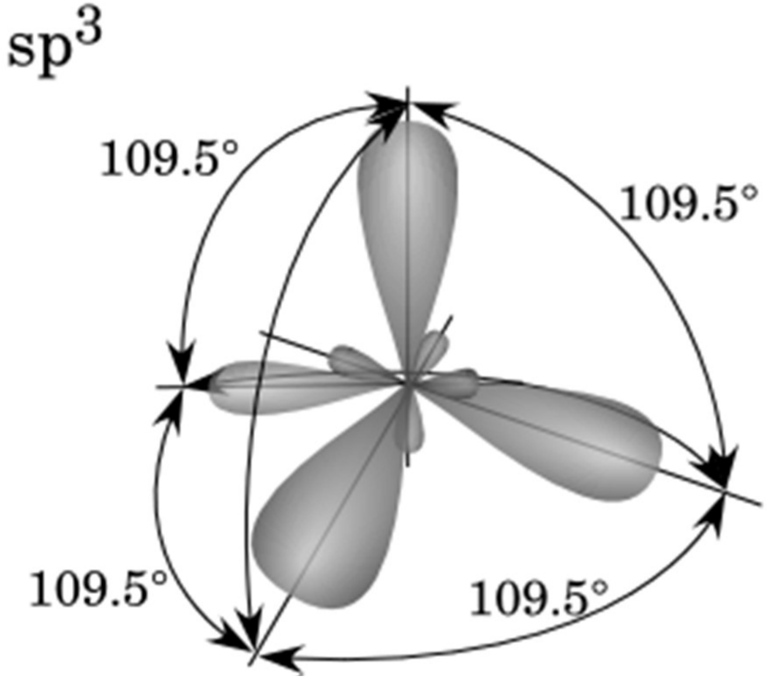
a) No hybridization

b) Hybridization –sp^3

H_2O

Inequivalent sp^3 hybridization of O(2sp) AO′s!

c. Why do atomic orbitals need hybridization?



CH_4

- Carbon has four valence electrons that are typically involved in the formation of 4 C-H bonds.

- For a carbon atom bonded to four other atoms, evidences suggested that all of the bonds have similar bonding orbitals.

Hybrid Orbital Theory is phenomenological!

d. How do atomic orbitals hybridize?

- Hybridization of ***n*** AO’s of an atom gives rise to ***n*** hybrid orbitals (HO)!

$$\{\phi_i^{AO}\}(i=1,\ldots,n)\rightarrow\{\phi_j^{HO}=\sum_{i=1}^{n}c_{ji}\phi_i^{AO}\}(j=1,\ldots,n)$$

e.g., a sp^3-hybridized orbital can be expressed as:

$$\phi_h=c_1\phi_{2s}+c_2\phi_{2px}+c_3\phi_{2py}+c_4\phi_{2pz}$$

- For *equivalent hybridization*, all ***n*** hybrid orbitals are equivalent in energy, but differ in directionality. The contribution of ***s*** orbital, if involved, to each HO is equal.

2. Construction of hybrid orbitals

a. sp hybridization

b. sp^2 hybridization

c. sp^3 hybridization

d. dsp^3 (sp^3d) hybridization (trigonal bipyramidal or square pyramidal)

e. dsp^2 (sp^2d) hybridization (square planar)

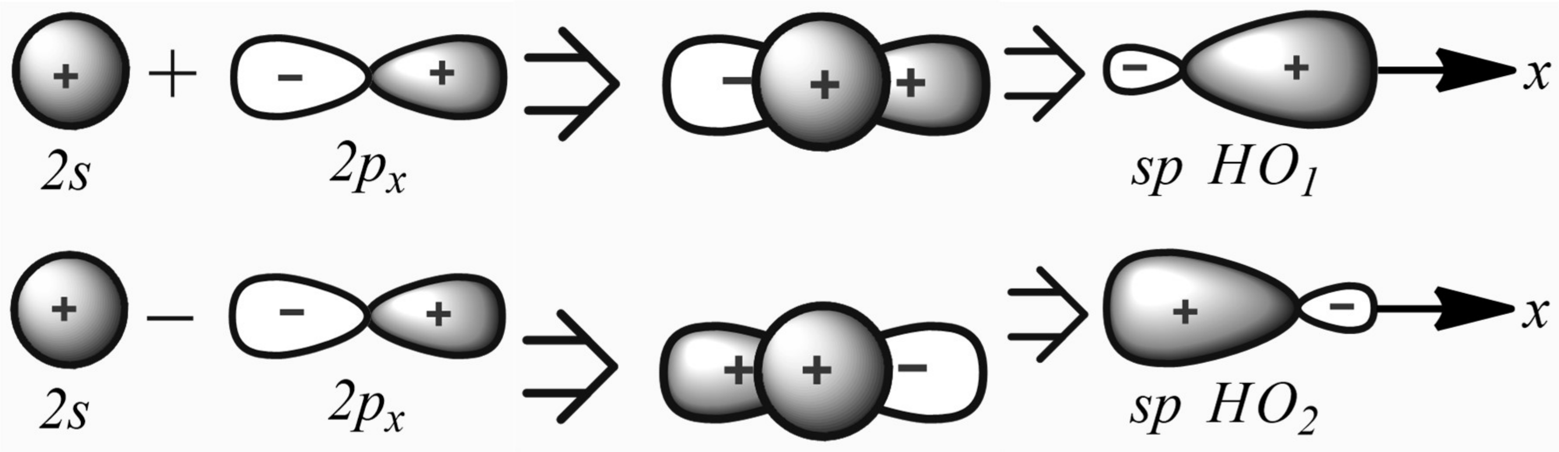
f. d^2sp^3 (sp^3d^2)hybridization (octahedral)

g. More … (e.g., sp^3d^3f, or sp^3d^3)

Bonding ability of AO: $\boxed{F = \sqrt{2l+1}}$ $\boxed{F_s = 1, F_p = \sqrt{3}, F_d = \sqrt{5} \ldots}$

a. sp hybridization (linear species)

- One ***s*** and one ***p*** AO′s mix to form a set of two hybrid orbitals.



- Accordingly, equivalent sp-hybridization results in two hybrids:

$$\phi_{h1} = \frac{1}{\sqrt{2}}(\phi_{2s} + \phi_{2px})$$

$$\phi_{h2} = \frac{1}{\sqrt{2}}(\phi_{2s} - \phi_{2px})$$

s-character

i) Each having 50% contribution from ***s*** orbital: $\alpha = |c_{2s}|^2 = 1/2$.

ii) Normalization and orthogonality: $\int \phi_{hj}\,\phi_{hi}\,d\tau = \delta_{ij}$

iii) Linearly aligned with a bond angle θ = **180°**.

Equivalent /inequivalent sp-hybridization

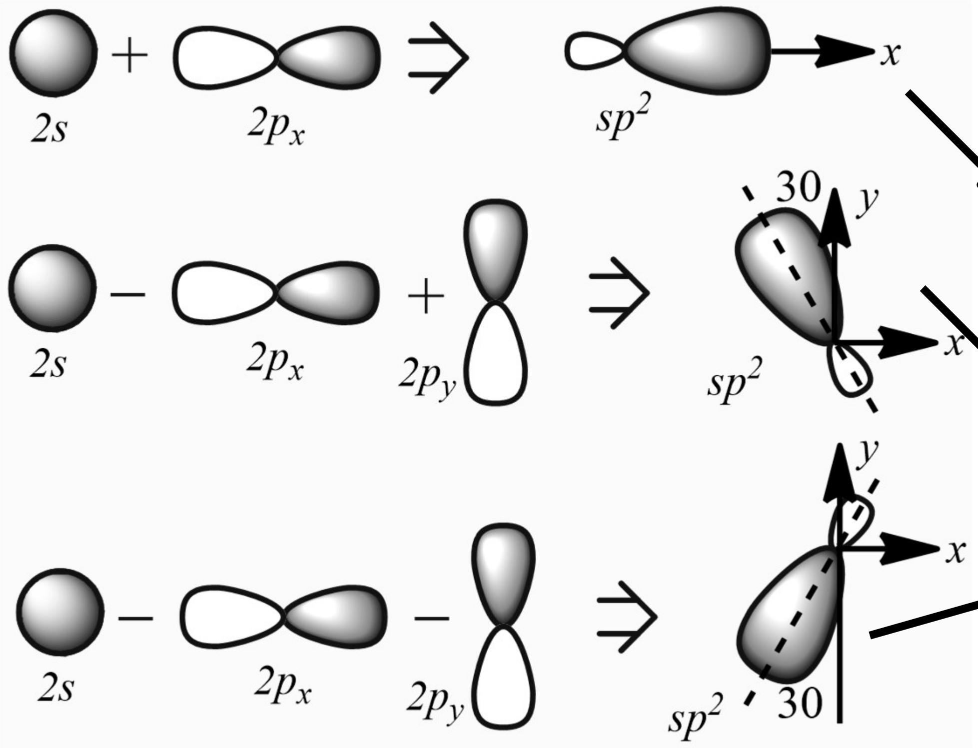
Whether an atom adopts equivalent or inequivalent hybridization depends on its chemical environment!

sp-hybridization at Be atom

Cl-Be-Cl	equivalent
Cl-Be-Br	inequivalent

b. sp^2 hybridization (trigonal planar)

- One **s** and two **p** (***p$_x$*** and ***p$_y$***) AOs mix to form a set of three hybrid orbitals.

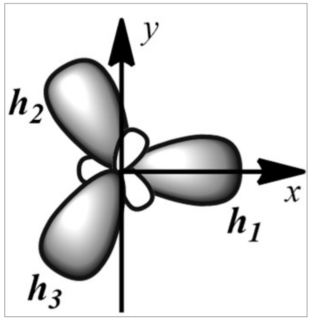


- Equivalent sp^2:

$$\phi_{h1} = \frac{1}{\sqrt{3}}\phi_s + \frac{\sqrt{2}}{\sqrt{3}}\phi_{2px}$$

$$\phi_{h2} = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{2px} + \frac{1}{\sqrt{2}}\phi_{2py}$$

$$\phi_{h3} = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{2px} - \frac{1}{\sqrt{2}}\phi_{2py}$$



sp^2, D_{3h}, θ=120°, trigonal

α = **1/3** (component of ***s***-orbital)

In general, an sp^2 hybrid orbital can be expressed as,

$$\phi_{hi} = a_i\phi_s + b_i\phi_{2px} + c_i\phi_{2py}$$

For equivalent hybridization: the weighting of ***s*** orbital in each hybrid orbital is $\alpha = \mathbf{a_i^2 = 1/3}$, and therefore $\boldsymbol{a_i = 3^{-1/2}}$

$$\Rightarrow \phi_{hi} = (1/\sqrt{3})\phi_s + b_i\phi_{2px} + c_i\phi_{2py}$$

Supposing $\boldsymbol{\phi_{h1}}$ is parallel to the ***x***-axis, but perpendicular to the ***y***-axis, then we have

$$\phi_{h1} = \sqrt{1/3}\phi_s + b_i\phi_{2px}$$

Normalization

$$\phi_{h1} = \sqrt{1/3}\phi_s + \sqrt{2/3}\phi_{2px}$$

$$\phi_{h1} = \sqrt{1/3}\phi_s + \sqrt{2/3}\phi_{2px}$$

$$\phi_{hi} = \sqrt{1/3}\phi_s + b_i\phi_{2px} + c_i\phi_{2py}$$ **(*i* = 2 or 3)**

Normalization and orthogonality

$$a_1a_2 + b_1b_2 + c_1c_2 = 0 \rightarrow 1/3 + \sqrt{2/3}b_2 + 0 \cdot c_2 = 0$$

$$a_2{}^2 + b_2{}^2 + c_2{}^2 = 1 \rightarrow 1/3 + b_2{}^2 + c_2{}^2 = 1$$

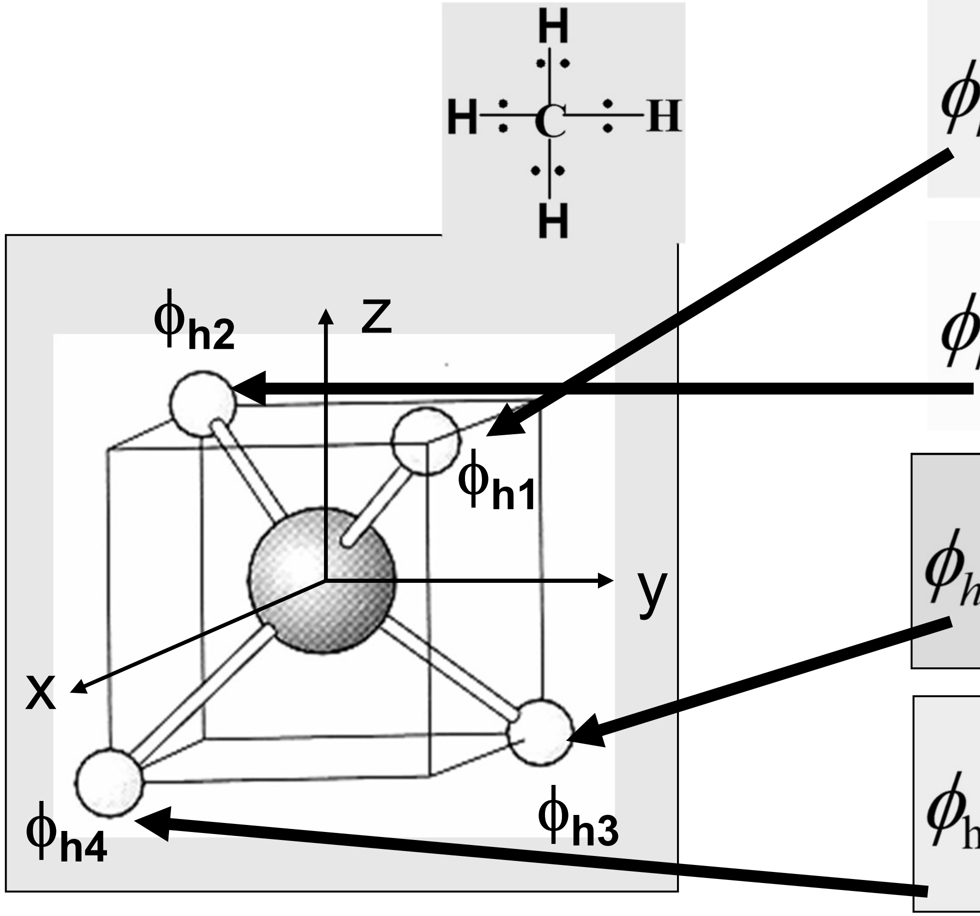
$$\rightarrow b_2 = -\sqrt{1/6} \qquad c_2 = \pm\sqrt{1/2} \rightarrow$$

$$\phi_{h2} = \sqrt{1/3}\phi_s - \sqrt{1/6}\phi_{2px} + \sqrt{1/2}\phi_{2py}$$

$$\phi_{h3} = \sqrt{1/3}\phi_s - \sqrt{1/6}\phi_{2px} - \sqrt{1/2}\phi_{2py}$$

c. sp^3 hybridization (tetrahedral)

- One ***s*** and 3 ***p*** AO's mix to form a set of four hybrid sp^3 orbitals.
- For equivalent sp^3 hybridization ***(α=1/4), e.g, CH_4***



$$\phi_{h1} = \frac{1}{2}[s + p_x + p_y + p_z]$$

$$\phi_{h2} = \frac{1}{2}[s - p_x - p_y + p_z]$$

$$\phi_{h3} = \frac{1}{2}[s - p_x + p_y - p_z]$$

$$\phi_{h4} = \frac{1}{2}[s + p_x - p_y - p_z]$$

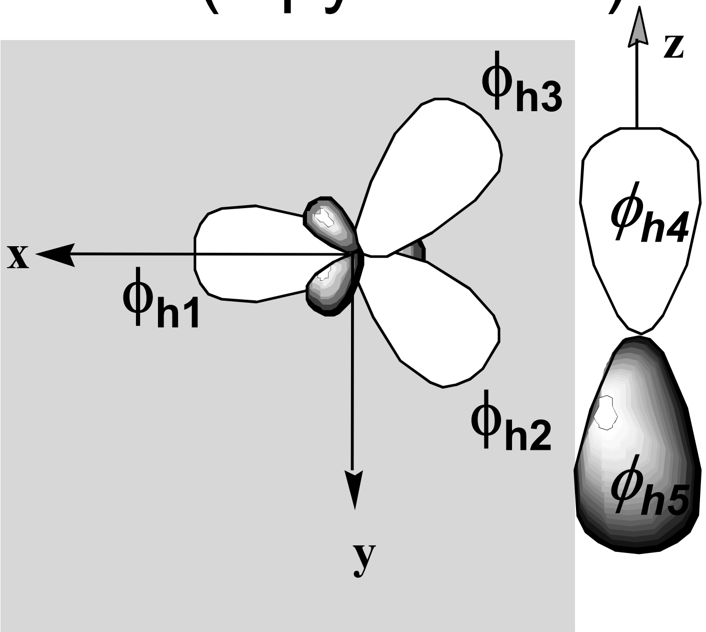
$$CH_4, SiH_4, GeH_4, PX_4, SO_4^{\ 2-}, PO_4^{\ 3-}$$

d. dsp^3 (sp^{3}d) hybridization (bipyramidal)

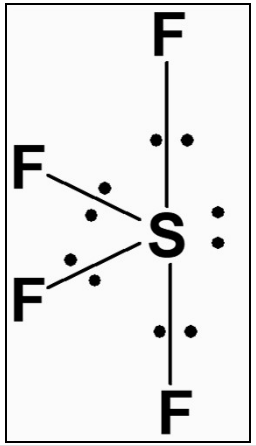
$$\phi_{h1} = \frac{1}{\sqrt{3}} s + \sqrt{\frac{2}{3}} p_x$$

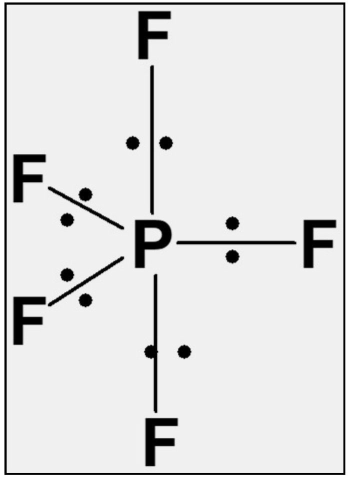
$$\phi_{h2} = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \sqrt{\frac{1}{2}} p_y$$

$$\phi_{h3} = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \sqrt{\frac{1}{2}} p_y$$



$$\phi_{h4} = \frac{1}{\sqrt{2}} [p_z + d_{z^2}]; \qquad \phi_{h5} = \frac{1}{\sqrt{2}} [p_z - d_{z^2}]$$





The bond lengths will not be the same because there is more ***d*** contribution to the axial hybrid orbitals.

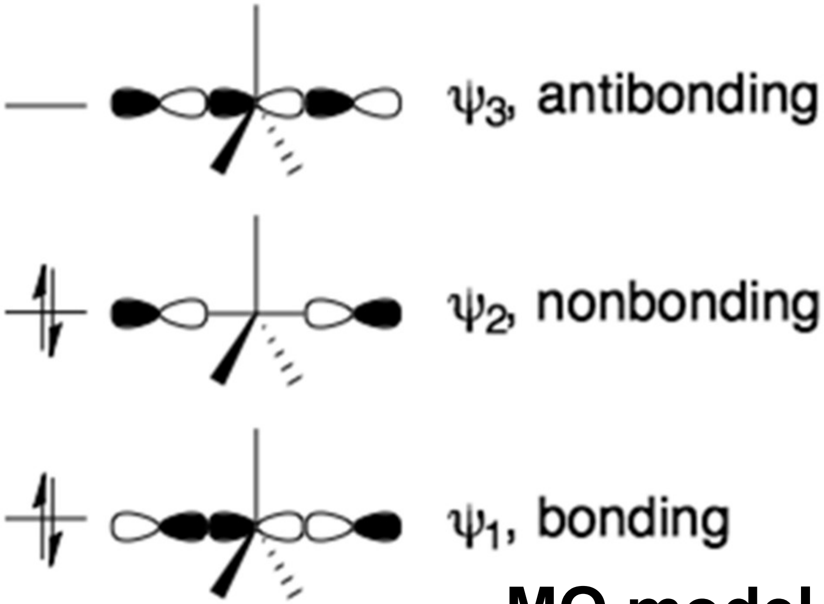
- For dsp^3, the axial bonds are shorter.
- For sp^{3}d, the axial bonds are longer, e.g., in PF$_5$.

(But mostly exaggerating the contribution of d orbitals!)

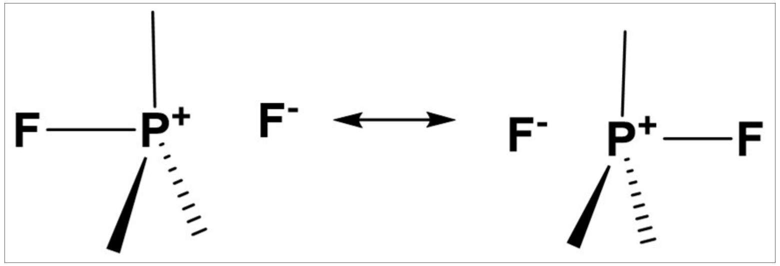
- However, in MOT, the 3d orbitals of P is not involved in the P-X bonds in PX_5(X = Cl, F) .
- An alternative model to describe the axial bonding in such bipyramidal molecules as PX_5:

Key points：

- The equatorial P-F bonds are normal σ-bond.
- The axial **F-P-F** bond: a **3-center 4-electron bond**.



MO model



Equivalent VB model:
resonance of VB structures

Axial P-F bond order

= 1/2

e. dsp^2 hybridization (square planar)

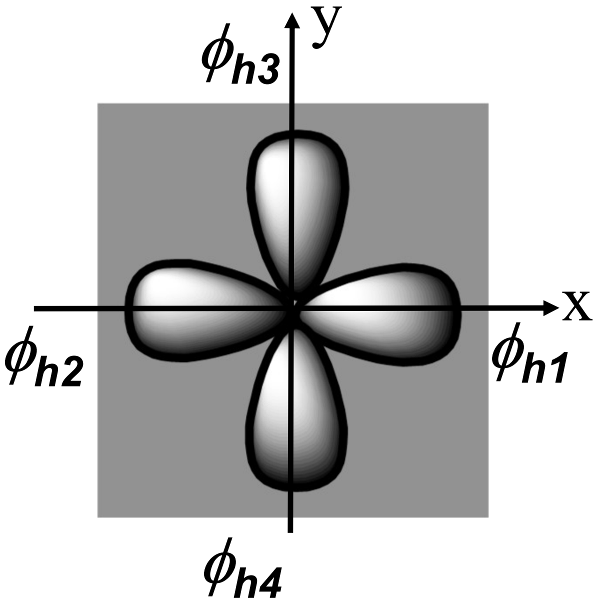
$$d_{x^2-y^2}, s, p_x, p_y$$

Square planar: D_{4h}

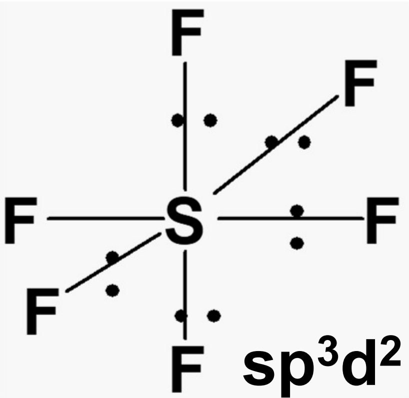
e.g., $Ni(CN)_4^{2-}$, $AuCl_4^-$

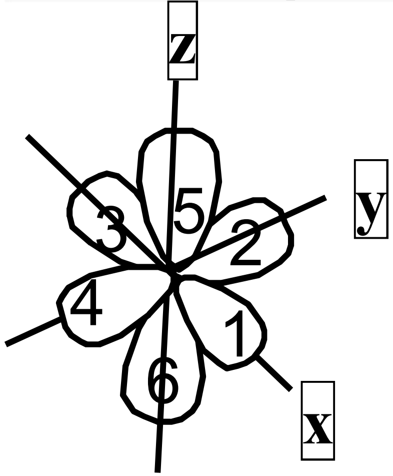
- **Equivalent case ($\alpha = ¼$)**

$$\left.\begin{aligned}
\phi_{h1} &= \frac{1}{2}\phi_s + \frac{1}{\sqrt{2}}\phi_{px} + \frac{1}{2}d_{x^2-y^2} \\
\phi_{h2} &= \frac{1}{2}\phi_s - \frac{1}{\sqrt{2}}\phi_{px} + \frac{1}{2}d_{x^2-y^2} \\
\phi_{h3} &= \frac{1}{2}\phi_s + \frac{1}{\sqrt{2}}\phi_{py} - \frac{1}{2}d_{x^2-y^2} \\
\phi_{h4} &= \frac{1}{2}\phi_s - \frac{1}{\sqrt{2}}\phi_{py} - \frac{1}{2}d_{x^2-y^2}
\end{aligned}\right\}$$



f. d^{2}sp^3 (sp^{3}d^2) hybridization (Octahedral)





$$d_{z^2}, d_{x^2-y^2}, s, p_x, p_y, p_z$$

- **Equivalent case**

$$\left\{\begin{aligned}
oc_1 &= \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_x + \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} \\
oc_2 &= \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_y - \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} \\
oc_3 &= \frac{1}{\sqrt{6}}s - \sqrt{\frac{1}{2}}p_x + \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} \\
oc_4 &= \frac{1}{\sqrt{6}}s - \sqrt{\frac{1}{2}}p_y - \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}
\end{aligned}\right.$$

$$oc_5 = \frac{1}{\sqrt{6}}s + \sqrt{\frac{1}{2}}p_z + \sqrt{\frac{1}{3}}d_{z^2} \qquad oc_6 = \frac{1}{\sqrt{6}}s - \sqrt{\frac{1}{2}}p_z + \sqrt{\frac{1}{3}}d_{z^2}$$

Hybridization schemes

- ***$sp^n d^m$*** **gives a "complete" set of hybrid orbitals for "any" geometry.**

sp	linear
sp^2	trigonal planar
sp^3	tetrahedral
sp^3d (d_{z^2})	trigonal bipyramidal
sp^3d($d_{x^2-y^2}$)	square pyramidal
sp^2d^2	square pyramidal
sp^3d^2	octahedral
sp^2d	square planar

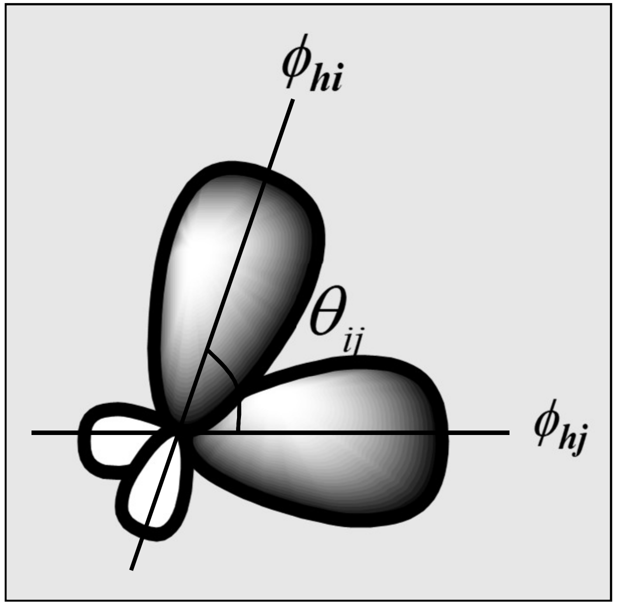
3. The angle between two hybrid orbitals

1) sp^n hybridization

Let's define
$$\phi_h = \sqrt{\alpha}\phi_s + \sqrt{1-\alpha}\phi_p$$

$$\phi_{hi} = \sqrt{\alpha_i}\phi_s + \sqrt{1-\alpha_i}\phi_{p_i}$$

$$\phi_{hj} = \sqrt{\alpha_j}\phi_s + \sqrt{1-\alpha_j}\phi_{pj}$$



where ϕ_{pi} is

$$\phi_{p_i} = x_i\phi_{px} + y_i\phi_{py} + z_i\phi_{pz}$$

Note the angle between the two vectors ϕ_{pi} and ϕ_{pj} is the angle θ_{ij} between the two hybrid orbitals ϕ_{hi} and ϕ_{hj} , i.e.,

$$\cos\theta_{ij} = \int \phi_{pi}\phi_{pj}\,d\tau$$

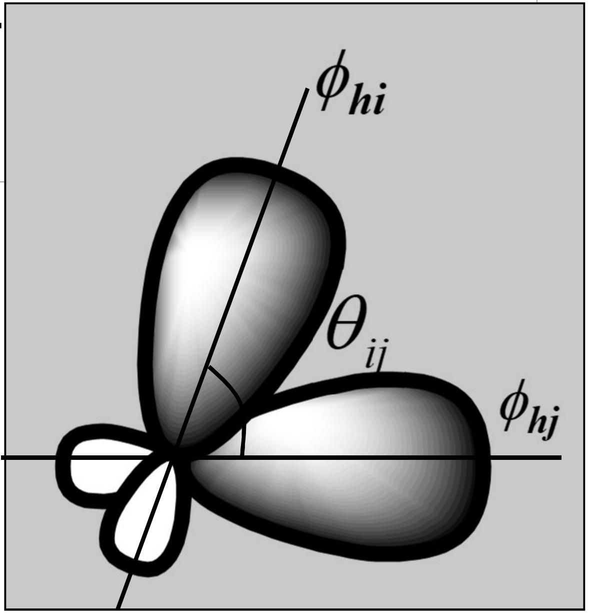
Normalization and orthogonality

$$0=\int \phi_{hi}\phi_{hj}d\tau=\int(\sqrt{\alpha_i}\phi_s+\sqrt{1-\alpha_i}\phi_{pi})(\sqrt{\alpha_j}\phi_s+\sqrt{1-\alpha_j}\phi_{pj})d\tau$$

$$=\sqrt{\alpha_i\alpha_j}\int\phi_s^2d\tau+\sqrt{(1-\alpha_i)(1-\alpha_j)}\underline{\int\phi_{pi}\phi_{pj}d\tau}+0+0$$

$$\Rightarrow 0=\sqrt{\alpha_i\alpha_j}+\sqrt{(1-\alpha_i)(1-\alpha_j)}\,\underline{\cos\theta_{ij}}$$

$$\Rightarrow\cos\theta_{ij}=-\frac{\sqrt{\alpha_i\alpha_j}}{\sqrt{(1-\alpha_i)(1-\alpha_j)}}<0\Rightarrow\theta_{ij}>90^\circ$$



$\alpha_i=\alpha_j$ Equivalent hybridization. e.g., CH_4

$\alpha_i\neq\alpha_j$ Non-equivalent hybridization. e.g., $CHCl_3$, CH_3Cl

sp: $\alpha = 0.5$ ➔ $\cos\theta = -1$ ➔ $\theta = 180.0^\circ$

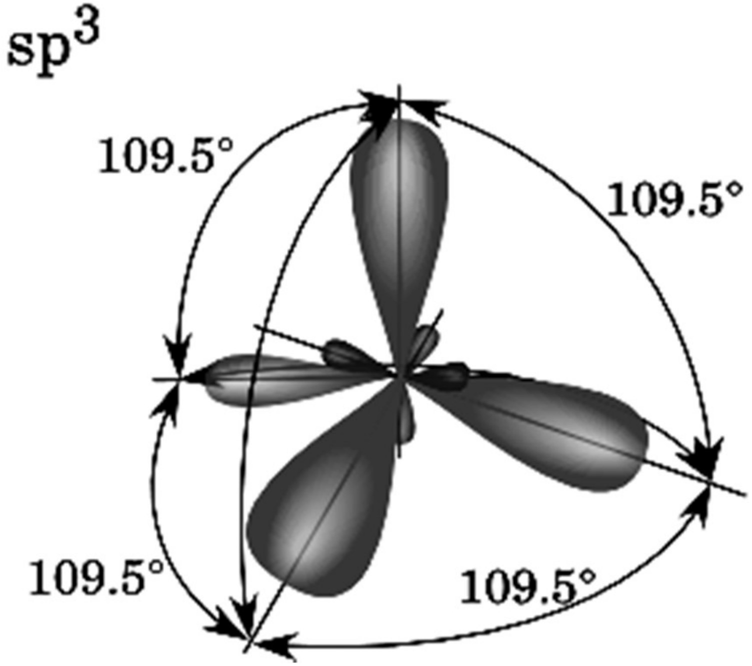
sp^2 : $\alpha = 1/3$ ➔ $\cos\theta = -0.5$ ➔ $\theta = 120.0^\circ$

Equivalent hybridization

$$sp^3 - hybridization \quad \alpha = \frac{1}{4} \Rightarrow$$

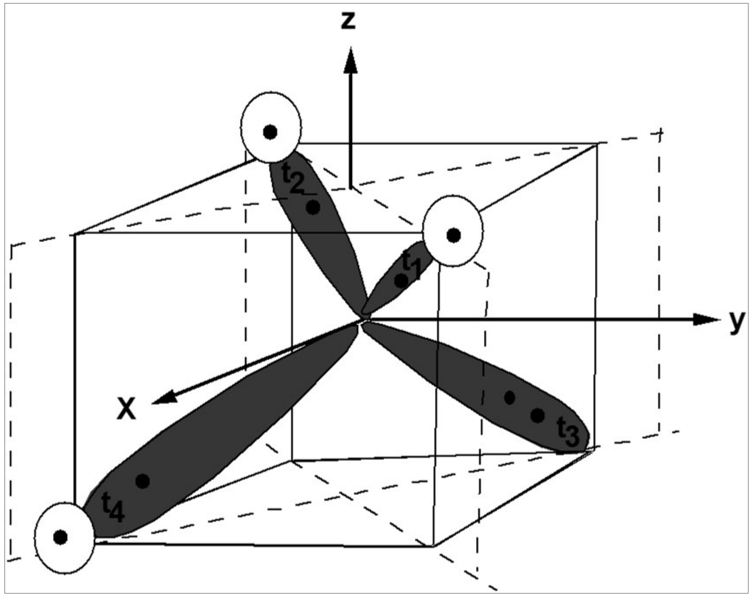
$$\cos\theta_{ij} = -\frac{\sqrt{\alpha_i \alpha_j}}{\sqrt{(1-\alpha_i)(1-\alpha_j)}} = -\frac{1}{3}$$

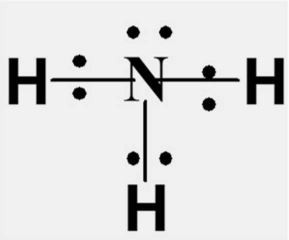
$$\Rightarrow \theta = 109^0 28''$$



Non-equivalent hybridization

$sp^3 - hybridization$





Other examples

PH_3, PF_3, NF_3,

s-component of the ***N*** sp^3 HO′s to form the N-H bonds.

$$For\ \ NH_3:\ \ \theta = \angle HNH = 107.3^\circ$$

$$\alpha + (1-\alpha)\cos 107.3^\circ = 0 \qquad \Rightarrow\ \alpha = 0.23$$

$$\Rightarrow \psi_{HO(N-H)} = \sqrt{0.23}s + \sqrt{0.77}p = 0.48s + 0.88p$$

$$\Rightarrow L_s = 1 - 3*0.23 = 0.31$$ *s*-component of the lone pair

$$\Rightarrow L_p = 3 - 3*0.77 = 0.69$$ *p*-component of the lone pair

$$\psi_{lone-pair} = \sqrt{0.31}s + \sqrt{0.69}p = 0.56s + 0.83p$$

For d-s-p hybridization, the angles between two hybrid orbitals can be calculated by: (where *α, β* ***and*** *γ* are the component of s, p and d orbitals)

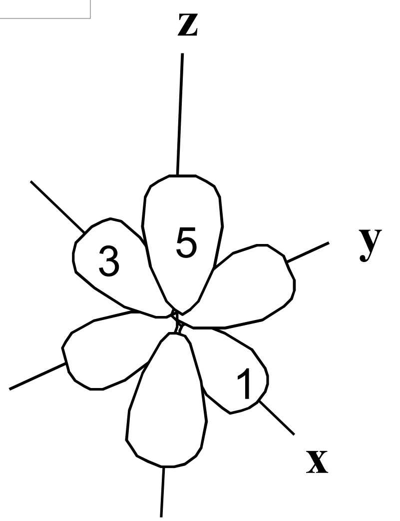
$$\alpha + \beta\cos\theta + \gamma\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) = 0$$

$$\mathrm{d^2sp^3}:\ \underline{\alpha = \frac{1}{6},\quad \beta = \frac{1}{2},\quad \gamma = \frac{1}{3}}$$

$$\frac{1}{6} + \frac{1}{2}\cos\theta + \frac{1}{3}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) = 0$$

$$\Rightarrow \cos\theta_1 = 0, \qquad \cos\theta_2 = -1$$

$$\Rightarrow \theta_1 = 90^\circ, \quad \theta_2 = 180^\circ$$



Octahedral

4. The bonding ability of hybrid orbitals

$$F_{AO} = \sqrt{2l+1}$$

Atomic orbital bonding ability : s, p, d, f : $1, \sqrt{3}, \sqrt{5}, \sqrt{7}$

The bonding ability of a hybrid orbital is given by :

$$\boldsymbol{f_h = \sqrt{\alpha} + \sqrt{3\beta} + \sqrt{5\gamma}}$$

for the sp^n hybridizations,

$\alpha = \frac{1}{2}, \beta = \frac{1}{2}$	$f_h = 1.932$	sp
$\alpha = \frac{1}{3}, \beta = \frac{2}{3}$	$f_h = 1.992$	sp^2
$\alpha = \frac{1}{4}, \beta = \frac{3}{4}$	$f_h = 2.00$	sp^3
$\alpha = 0,$	$f_h = \sqrt{3}$	p
$\alpha = 1,$	$f_h = 1$	s

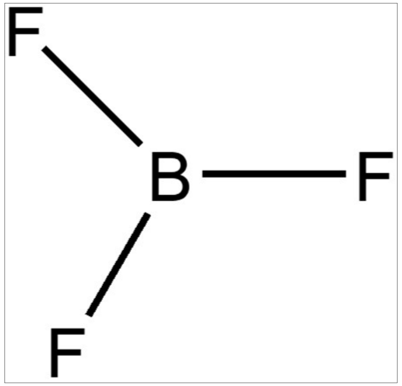
Hybridization enhances the bonding ability of atomic valence orbitals!!

$$\boxed{\alpha = \frac{1}{6}, \beta = \frac{1}{2}, \gamma = \frac{1}{3} \qquad f_h = 2.925 \quad \mathrm{d^2sp^3}}$$

5. Discussions

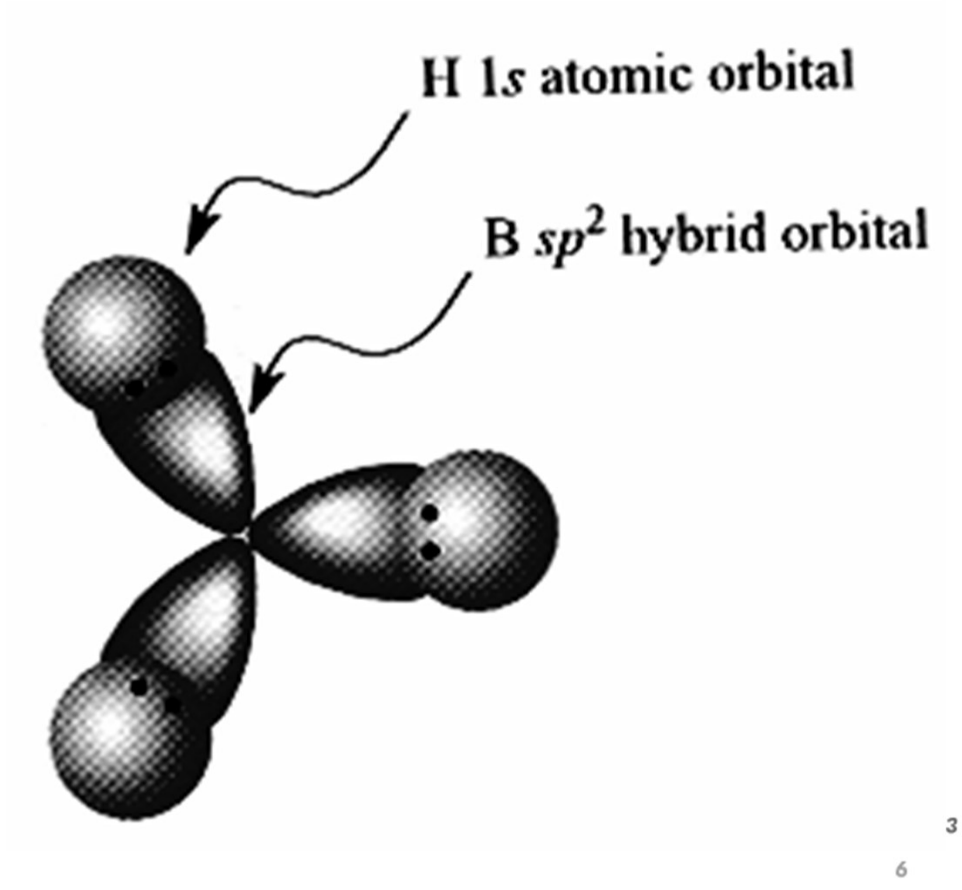
sp^2

e.g., $BF_3(D_{3h})$, BH_3 (D_{3h}), NO_3^-, CO_3^{2-}

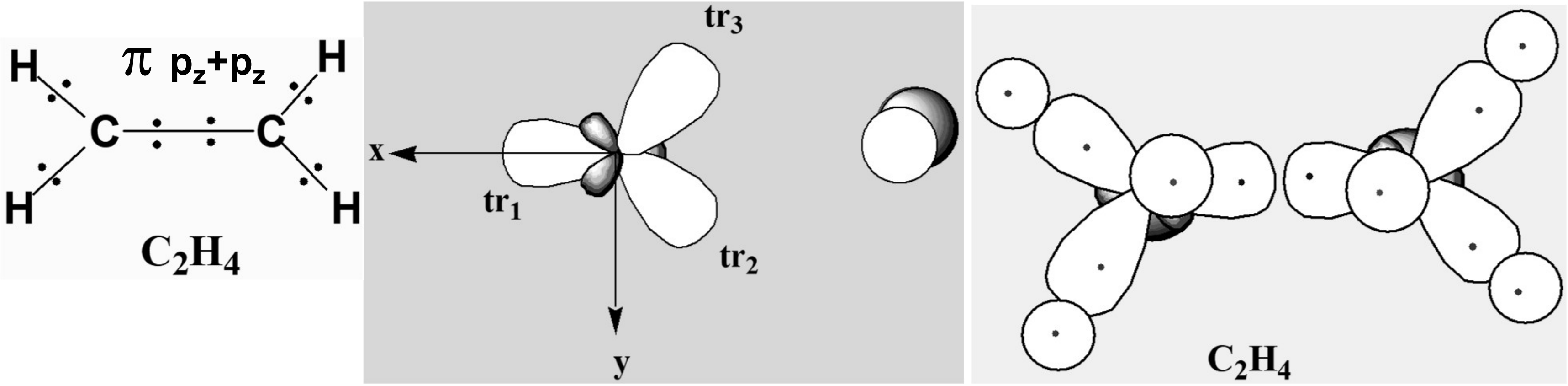


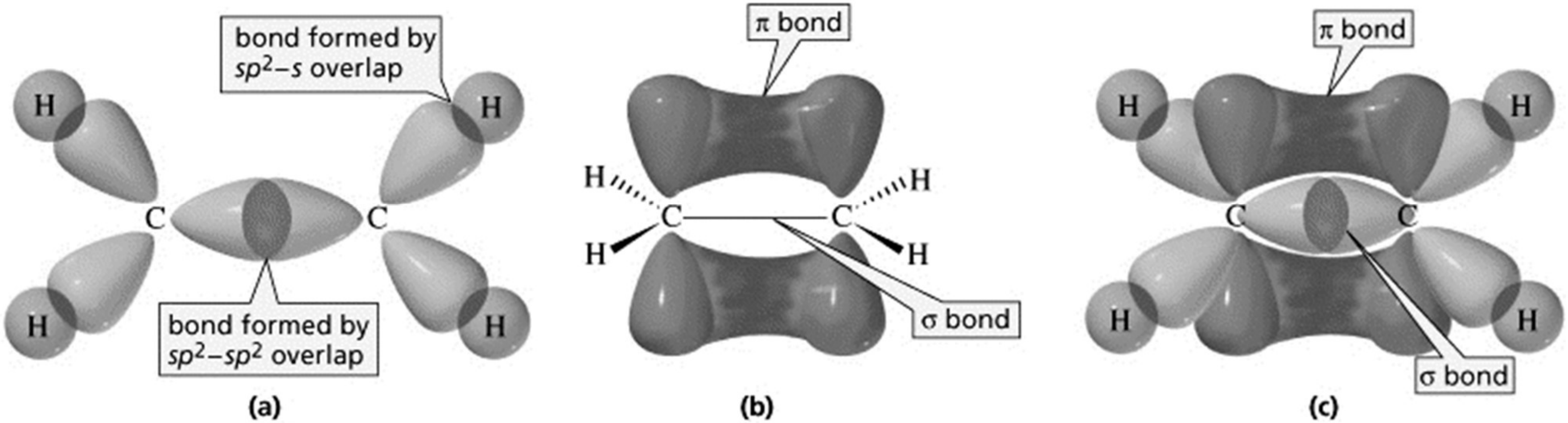
Example: BH_3

- The B atom has 3 sp^2 hybrid orbitals each with one electron.
- This one electron pairs with the hydrogen 1s electron.
- The $2p_z$ AO of B atom is thus empty.



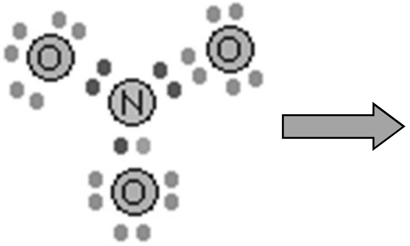
Example:



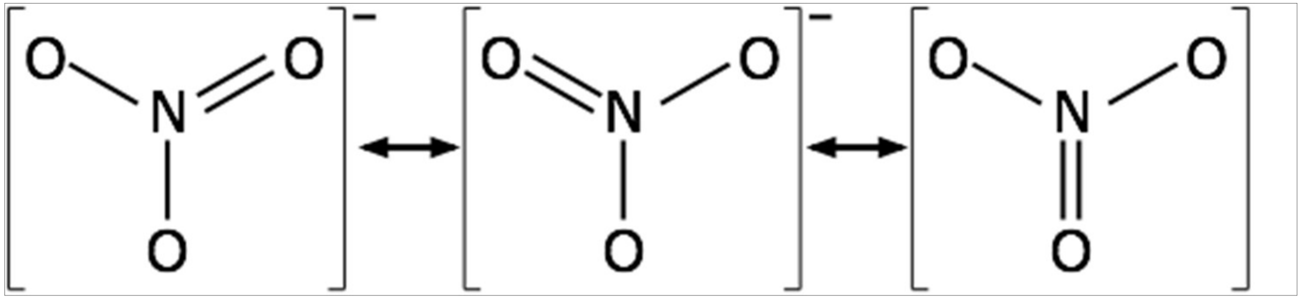


The sp^2-hybridization and chemical bonding in C_2H_4.

Example: nitrate (NO_3^-) --hybridization and delocalization



dot-electron structure



Resonance of three equivalent dot-electron structures (or VB structures)–delocalization of π-electrons

VB model:

i) N~sp^2 hybridization.

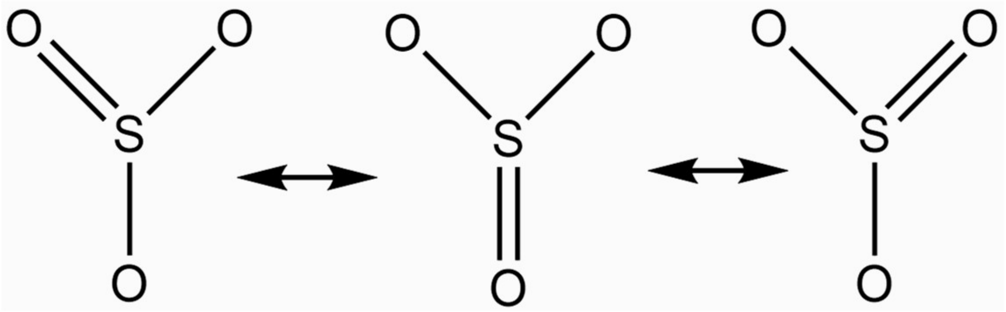
ii) Three N-O σ-bonds (One N→O type!) plus a N-O π-bond.

Thus N is hexavalent!

iii) Resonance of the three VB structures thus gives a delocalized 4-center 6-electron π-bond (Π_4^6).

(Valence) Isoelectronic: **SO_3**

SO_3 D_{3h}



VB model:

i) S~sp^2 hybridization.

ii) Three S-O σ-bonds (two of them are S→O type!) plus a S-O π-bond. ***Thus S is hexavalent***!

iii) Resonance of the three VB structures thus gives a delocalized 4-center 6-electron π-bond (Π_4^6).

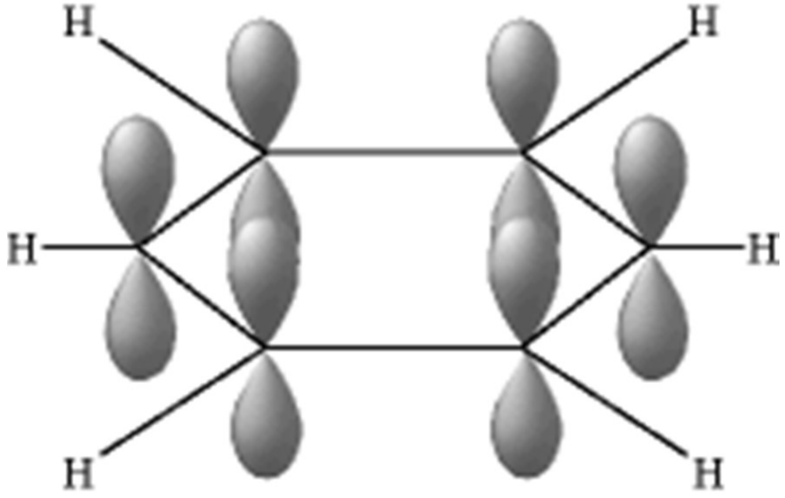
MO model:

i) VE ~ 24e; S~sp^2 hybridization;

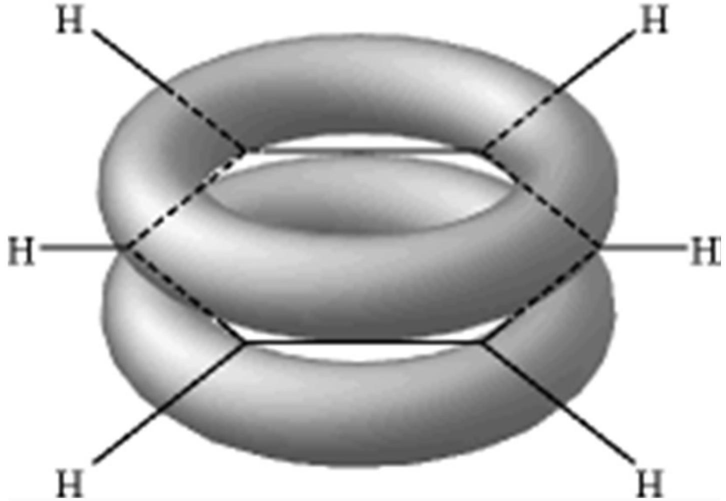
ii) Three S-O σ-bonds(6e) ; 6 lone pairs on the three O atoms(12e);

iii) The rest 6e (= 24e-6e-12e) should be accommodated in the delocalized 4-center π-bond, i.e., a Π_4^6.

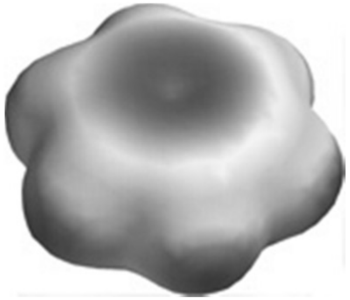
Example: Benzene --hybridization and delocalization



The sp^2 hybrid orbitals of C atoms and the 1s AO′s of H atoms form the σ-framework of benzene.



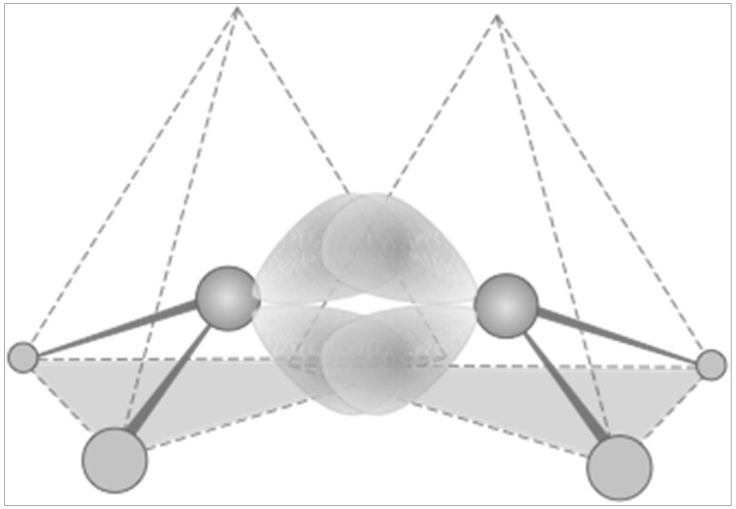
The unhybridized p_z AO′s of C atoms form a continuous cyclic Π_6^6 bond of benzene.

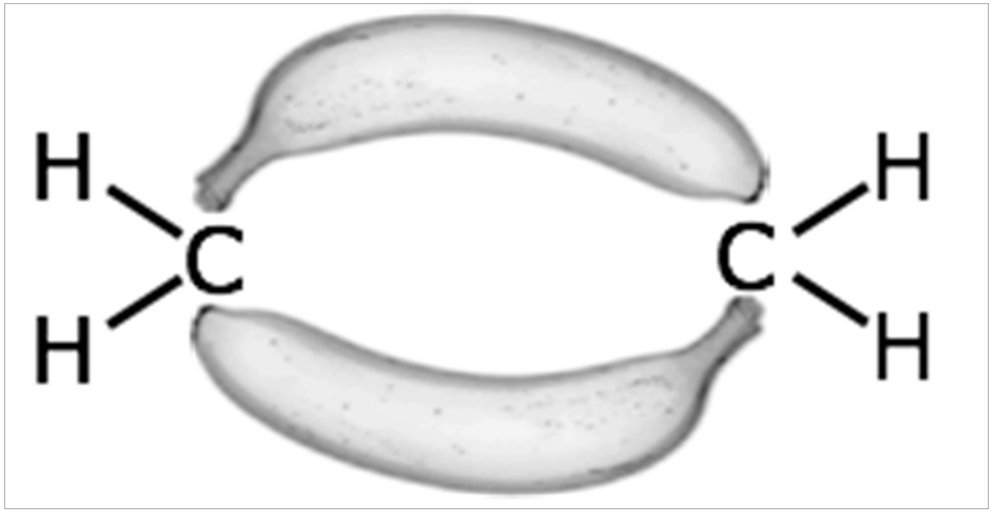


6. “Bent bond” model -- An alternative of hybrids

(obsolete!)

“Bent bond” model of ethylene

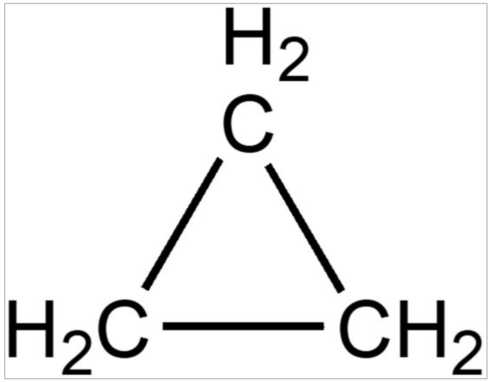




- No need to assume hybridization in the C atoms at all.
- Directions of the p-orbitals in C atoms should be distorted sufficiently to provide the overlap for bonding. These bent bonds are called “banana bonds”.

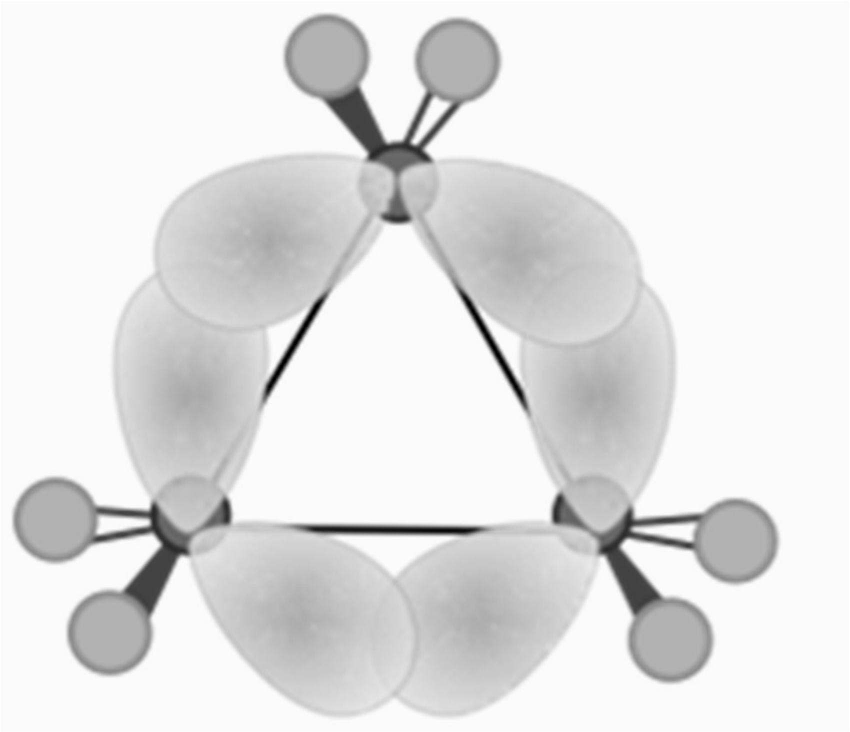
6. “Bent-bond” Model -- an alternative of hybrids

cyclopropane



Note the C–C bond angles are 60° — quite a departure from the tetrahedral angle of 109.5° associated with *sp*^{3} hybridization!

sp^3 hybridization of C



Three “banana bonds” formed!

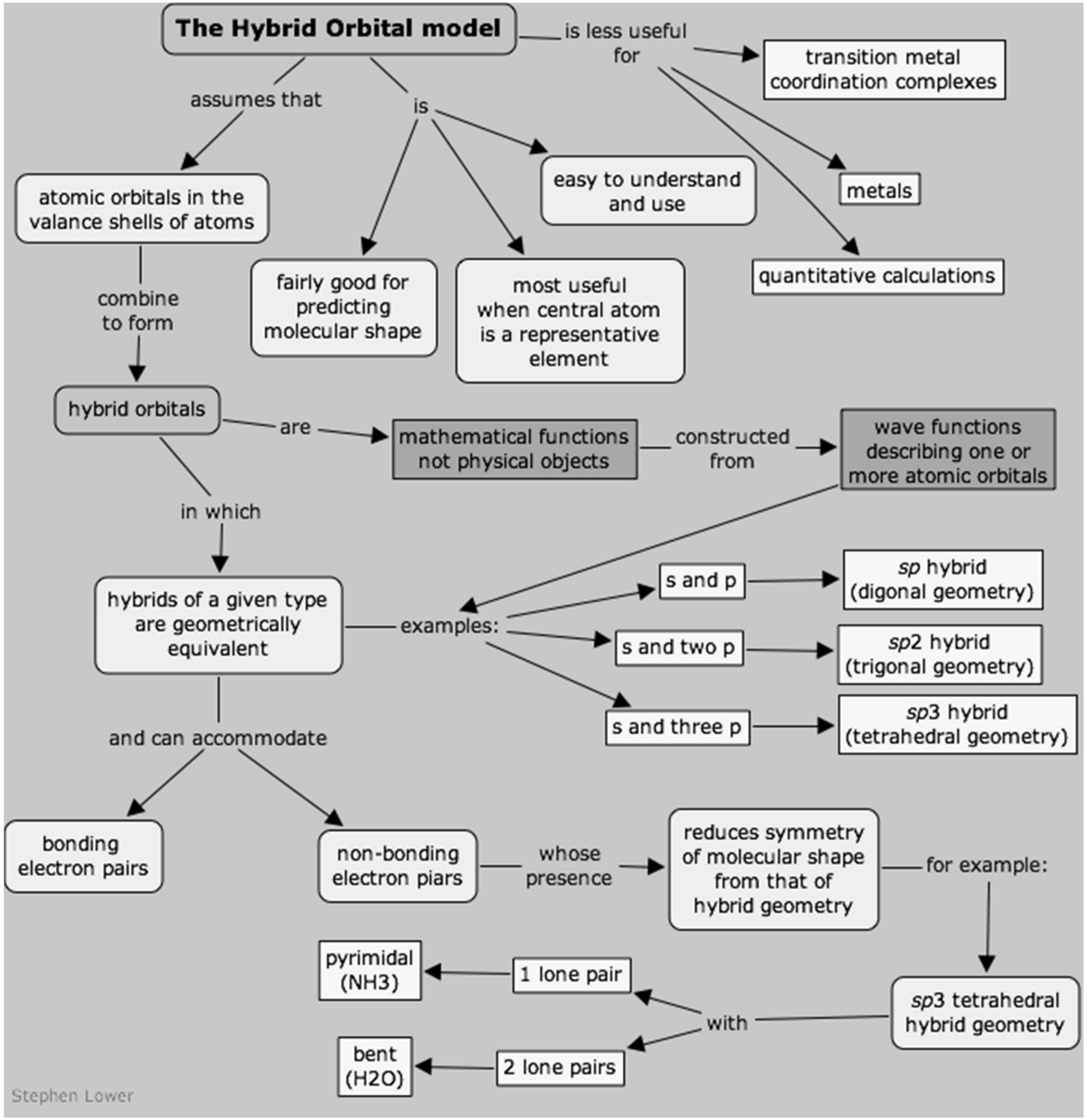
However, in terms of MO theory, Dewar proposed that this molecule has σ-aromaticity! *Dewar, M. J. J. Am. Chem. Soc. 1984,* ***106*** *(3): 669;* Wu, W. *Chem. Eur. J. 2009,* **15** (38): 9730 .

You should understand that

- ***Hybridization is not a physical phenomenon*****; it is merely a** ***mathematical operation*** that combines the atomic orbitals we are familiar with in such a way that the new (hybrid) orbitals possess the geometric and other properties that are reasonably consistent with what we observe in a wide range (but certainly not in all) molecules.

- Hybrid orbitals are abstractions that describe reality fairly well in certain classes of molecules (and fortunately, in much of the very large class of organic substances) and are therefore a useful means of organizing a large body of chemical knowledge... but they are far from infallible.

Concept Map (I)



The Hybrid Orbital model

is less useful for

transition metal coordination complexes

metals

quantitative calculations

assumes that

atomic orbitals in the valance shells of atoms

combine to form

hybrid orbitals

are

mathematical functions not physical objects

constructed from

wave functions describing one or more atomic orbitals

is

fairly good for predicting molecular shape

most useful when central atom is a representative element

easy to understand and use

in which

hybrids of a given type are geometrically equivalent

examples:

s and p

sp hybrid (digonal geometry)

s and two p

*sp*2 hybrid (trigonal geometry)

s and three p

*sp*3 hybrid (tetrahedral geometry)

and can accommodate

bonding electron pairs

non-bonding electron piars

whose presence

reduces symmetry of molecular shape from that of hybrid geometry

for example:

*sp*3 tetrahedral hybrid geometry

with

1 lone pair

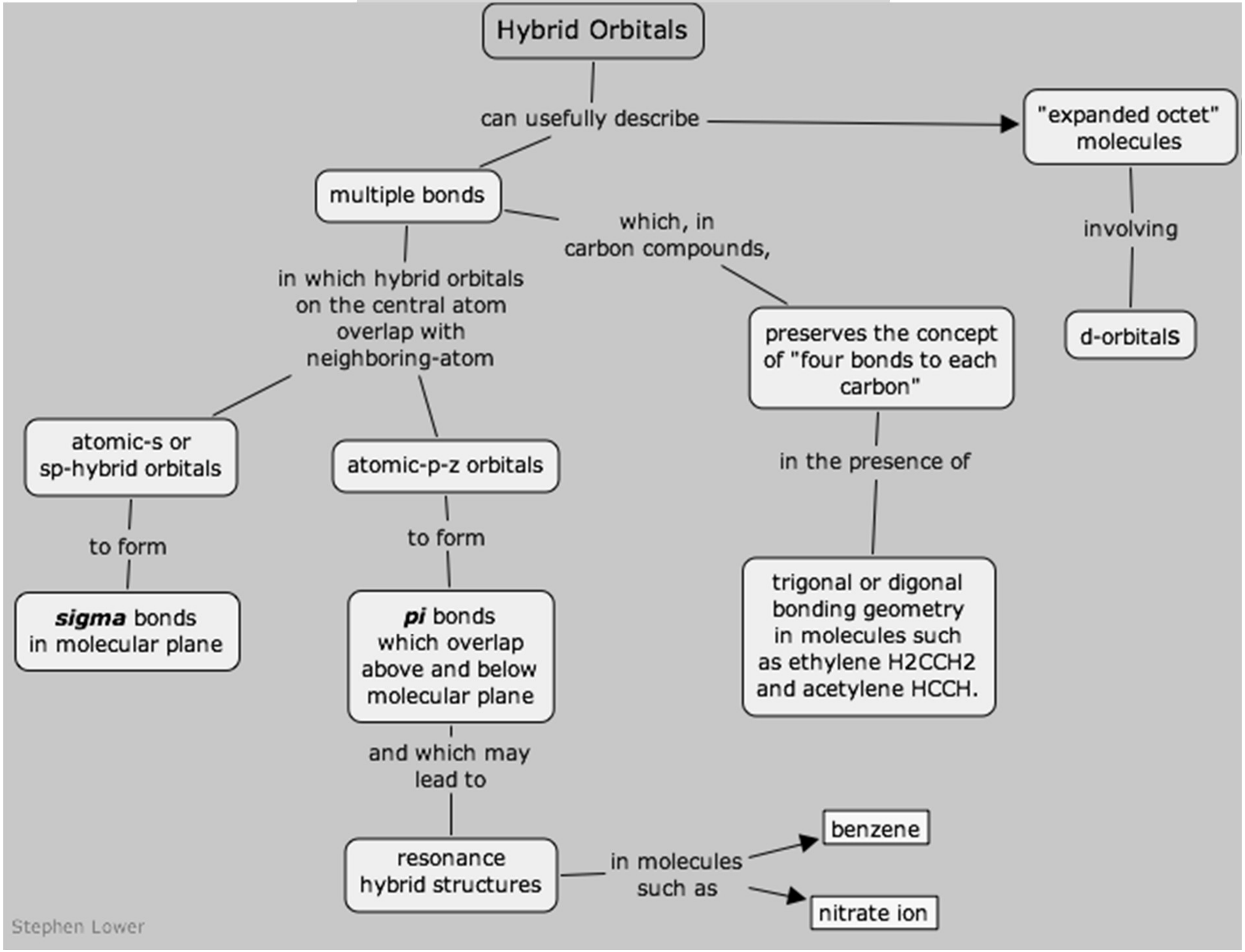
pyrimidal (NH3)

2 lone pairs

bent (H2O)

Stephen Lower

Concept Map II



Hybrid Orbitals

can usefully describe

"expanded octet" molecules

involving

d-orbitals

multiple bonds

which, in carbon compounds,

preserves the concept of "four bonds to each carbon"

in the presence of

trigonal or digonal bonding geometry in molecules such as ethylene H2CCH2 and acetylene HCCH.

in which hybrid orbitals on the central atom overlap with neighboring-atom

atomic-s or sp-hybrid orbitals

to form

sigma bonds in molecular plane

atomic-p-z orbitals

to form

pi bonds which overlap above and below molecular plane

and which may lead to

resonance hybrid structures

in molecules such as

benzene

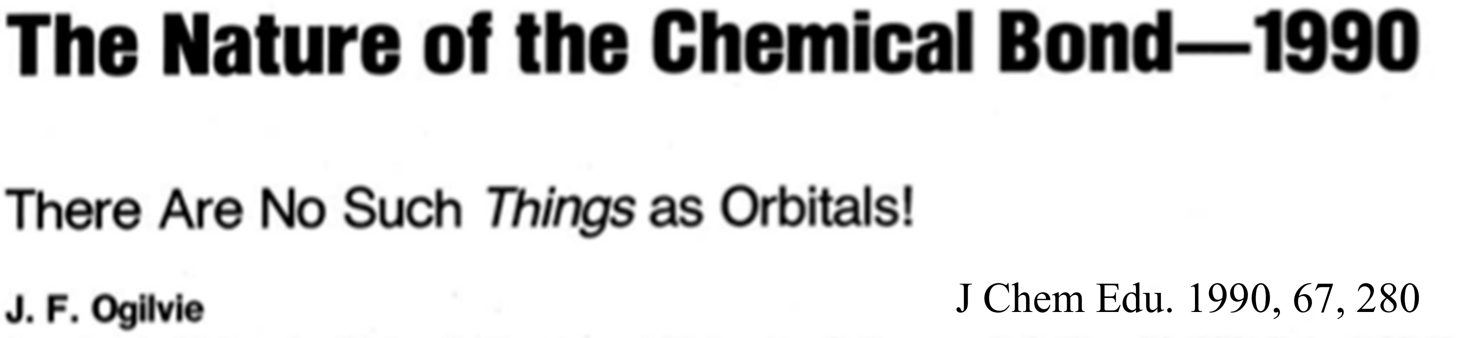
nitrate ion

Stephen Lower

After-class Discussion:

Real or Imagination:

- **Chemical Bond**
- **Orbital**
- **Atomic Orbital**
- **Molecular Orbital**
- **Hybridized Orbital**



The Nature of the Chemical Bond—1990

There Are No Such *Things* as Orbitals!

J. F. Ogilvie

J Chem Edu. 1990, 67, 280

The Nature of the Chemical Bond —1992

Linus Pauling

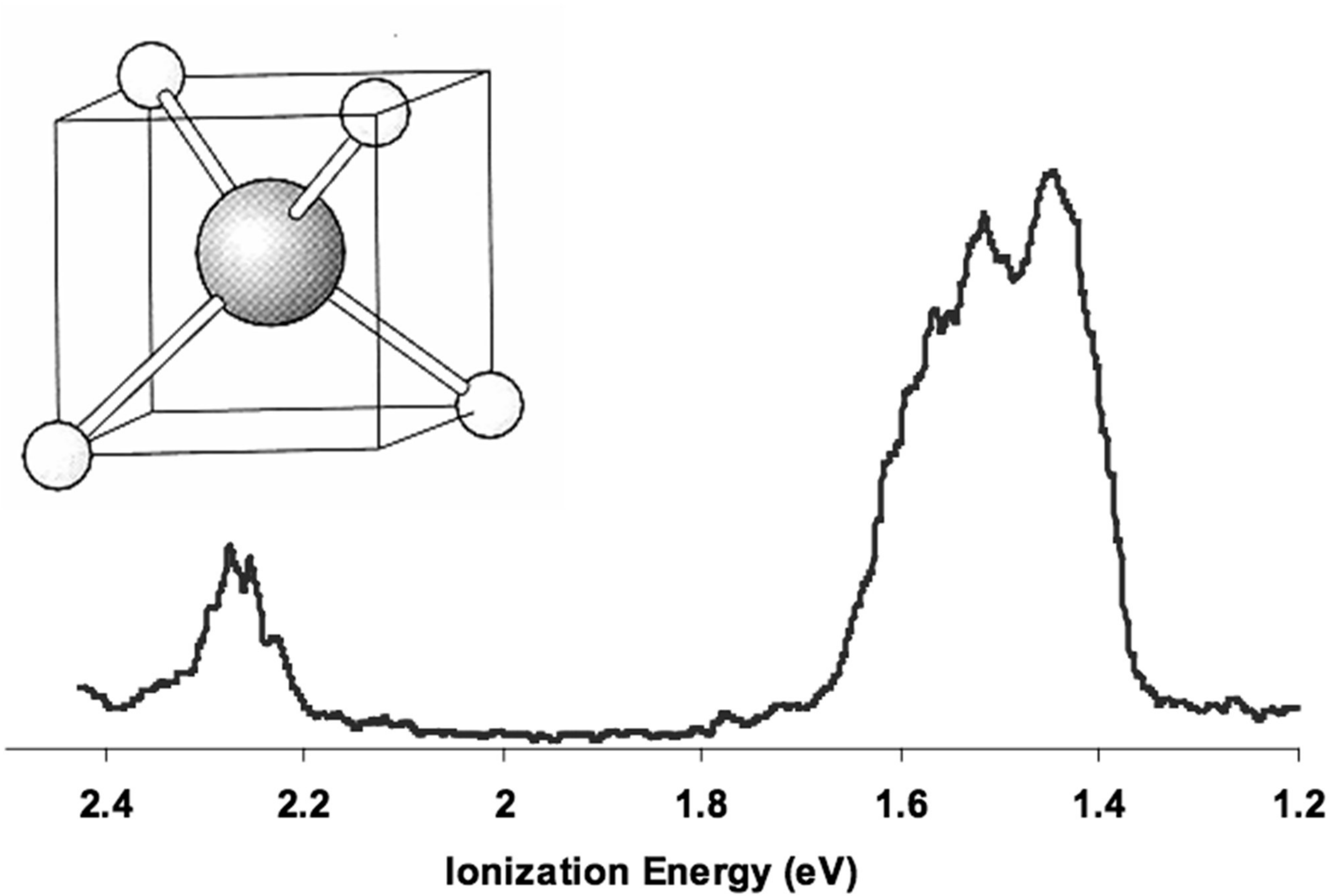
Linus Pauling Institute of Science and Medicine, 440 Page Mill Road, Palo Alto, CA 94306

J Chem Edu. 1992, 69, 519

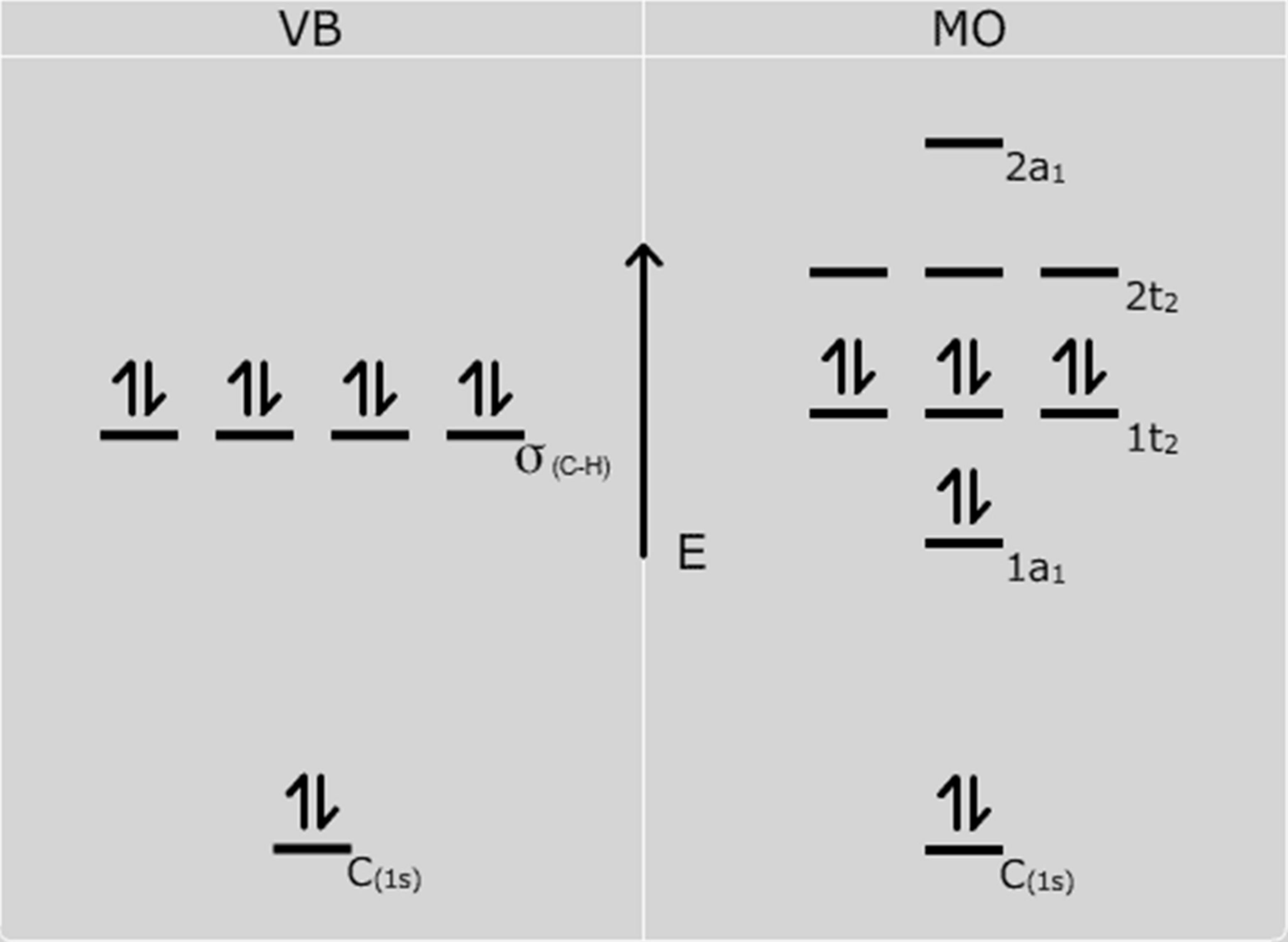
Editor's Note

In this issue we bring to closure the current discussion of the nature of the chemical bond. Readers will recall the paper by Ogilvie [J. Chem. Educ. **1990,** 67, 28&289] giving one modern point of view of the chemical bond. In this issue, we publish another modern point of view by Pauling together with three letters (page 600) that the Ogilvie paper engendered. These letters have been selected from a larger number (which we are unable to print) and are representative of the kinds of responses that the paper generated. Since both Pauling and Ogilvie use the photoelectron spectra of methane to provide evidence for their (divergent) views, we also publish in this issue (page 522) a paper by Simons on photoelectric spectroscopy of methane.

PES Spectrum of Methane



Electron configuration



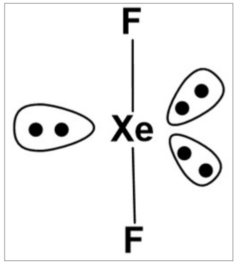
An alternative view on the chemical bonding within hypervalent compounds

3-center 4-electron bond

[**VB (**Coulson model**) vs. MO (**Rundle–Pimentel model **)]**

Example 1. XeF_2

a) Classic view – Pauling's model (involving d-orbital).



sp^3d hybridization,

3 lone pairs + 2 axial Xe-F bonds

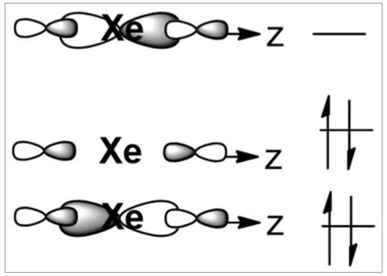
b) 3-center 4-electron bond (excluding d-orbital).

sp^2 hybridization → 3 lone pairs (equatorial)

Axial 3c4e bond: Xe $5p_z$ (2e) + 2F $2p_z$ (2 x 1e)

VB: $\text{F-Xe}^+\ \text{F}^- \longleftrightarrow \text{F}^-\ \text{Xe}^+\text{-F}$ **∴ Xe-F bond order =1/2**

MO:



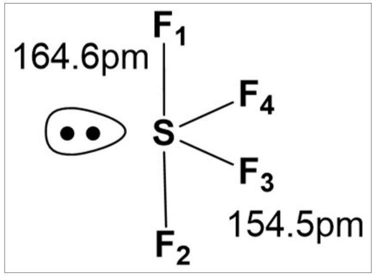
$\psi_3 = A(\phi_{F1} + 2\phi_{Xe} + \phi_{F2})$ **(anti-bonding)**

$\psi_2 = A(\phi_{F1} - \phi_{F2})$ **(non-bonding)**

$\psi_1 = A(\phi_{F1} - 2\phi_{Xe} + \phi_{F2})$ **(bonding)**

Example 2. SF_4

a) Classic view (involving valence d orbital).



sp^3d hybridization,
1 lone pair + 4 S-F bonds

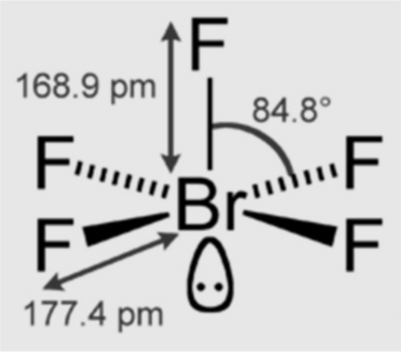
b) 3-center 4-electron bond (excluding d orbital).

- **sp^2 hybridization → 1 lone pair + 2 S-F (equatorial)**
- **Axial 3c4e bond (MO): S $3p_z$ (2e) + 2F $2p_z$ (1e)**

$$\psi_1 = A\phi_{F1} - B\phi_S + A\phi_{F2} \qquad \psi_2 = A'(\phi_{F1} - \phi_{F2})$$

$$\psi_{LUMO} = A\phi_{F1} + B\phi_S + A\phi_{F2} \quad (A < B)$$

- This model accounts well for the fact that the axial S-F bonds are longer than the equatorial ones.



- Such bonding model can be used for similar hypervalent compounds, e.g., XeF_4, BrF_5 etc!

§ **5.2** Valence Shell Electron-Pair Repulsion (VSEPR) Model (After-class reading)

- Quantum mechanical treatments have a number of advantages. However, the VSEPR model allows a simple qualitative prediction of molecular geometry.
- In a molecule, the valence electron pairs：

i) Stabilized by electrostatic attraction by the nucleus,

ii) Destabilized by Pauli repulsion between their neighbors.

- A lone pair is more diffuse than a bonding pair, exerting larger repulsion to a neighboring pair.

A stable molecule should adopt such a geometry that minimizes the repulsions among its various electron pairs!

VSEPR

Overall spatial distribution pattern of valence electron pairs of central atom.

Atom B in AB_n lies on the surface of a sphere; electron pairs are "localized" on a sphere of smaller radius at maximum distances apart, so as to minimize overlap of different electron pairs.

1. Repulsion between two lone pairs (**LP**s) is the greatest.
2. Repulsion between a lone electron pair and a bonding electron pair (**BP**) is less.
3. Repulsion between two bonding pairs is the least.
4. π electron pair does not influence stereochemistry.

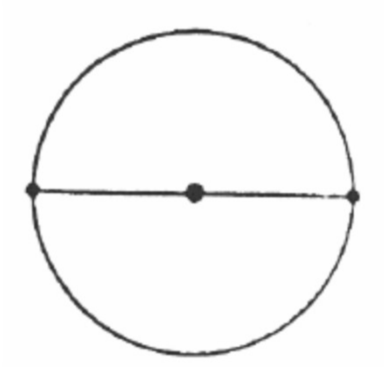
Repulsion of electron pairs

LP-LP > LP-BP > BP-BP ⇨ The position of lone pair(s) matters!

VSEPR model is sometimes used in combination with the Lewis dot-electron structures and hybrid orbital theory.

Arrangements of Maximum distance between valence shell electron pairs.

No. of pairs	arrangement
2	Linear
3	Equilateral triangle
4	Tetrahedron
5	Trigonal bipyramid
6	Octahedron

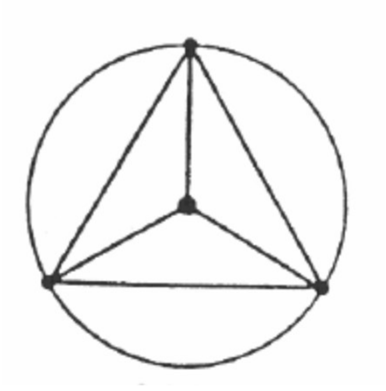


AX_2
$BeCl_2$, $CaCl_2$
(linear)

(2+2)/2=2

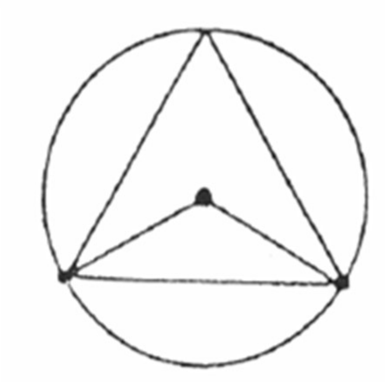
AX_3
BF_3
(trigonal plane)

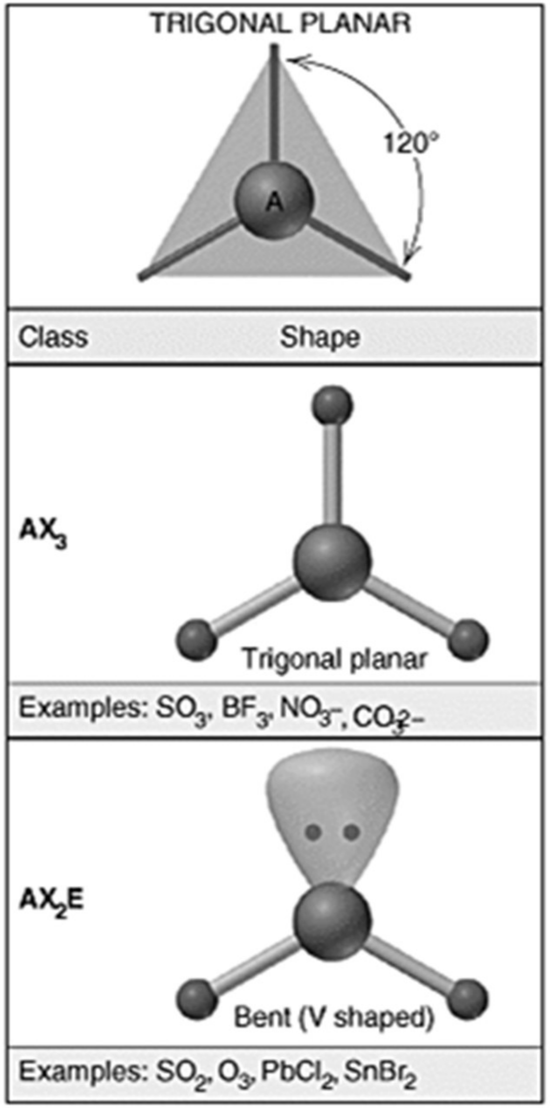
(3+3)/2=3

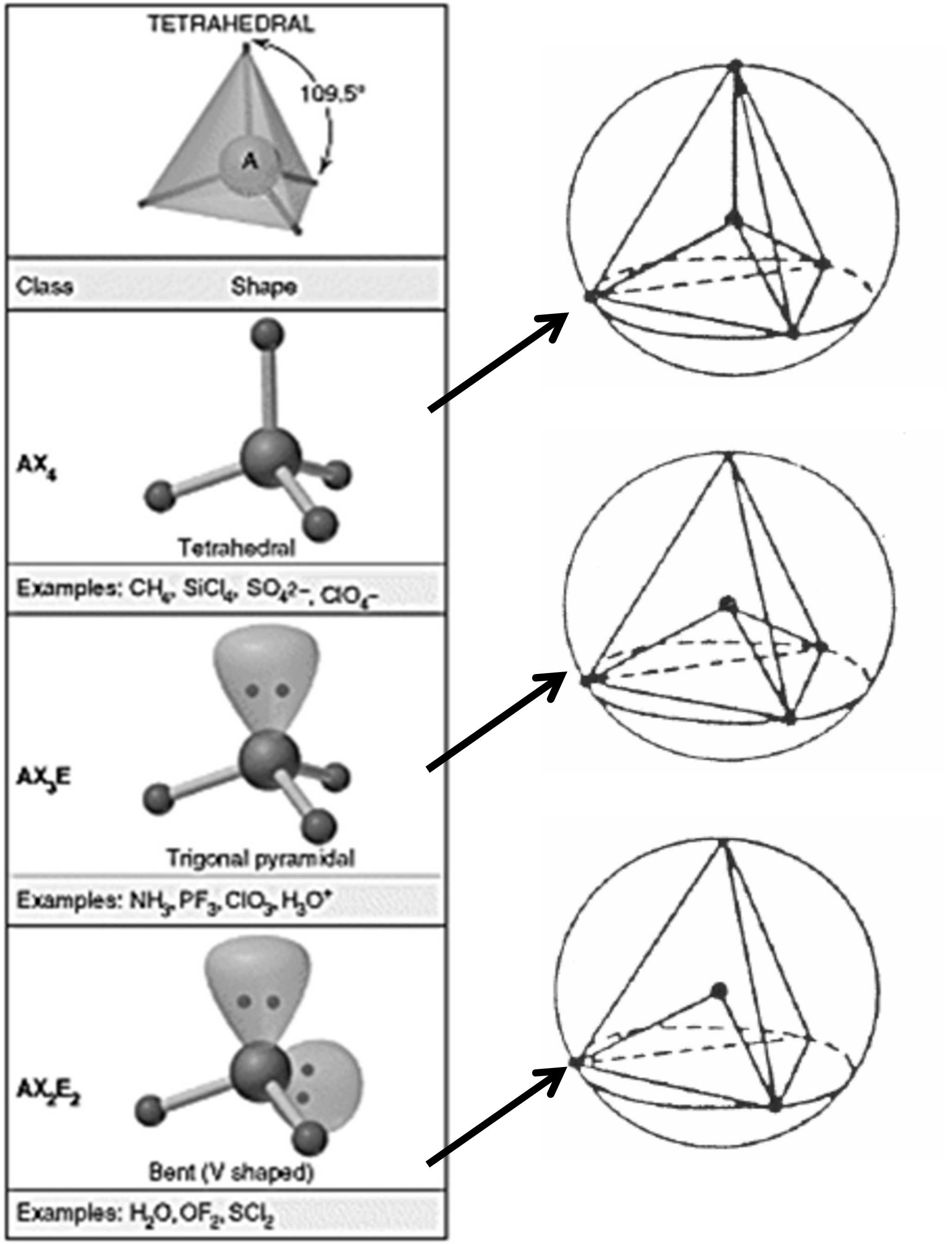


AX_2E
CCl_2, $SnCl_2$
(bent)

(4+2)/2=3







AX_4
CH_4, AlH_4^-, CCl_4, NH_4^+
(tetrahedral)

(4+4)/2=4

AX_3E
NH_3, NF_3
(pyramidal)

(5+3)/2=4

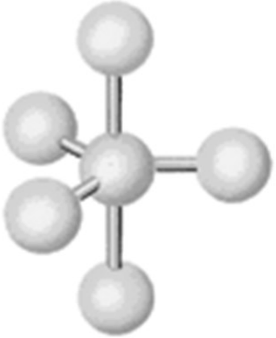
AX_2E_2
H_2O, H_2S
(bent)

(6+2)/2=4

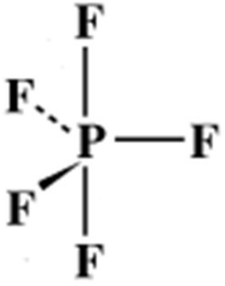
Electron-pair geometries and molecular shapes

Five electron pairs:

No lone pairs

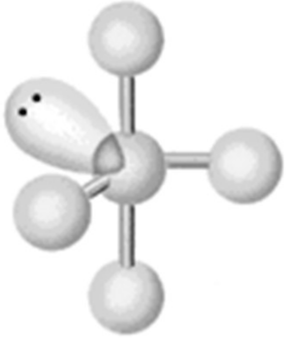


Triangular bipyramidal

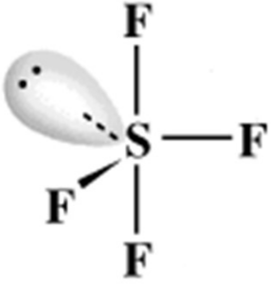


(5+5)/2=5

One lone pair

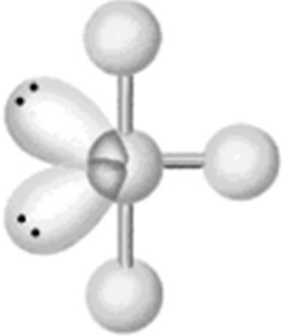


Seesaw

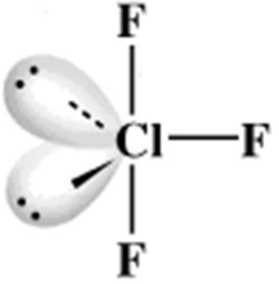


(6+4)/2=5

Two lone pairs

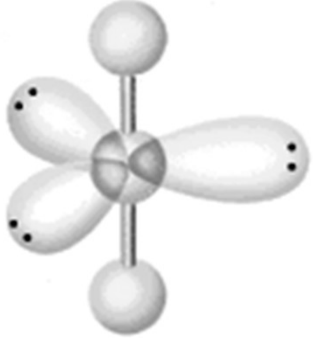


T shaped

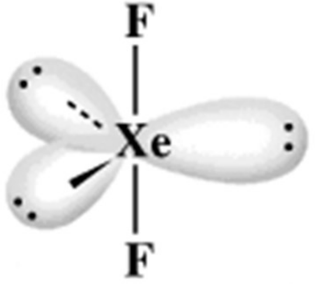


(7+3)/2=5

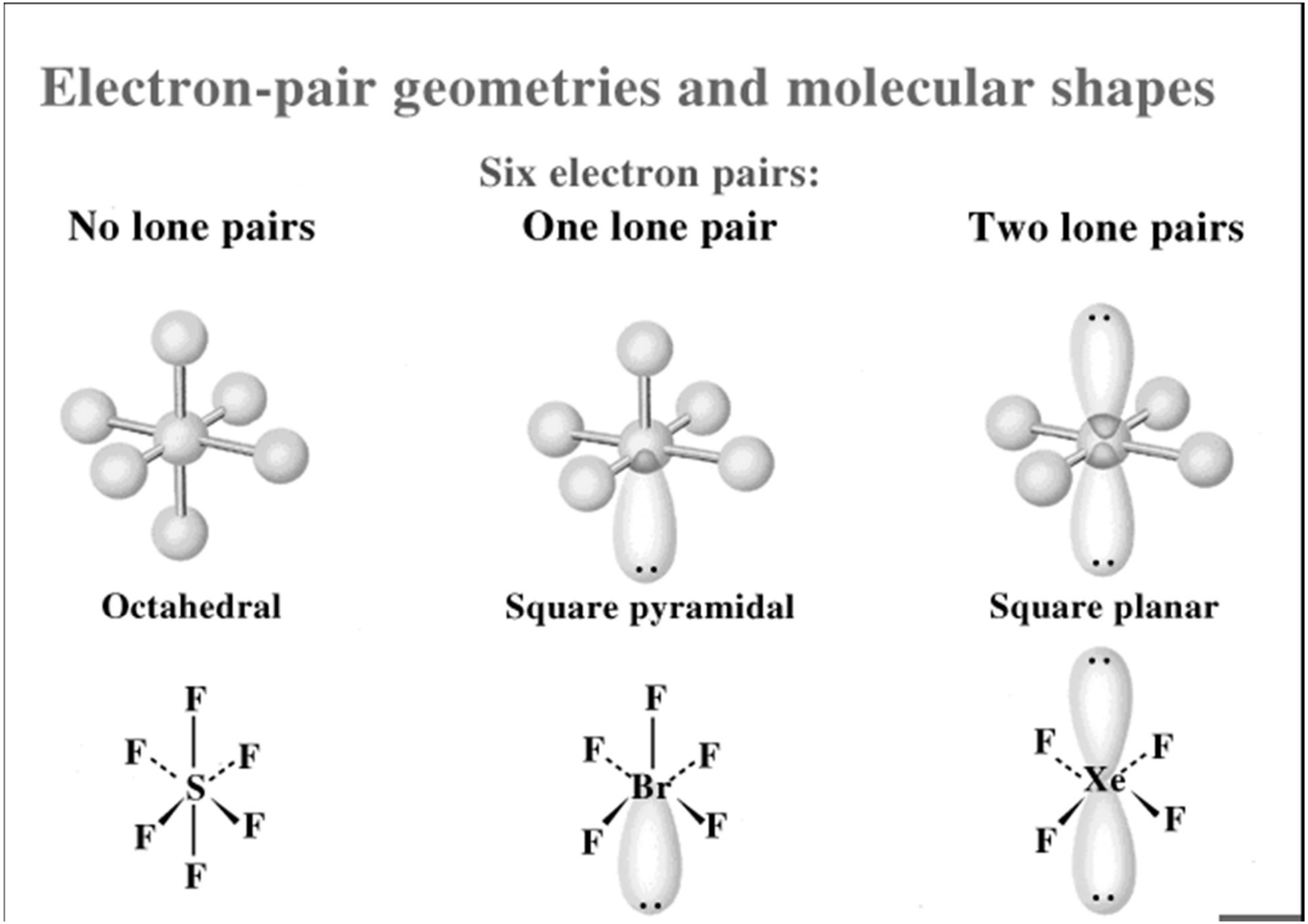
Three lone pairs



Linear



(8+2)/2=5



Electron-pair geometries and molecular shapes

Six electron pairs:

No lone pairs	One lone pair	Two lone pairs
Octahedral	Square pyramidal	Square planar

(6+6)/2

(7+5)/2=6

(8+4)/2=6

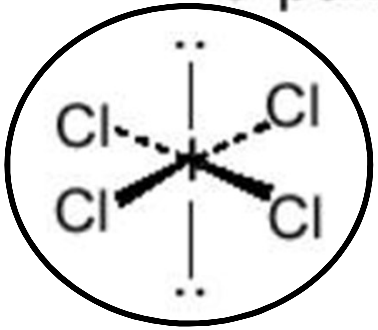
For such molecule as XeF_4, isomers exist!

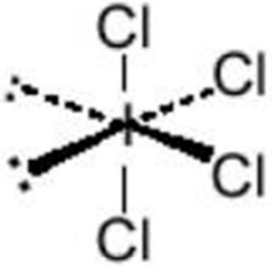
Repulsion of electron pairs

LP -LP > LP-BP > BP-BP

ICl_4^- AB_4e^2 6-pair case

possible structures:





	D_{4h}	C_{2v}
e/e	0	1
bp/e	8	6
bp/bp	4	5

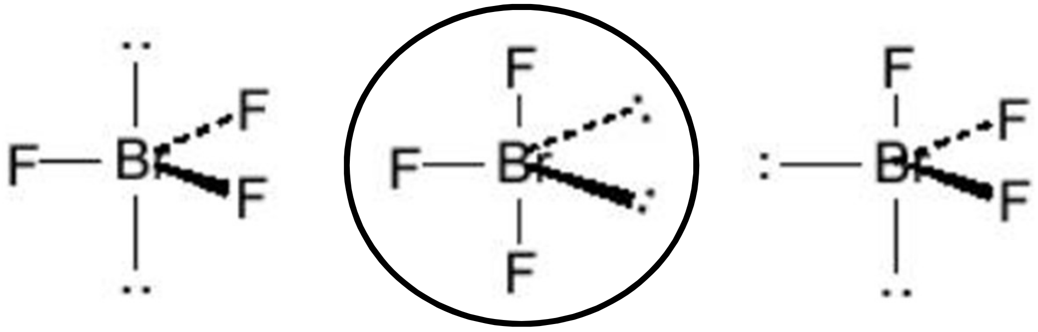
- **N(VEP) = (7 + 4 + 1)/2 = 6; N(BP) = 4; N(LP) = 2**
- **Simply considering the pairs with a bond angle ~ 90º!!!!!!!**
- **The first structure is preferred!**

Repulsion of electron pairs

BP-BP < BP-LP < LP-LP

BrF_3 AB_3e^2 5-pair case

possible structures:



	D_{3h}	C_{2v}	C_s
e/e	0	0	1
bp/e	6	4	3
bp/bp	0	2	2

- **N(VEP) = (7+3)/2 =5; N(BP) = 3; N(LP) = 2**
- **The second structure is preferred!**

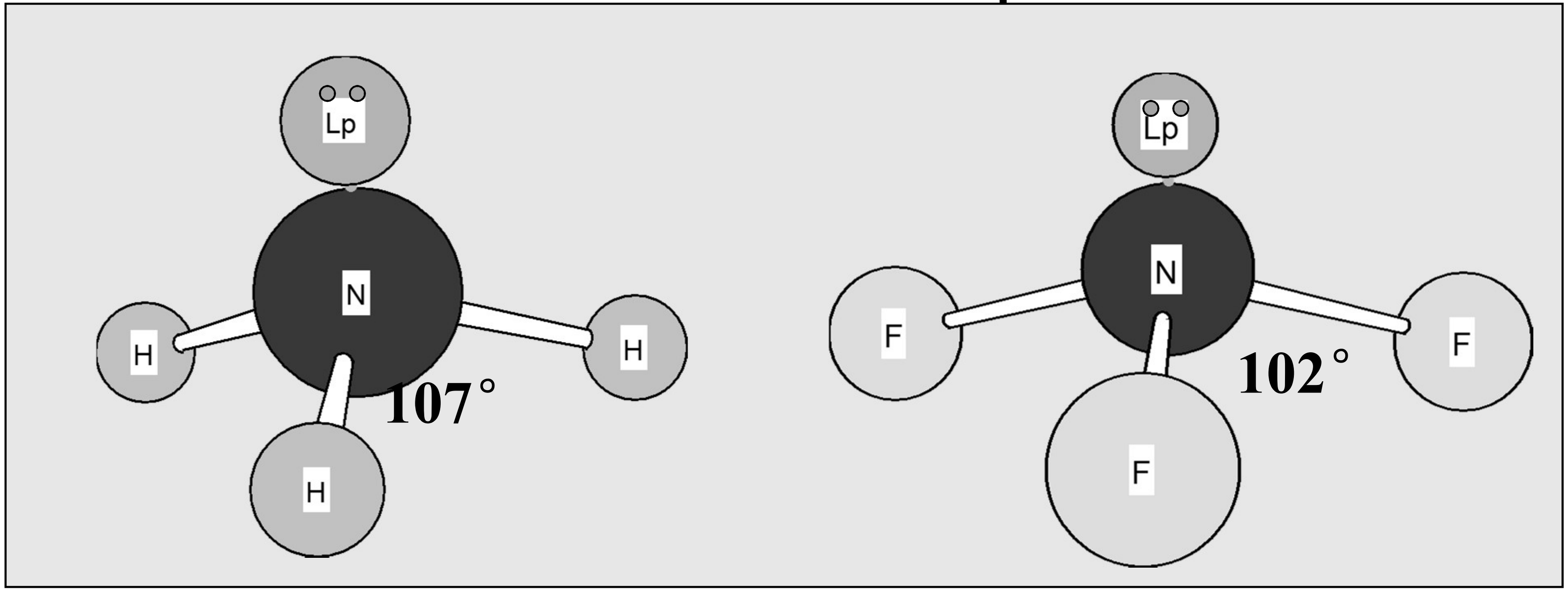
Molecular Stereochemistry

No. of pairs of e	formula	stereochemistry	point group
1	A_2, AB	none	$D_{\infty h}$ or $C_{\infty v}$
2	AB_2	linear	$D_{\infty h}$
3	AB_2e^1	bent	C_{2v}
3	AB_3	triangular	D_{3h}
4	AB_2e^2	bent	C_{2v}
4	AB_3e^1	pyramidal	C_{3v}
4	AB_4	tetrahedral	T_d

Molecular Stereochemistry

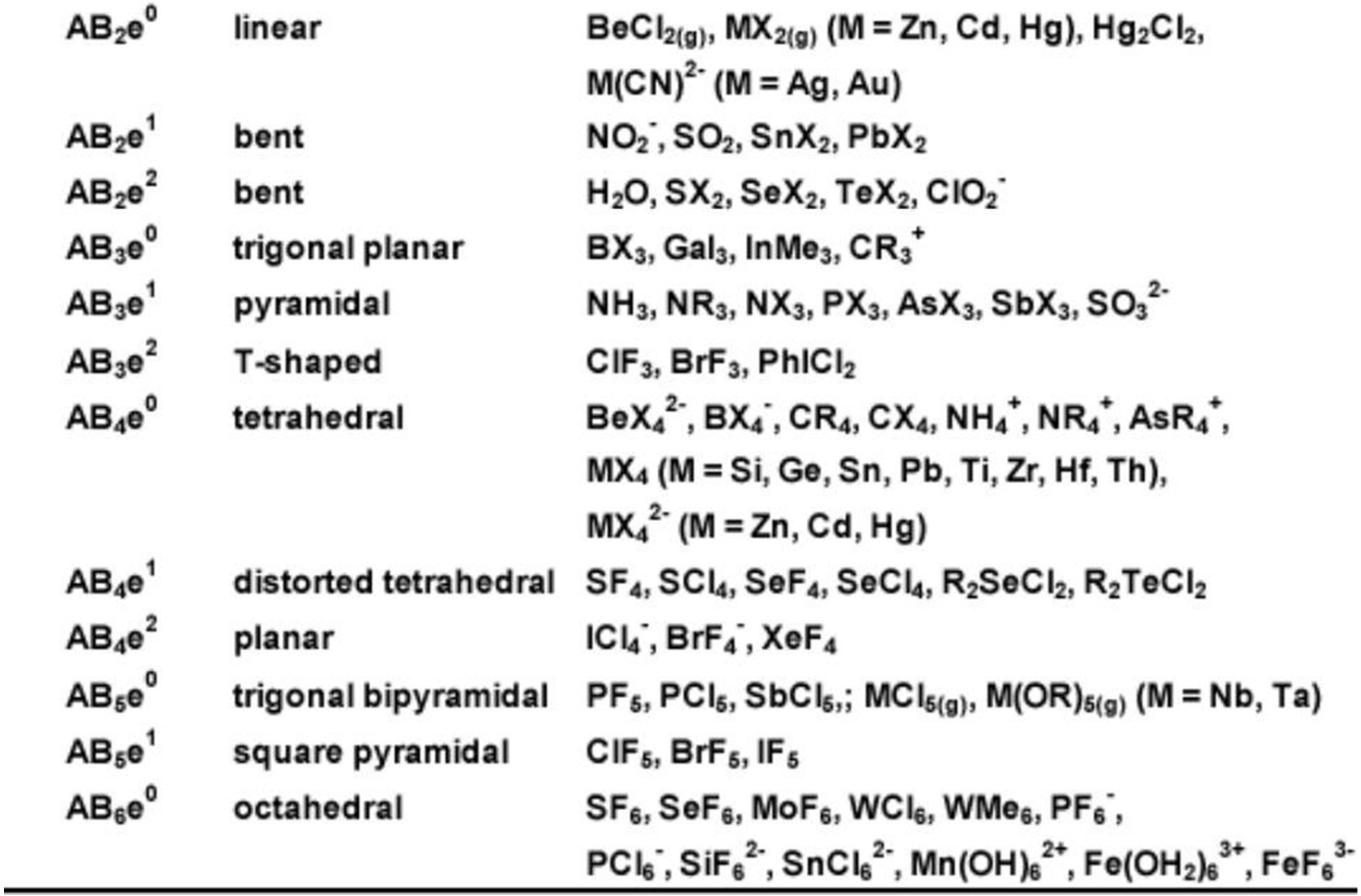
No. of pairs of e^-	formula	stereochemistry	point group
5	AB_2e^3	linear	$D_{\infty h}$
5	AB_3e^2	T-shaped	C_{2v}
5	AB_4e^1	distorted tetrahedron	C_{2v}
5	AB_5	trigonal bipyramid	D_{3h}
6	AB_4e^2	square planar	D_{4h}
6	AB_5e^1	square pyramid	C_{4v}
6	AB_6	octahedron	O_h

VSEPR Example



- **Bond angles decrease with increasing electronegativity of the ligand or decreasing electronegativity of the central atom.**
- **Why? The BP is more distant from the central atom upon increasing electronegativity of the ligand.**

AB_ne^m (n = coordination number; m = number of lone pairs)



AB_2e^0	linear	$BeCl_{2(g)}$, $MX_{2(g)}$ (M = Zn, Cd, Hg), Hg_2Cl_2, $M(CN)^{2-}$ (M = Ag, Au)
AB_2e^1	bent	NO_2^-, SO_2, SnX_2, PbX_2
AB_2e^2	bent	H_2O, SX_2, SeX_2, TeX_2, ClO_2^-
AB_3e^0	trigonal planar	BX_3, GaI_3, $InMe_3$, CR_3^+
AB_3e^1	pyramidal	NH_3, NR_3, NX_3, PX_3, AsX_3, SbX_3, SO_3^{2-}
AB_3e^2	T-shaped	ClF_3, BrF_3, $PhICl_2$
AB_4e^0	tetrahedral	BeX_4^{2-}, BX_4^-, CR_4, CX_4, NH_4^+, NR_4^+, AsR_4^+, MX_4 (M = Si, Ge, Sn, Pb, Ti, Zr, Hf, Th), MX_4^{2-} (M = Zn, Cd, Hg)
AB_4e^1	distorted tetrahedral	SF_4, SCl_4, SeF_4, $SeCl_4$, R_2SeCl_2, R_2TeCl_2
AB_4e^2	planar	ICl_4^-, BrF_4^-, XeF_4
AB_5e^0	trigonal bipyramidal	PF_5, PCl_5, $SbCl_5$,; $MCl_{5(g)}$, $M(OR)_{5(g)}$ (M = Nb, Ta)
AB_5e^1	square pyramidal	ClF_5, BrF_5, IF_5
AB_6e^0	octahedral	SF_6, SeF_6, MoF_6, WCl_6, WMe_6, PF_6^-, PCl_6^-, SiF_6^{2-}, $SnCl_6^{2-}$, $Mn(OH)_6^{2+}$, $Fe(OH_2)_6^{3+}$, FeF_6^{3-}

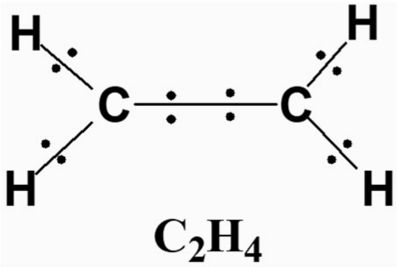
§ 5.3 Delocalized π-electrons/conjugation and Delocalized Molecular Orbital Theory

From the qualitative viewpoint, we can always consider separately the σ- and π-electrons within a molecule!

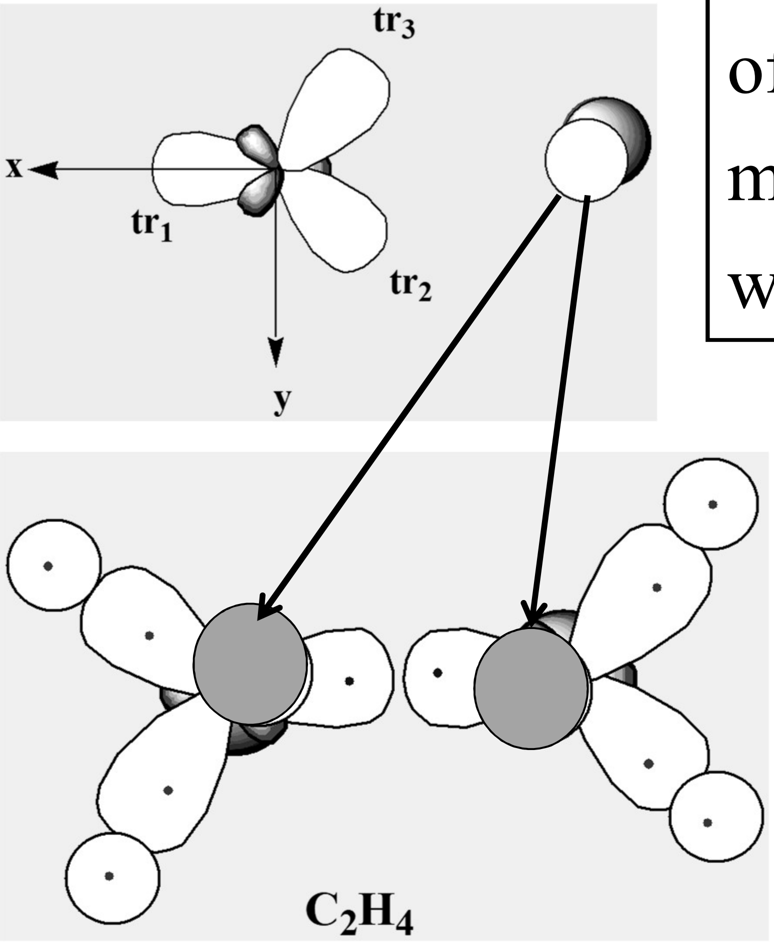
5.3.1 Normal π bond

i.e., two-center-two-electron π-bond (2c-2e)

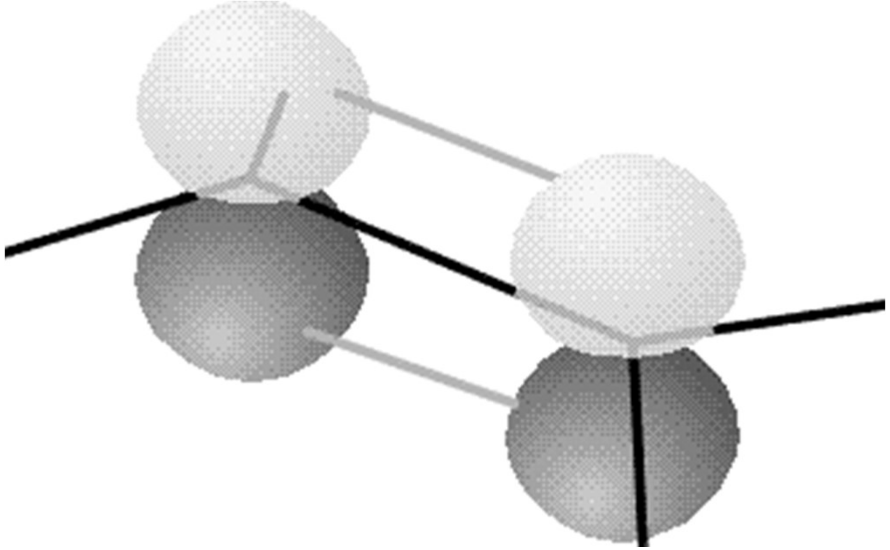
Except the σ-framework, the remaining, unhybridized *p* orbital of C atom is perpendicular to the molecular plane, forming a π bond with that of a neighboring C atom.



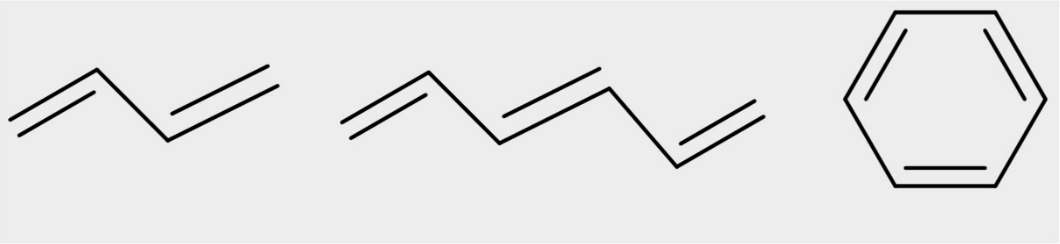
C_2H_4



C_2H_4

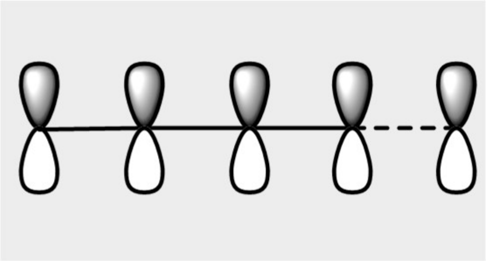


5.3.2 Delocalized π bond



Several 2c-2e π-bonds are continuously aligned !

→ **π-conjugation & formation of a delocalized π-bond**.



$$\Pi_n^m$$

***n*-orbital numbers,**

***m*-electron numbers (n>2)**

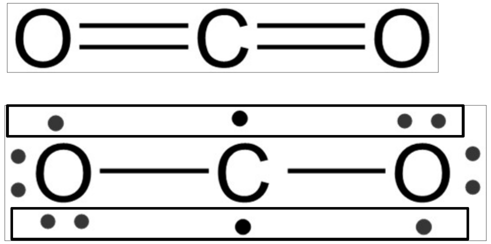
Conditions for the formation of a delocalized π bond:

- The atoms are coplanar, with every atom contributing a ***p***-orbital orientated in the same direction. (?exceptions)
- The number of *π* electrons is less than twice of the number of participating ***p***-orbitals.

Q: Can d-type AO′s be involved in a delocalized π-bond?

A. Some Inorganic conjugated molecules

i. Linear type (AB_2 16 valence electron) C: sp-hybridization + p_x + p_y



$$\pi \text{ electrons} : 16 - 4 - 4 = 8$$

$$2\Pi_3^4 : \quad \Pi_3^4(x) \quad \Pi_3^4(y)$$

3c-4e π-bond, Π_3^4

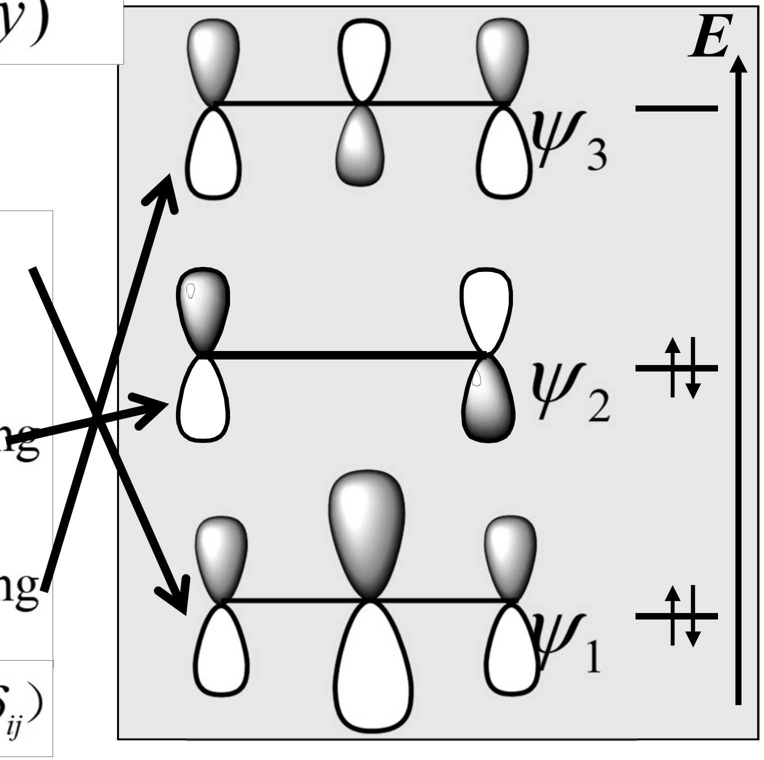
For Π_x or Π_y, we have three π-MOs,

$$\psi_1 = \frac{1}{\sqrt{2+\lambda^2}}[\phi_O(1) + \lambda\phi_C + \phi_O(2)] \quad \text{bonding}$$

$$\psi_2 = \frac{1}{\sqrt{2}}[\phi_O(1) - \phi_O(2)] \quad \text{non-bonding}$$

$$\psi_3 = \frac{1}{\sqrt{2+\lambda^2}}[\phi_O(1) - \lambda\phi_C + \phi_O(2)] \quad \text{anti-bonding}$$

$$(define \int \phi_i \phi_j = \delta_{ij})$$



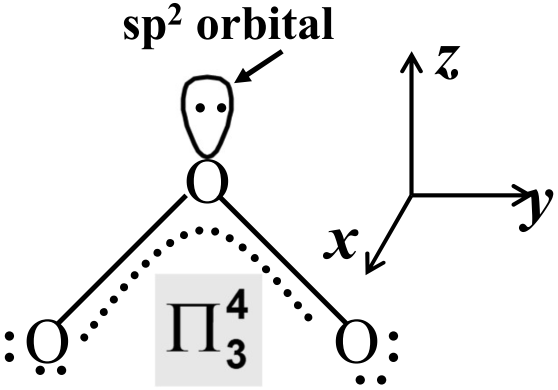
Isoelectronic analogy: NO_2^+, N_2O, N_3^-; COS; $BeCl_2$, $HgCl_2$

* NO_2^+ has two equivalent Π_3^4 bonds; NO_2 has just a Π_3^4 bond!

ii. Non linear type(bent) (17~19 valence electron)

e.g., O_3 (18 valence electrons)

Central atom O: sp^2 hybridization + $p_{\pi(x)}$



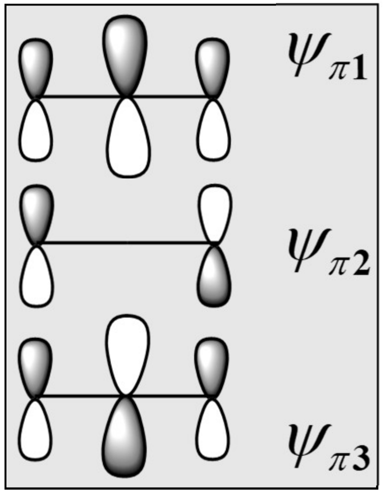
π **electrons : 18 - 6 - 8 = 4** Π_3^4

$\psi_{\pi 1} = \frac{1}{2}[\phi_1 + \sqrt{2}\phi_2 + \phi_3]$ bonding

$\psi_{\pi 2} = \frac{1}{\sqrt{2}}[\phi_1 - \phi_3]$ non - bonding(HOMO)

$\psi_{\pi 3} = \frac{1}{2}[\phi_1 - \sqrt{2}\phi_2 + \phi_3]$ anti - bonding(LUMO)

(define $\int \phi_i \phi_j = \delta_{ij}$)



Isoelectron analogy: SO_2

19 valence electrons: ClO_2

Π_3^4

$\boxed{\Pi_3^5}$

↑ **anti-bonding**

↑↓ **non-bonding**

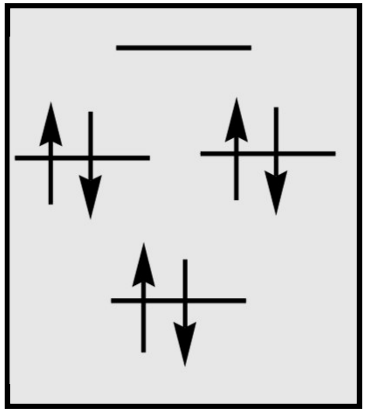
↑↓ **bonding**

iii. Equilateral triangular type: BCl_3 D_{3h}

24 valence electrons

Central atom B: sp^2 hybridization

$$\psi_\pi = c_1\varphi_B(1) + c_2\varphi_{Cl}(2) + c_3\varphi_{Cl}(3) + c_4\varphi_{Cl}(4)$$

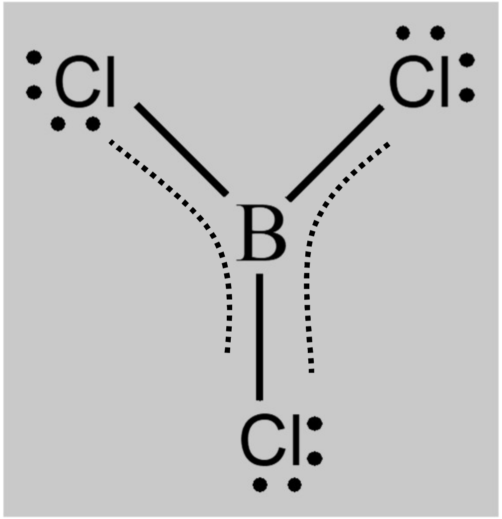


anti-bonding

non-bonding

bonding

24
-6
18
-12
6



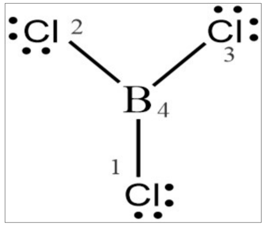
π electrons : Π_4^6

Isoelectronic analogy: AlF_3, NO_3^-, CO_3^{2-}, SO_3, Cl_2CO, $(H_2N)_2C{=}O$, $Cl_2C{=}S$

- For four-atom triangular type molecules, the p_π-orbitals form one bonding, two nonbonding and one antibonding orbitals, in general.
- For four-atom linear type molecules, the p_π-orbitals form two bonding and two antibonding orbitals!

After-class assignment:

Please construct the π-MOs of BCl_3 by using the p_π AOs.



3Cl p_π: $\{\phi_1, \phi_2, \phi_3\}$ *B* p_π : ϕ_4 *A;*

C_3	E	C_3	C_3^2		$\epsilon = e^{2\pi i/3}$
A	1	1	1	z, R_z	$x^2 + y^2, z^2$
E	$\left\{\begin{matrix}1 \\ 1\end{matrix}\right.$	$\begin{matrix}\epsilon \\ \epsilon^*\end{matrix}$	$\left.\begin{matrix}\epsilon^* \\ \epsilon\end{matrix}\right\}$	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (yz, xz)$
Γ_π	*3*	*0*	*0*	$\{3\ p_\pi\ Cl\}$	$\Gamma_\pi = A \oplus E$

$$\mathrm{SALC}^{\mathrm{A}} = \phi_1 + \phi_2 + \phi_3$$

$$\mathrm{SALC}_1^{E} = \phi_2 - \phi_3$$

$$\mathrm{SALC}_2^{E} = 2\phi_1 - \phi_2 - \phi_3$$

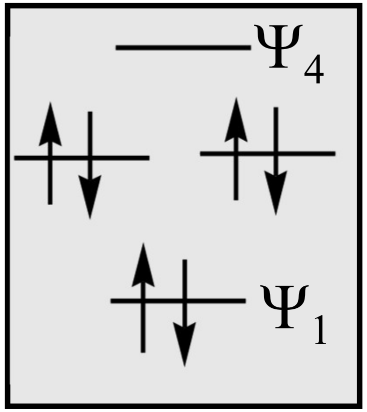
+ p_π(B)

$$\Psi_1^{\mathrm{A}} = \frac{1}{\sqrt{3+\lambda^2}}(\phi_1 + \phi_2 + \phi_3 + \lambda\phi_4)$$

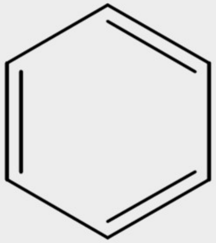
$$\Psi_4^{\mathrm{A}} = \frac{1}{\sqrt{3+\lambda^2}}(\phi_1 + \phi_2 + \phi_3 - \lambda\phi_4)$$

$$\Psi_2^{E} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

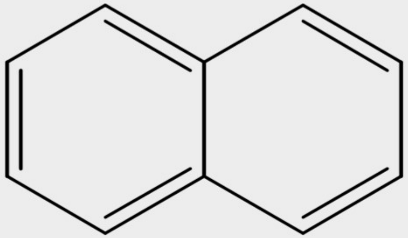
$$\Psi_3^{E} = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$$



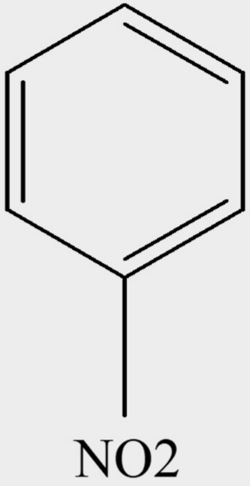
B. Some organic conjugated molecules



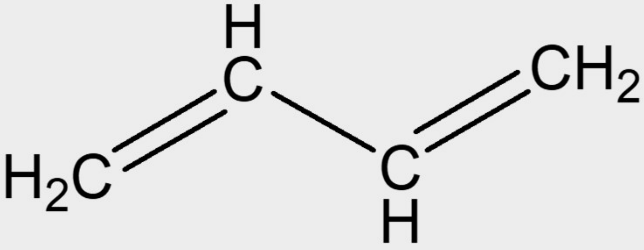
$$\Pi_6^6$$



$$\Pi_{10}^{10}$$



$$\Pi_9^{10} = \Pi_6^6 + \Pi_3^4$$



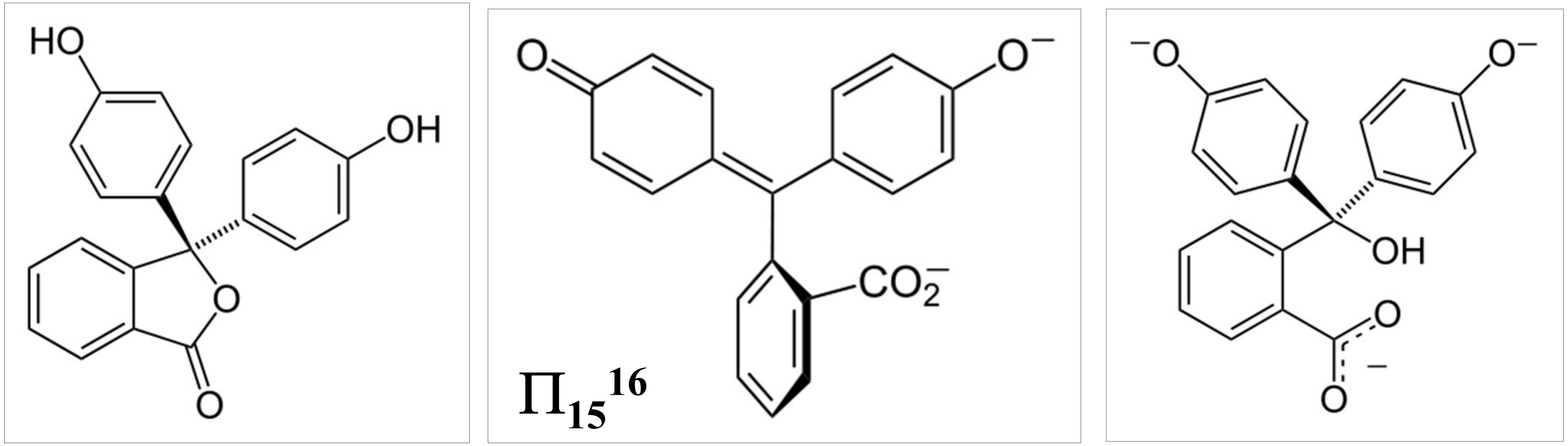
$$\Pi_4^4$$

5.3.3 The conjugation effects.

i. The electrical conductivity is enhanced by the delocalization of π bond, e.g., graphene.

ii. Color. The formation of delocalized π bonding increases the delocalized extent of the π electrons and causes the energy of the system to decrease.

Phenolphthalein - an indicator of basicity

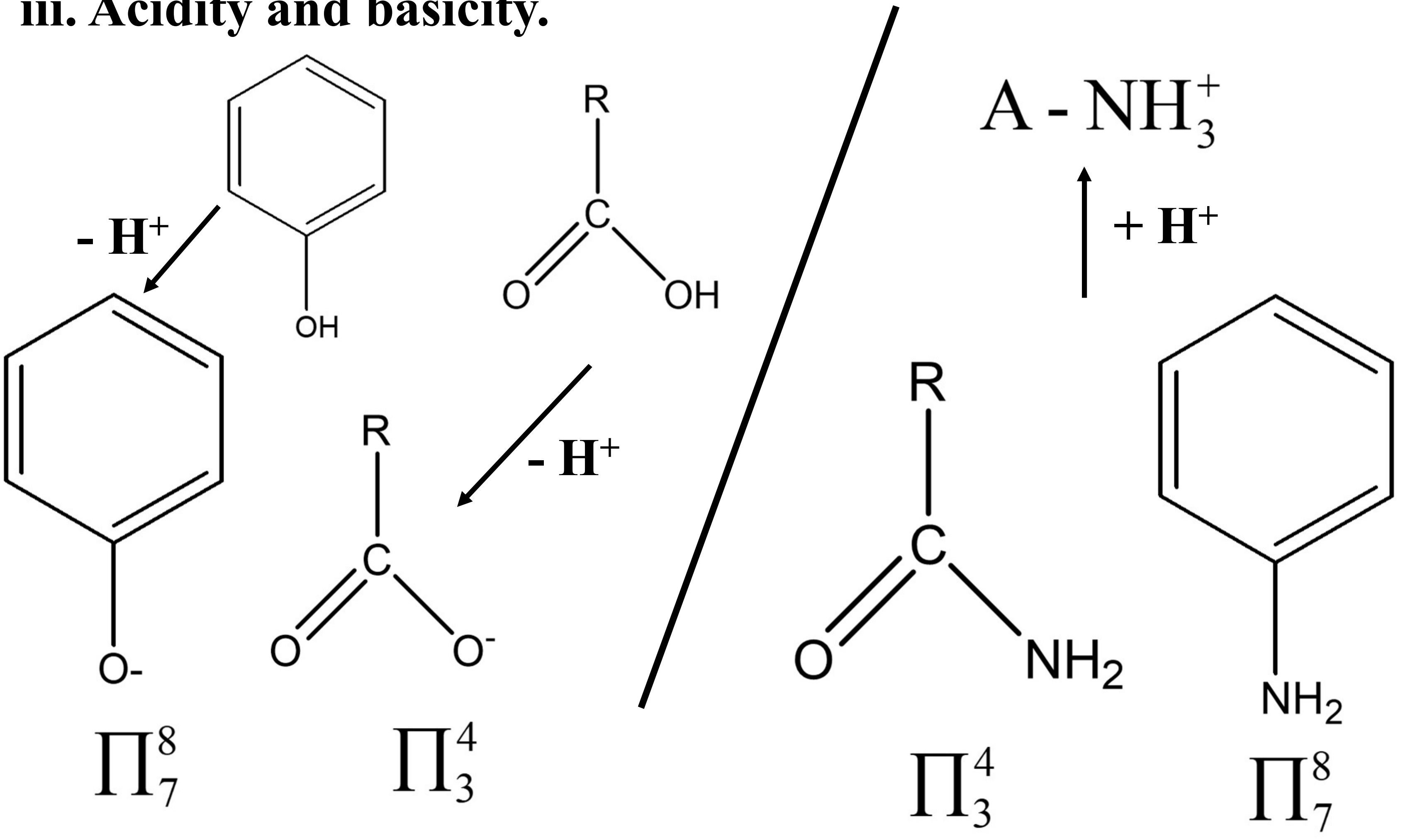


pH=0-8.2
colorless

pH=8.2-12.0
red

pH > 13.0
colorless

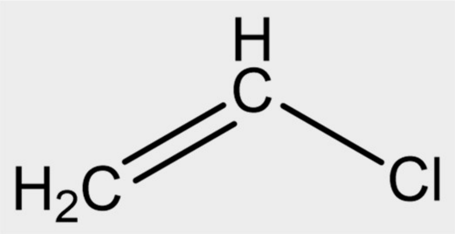
iii. Acidity and basicity.

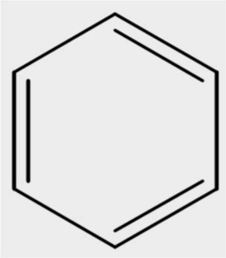


Electron delocalization: i) enhanced acidity of phenol and carboxylic acids; ii) weakened basicity of amides and aniline.

iv. Delocalization/conjugation effects on Chemical reactivity.

e.g. $H_2C=CH-Cl$. The formation of the Π_3^4-bond causes a contraction of the C-Cl bond, and reduces the lability of Cl.



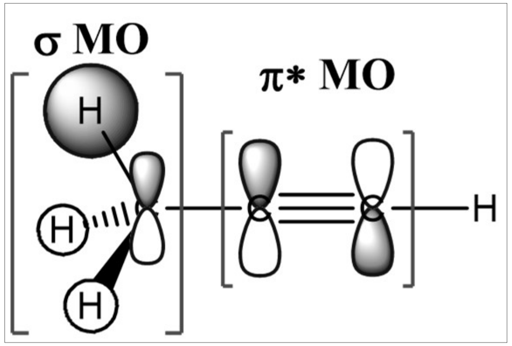


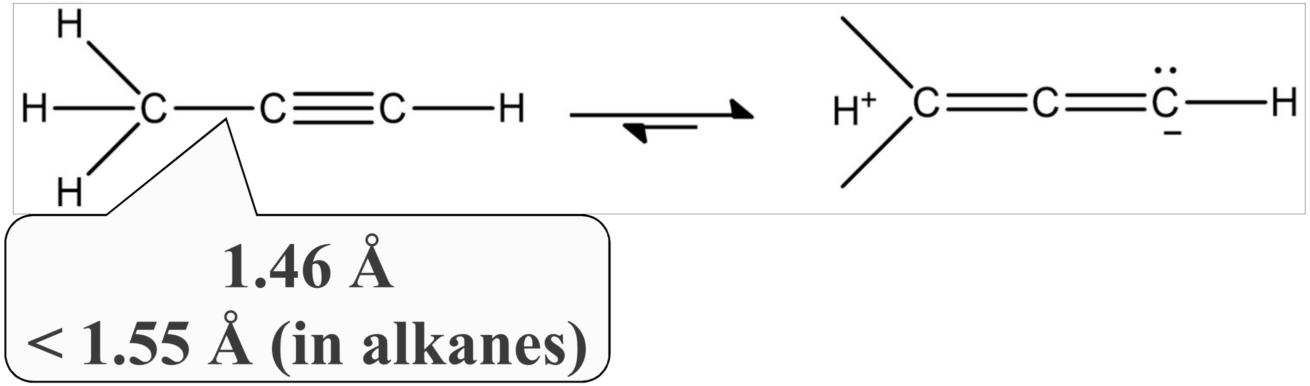
e.g. Benzene. The π-bond of Benzene exhibits much lower reactivity than that of simple alkenes.

5.3.4 Hyperconjugation.

- First introduced in 1939 by R.S. Mulliken.

- Hyperconjugation is ***the stabilizing interaction*** of the electrons in a ***σ-bond*** (usually C–H or C–C) with an adjacent empty (or partially filled) ***non-bonding p-orbital or antibonding π orbital***, which gives an extended molecular orbital that increases the stability of the system.





1.46 Å
< 1.55 Å (in alkanes)

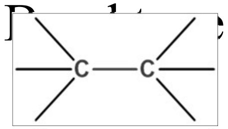
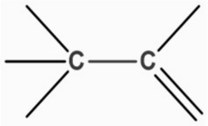
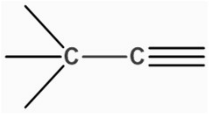
σ(C-H) --- π*(C≡C) > σ* (C-H) --- π (C≡C).

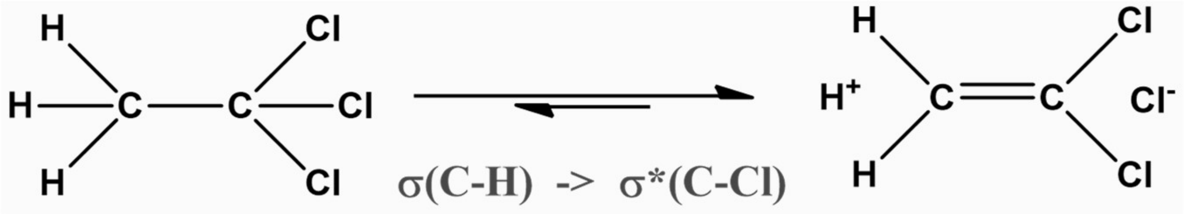
σ(C-H) --- π(C≡C)?

Effects of hyperconjugation on Chemical properties.

A. Bond length and bond energy:

σ-bond: Shortening of bond length and increasing of bond energy.

	Hybridization	C-C bond length (Å)	C-C bond energy(kJ.mol^{-1})
	**sp^3-sp^3**	**1.54**	**346.3**
	**sp^3-sp^2**	**1.51**	**357.6**
	**sp^3-sp**	**1.46**	**382.5**



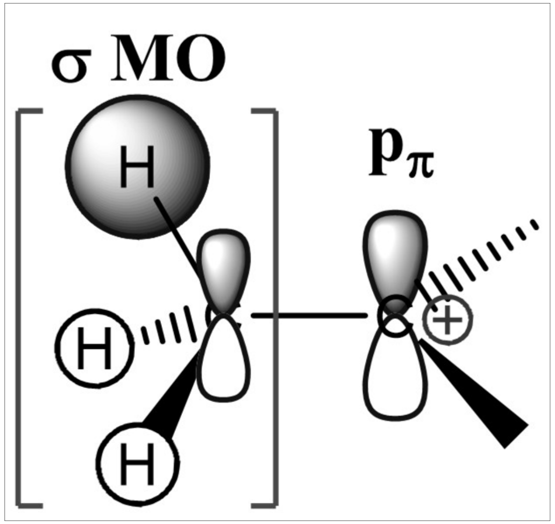
B. Dipole moment

The dipole moment of 1,1,1-trichloroethane with hyperconjugationis much larger than that of chloroform （$HCCl_3$).

C. Stabilizing carbocations:

Hyperconjugative interaction between the electron(s) in a bond that is β to the positively charged C can stabilize a carbocation.

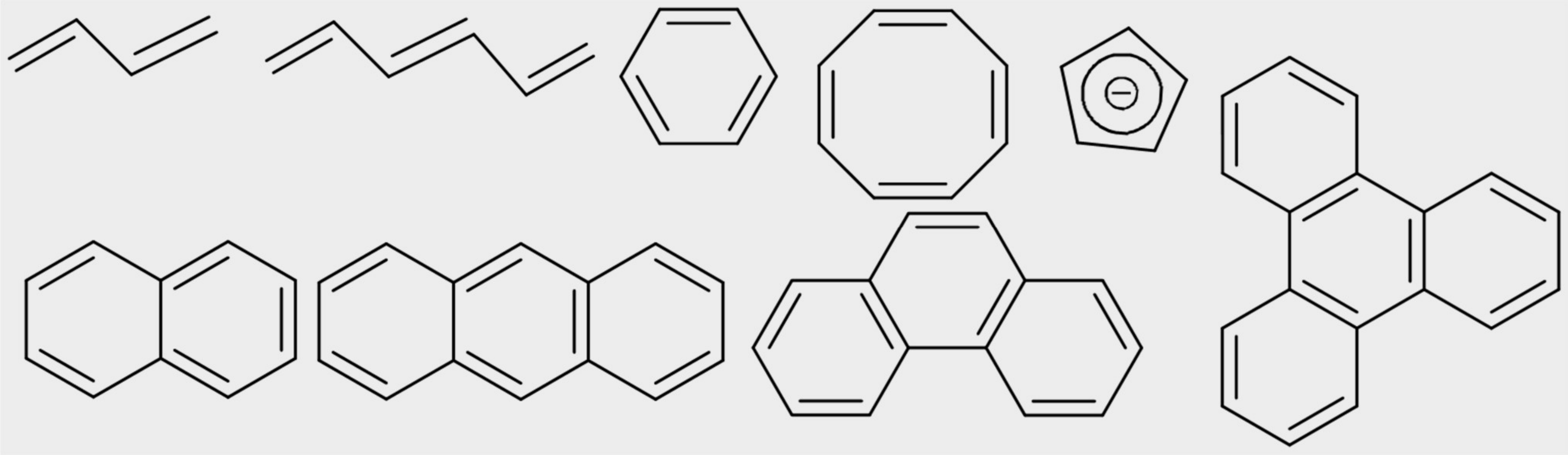
$\sigma(\text{C-H}) \rightarrow p_{\pi}(\text{C}^{+})$



Stability of carbocations:

$$(CH_3)_3C^+ > (CH_3)_2CH^+ > (CH_3)CH_2^+ > CH_3^+$$

§ 5.4 Hückel molecular orbital（HMO）theory and π-conjugation

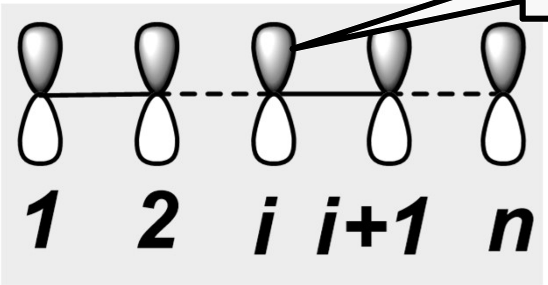


5.4.1 HMO method – A semiempirical treatment!

- Proposed in 1931 by Hückel to treat π-conjugation.
  - i) composition and energy of π-MO′s
  - ii) properties, stability, and even electronic spectra
- Modified in 1950s to treat σ-electrons/σ-MO′s -- **EHMO**

5.4.1 HMO method

π-type AO, ϕ_i



$$\Pi_n^m$$

(A ***n***-center ***m***-electron π-conjugation)

- **Single-particle approximation**: the total π-electron Hamiltonian for a Π_n^m system is approximated by the form,

$$\hat{H}_\pi = \sum_{j=1}^{m} \hat{h}_j^{eff}$$

(i.e., sum of one-electron effective Hamiltonians)

- The total wavefunction of the Π_n^m system can be expressed as,

$$\Psi_\pi = \prod_{j=1}^{m} \psi_j \quad \boxed{\& \quad \hat{\mathrm{H}}_\pi \Psi_\pi = E_\pi \Psi_\pi} \quad \Rightarrow \begin{cases} \hat{h}_j^{eff} \psi_j = \varepsilon_j \psi_j \\ E_\pi = \sum_j \varepsilon_j \end{cases}$$

$$\pi\text{ - MO}: \quad \psi_j = \sum_{i=1}^{n} c_i \phi_i$$

MO wavefunction of the *j*th π-electron

LCAO-MO

$$\hat{h}_j^{eff}\psi_j = \varepsilon_j\psi_j \quad (\psi_j = \sum_{i=1}^{n} c_i\phi_i \quad)$$

Suppose we have the form of ***h***

Suppose we have the form of $\boldsymbol{h^{eff}}$ ***!*** then use the variation theorem!

Variation integral $< \varepsilon >= \int \psi^* \hat{h}^{eff}\psi d\tau$ $let\ E =< \varepsilon >$

Then make $\dfrac{\partial E}{\partial c_1} = \dfrac{\partial E}{\partial c_2} = \text{......} = \dfrac{\partial E}{\partial c_n} = 0$

Variation Theorem-Minimization of E!

Thus we have ***n*** secular equations (in the matrix form),

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12}\ \dots & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22}\ \dots & \dots & H_{2n} - ES_{2n} \\ \text{......} & \text{......} & & \text{......} \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2}\ \dots & \dots & H_{nn} - ES_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \dots \\ 0 \end{pmatrix}$$

This demands the secular determinant to be zero, i.e.,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12}\ \dots & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22}\ \dots & \dots & H_{2n} - ES_{2n} \\ \text{......} & \text{......} & & \text{......} \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2}\ \dots & \dots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

Number of integrals:

H_{ij} ~ n(n+1)/2

S_{ij} ~ n(n+1)/2

Yet $\boldsymbol{h^{eff}}$ is unknown!

To solve it, Hückel further introduced the following approximations,

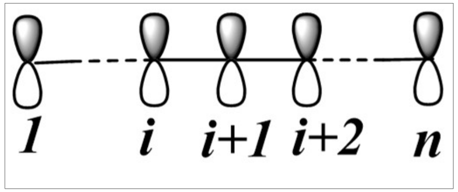
$$H_{ii} = \int \phi_i^* \hat{h} \phi_i d\tau = \alpha \ \textbf{(}\boldsymbol{e.g.,}\text{energy of } \pi \text{ - AO)}$$

$$H_{ij} = \int \phi_i^* \hat{h} \phi_j d\tau = \beta \ (\text{if } \mathrm{i} = \mathrm{j} \pm 1, \text{neighboring})$$

$$= 0 \ \ (\text{if } \ \mathrm{i} \neq \mathrm{j} \pm 1)$$

$$S_{ij} = \int \phi_i^* \phi_j d\tau = 1 \ \ (\mathrm{i} = \mathrm{j}\,, \text{the same atom})$$

$$= 0 \ \ (\mathrm{i} \neq \mathrm{j}, \text{different atom})$$



E.g., for a linear π-system,

$\boldsymbol{H_{11} = H_{22} = \dots = H_{nn} = \alpha}$

$\boldsymbol{S_{11} = \dots = S_{nn} = 1,}$

$\boldsymbol{\rightarrow H_{ii} - ES_{ii} = \alpha - E}$

$\boldsymbol{H_{i(i\pm1)} - ES_{i(i\pm1)} = \beta\,,}$

Its secular determinant thus becomes

$$\begin{vmatrix} \alpha - E & \beta & \dots & 0 & 0 \\ \beta & \alpha - E & \dots & 0 & 0 \\ 0 & \beta & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & & \beta & \alpha - E \end{vmatrix} = 0$$

Get {E_j} (*n* roots)

For each E_j, get {C_{ji}}

Now only need to know the α & β integrals, which can be determined semiempirically!

Semiempirical determination of the integrals:

$$H_{ii} = \int \phi_i^* \hat{h} \phi_i d\tau = \alpha$$

Coulombic integral ≈ energy of π-type AO! (e.g., C 2p AO)

$$H_{ij} = \int \phi_i^* \hat{h} \phi_j d\tau = \beta \quad (\text{if } i = j \pm 1)$$
$$= 0 \quad (\text{if } i \neq j \pm 1)$$

Resonance integral
(stabilization energy upon overlapping of two AO′s)

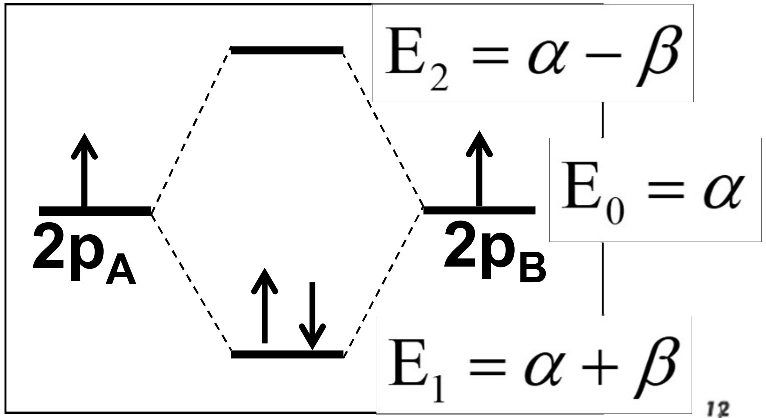
C_2H_4
(2c-2e π-MO, **i.e.,** a localized π-bond

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad \xrightarrow{x = (\alpha - E)/\beta} \quad \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

⇒ $x^2 - 1 = 0 \Rightarrow x = \pm 1 \Rightarrow E = \alpha \pm \beta$

⇒ $E_{\pi-bond} = 2E_1 - 2E_0 = 2\beta$

⇒ $\beta = E_{\pi-bond}/2$



$E_2 = \alpha - \beta$

$E_0 = \alpha$

$E_1 = \alpha + \beta$

The π-bond energy of ethene can be determined by UV-vis spectroscopy.

$$\Delta E = E_2 - E_1 = 2\beta = h\nu$$

5.4.2 The HMO treatment for the π-bonding within 1,3-butadiene

$H_2C=CH\text{-}CH=CH_2$

$$\psi_\pi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 \xrightarrow{\text{Variation theorem}}$$

Simplified secular equation by using Hückel approximations:

$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \longrightarrow$$

Seqular determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

HMO method

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

$$let\ x = \frac{\alpha - E}{\beta}, \quad E = \alpha\text{-}\beta x$$

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

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

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

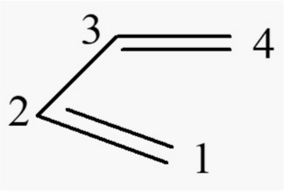
$$x^2\left(x^2 - 1\right) - x^2 - \left(x^2 - 1\right) = 0$$

$$x^4 - 3x^2 + 1 = 0$$

HMO method

$$\text{let } x = \frac{\alpha - E}{\beta}, \quad E = \alpha\text{-}x\beta$$

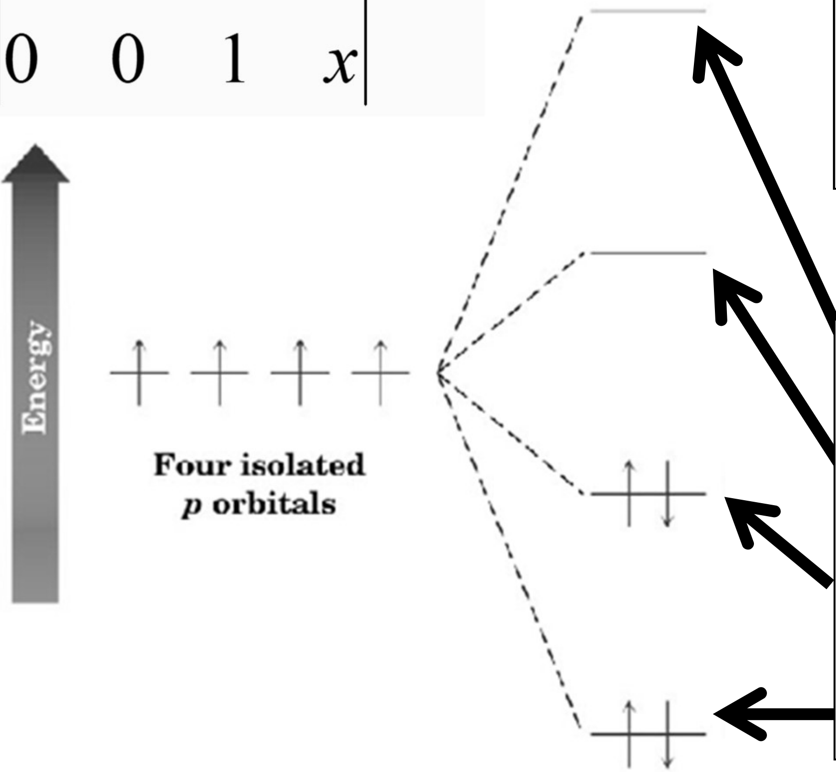
$H_2C{=}CH{-}CH{=}CH_2$



$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \Longrightarrow x^4 - 3x^2 + 1 = 0$$

$$\begin{cases} x^2 = 0.38 \Rightarrow \ x_{2,3} = \mp 0.618 \\ x^2 = 2.62 \Rightarrow \ x_{1,4} = \mp 1.618 \end{cases}$$

$\because E = \alpha\text{-}x\beta$ $(\alpha, \beta < 0)$



$E_4 = \alpha - 1.618\beta$	**Anti-bonding**
$E_3 = \alpha - 0.618\beta$	**Anti-bonding**
$E_2 = \alpha + 0.618\beta$	**Bonding**
$E_1 = \alpha + 1.618\beta$	**Bonding**

Now we can solve the secular equations to get the coefficients *{ci}*:

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \Rightarrow \begin{aligned} c_1 x + c_2 &= 0 \\ c_1 + c_2 x + c_3 &= 0 \\ c_2 + c_3 x + c_4 &= 0 \\ c_3 + c_4 x &= 0 \end{aligned}$$

normalization condition: $c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$

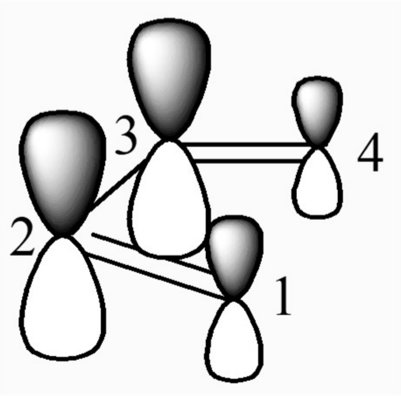
1) By substituting $x_1 = -1.618$, we get

$$c_1 = c_4 = 0.372, \quad c_2 = c_3 = 0.602$$

i.e., the π-MO is in the form

$$\psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$

with $E_1 = \alpha - x_1\beta = \alpha + 1.618\beta$



$$E_1 = \alpha + 1.618\beta$$
$$E_2 = \alpha + 0.618\beta$$
$$E_3 = \alpha - 0.618\beta$$
$$E_4 = \alpha - 1.618\beta$$

$$\psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$
$$\psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$
$$\psi_3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$
$$\psi_4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4$$

Antibonding MO
(three nodes)

— $E_4 = \alpha - 1.618\beta$

Antibonding MO
(two nodes)

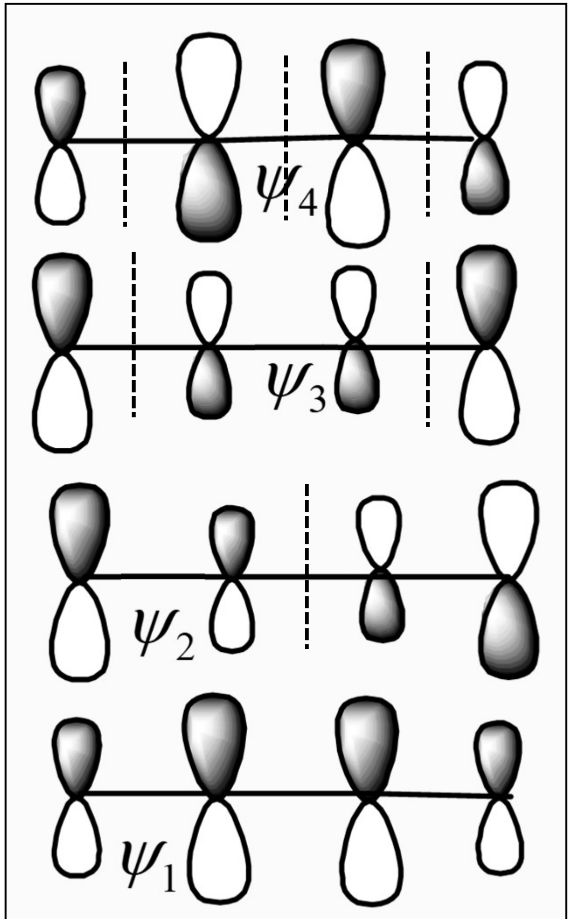
— $E_3 = \alpha - 0.618\beta$

Bonding MO
(One node)

⇅ $E_2 = \alpha + 0.618\beta$

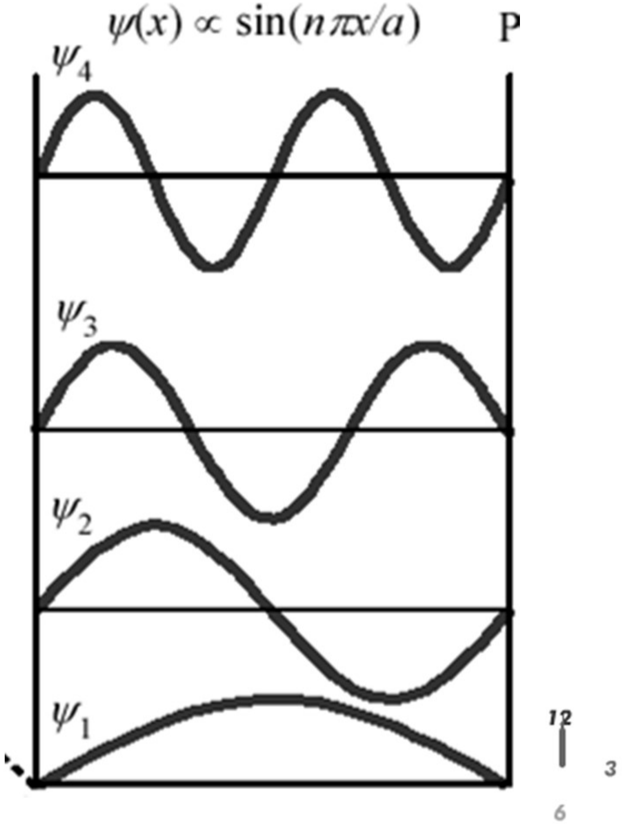
Bonding MO
(No node)

⇅ $E_1 = \alpha + 1.618\beta$



≅

1-D potential well!



Delocalized energy

Total π-electron energy in butadiene

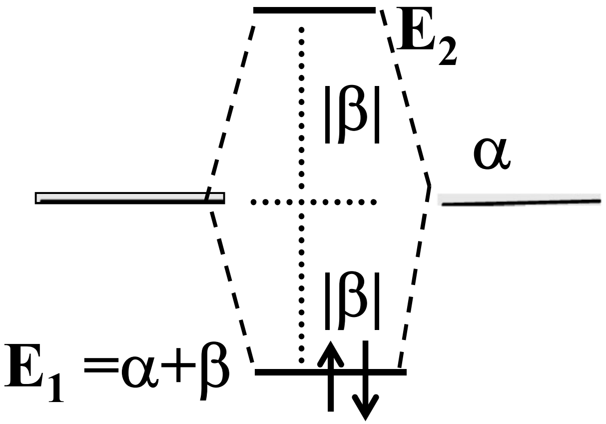
$$E_{\pi e}(C_4H_6) = 2E_1 + 2E_2 = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$

$$= 4\alpha + 4.48\beta$$

Total π-electron energy of two isolated C=C bonds (each akin a π-bond in C_2H_4)

$$E_{\pi e}(2C = C) = 2 \times 2(\alpha + \beta)$$

$$= 4\alpha + 4\beta$$



Thus, the delocalized energy or resonance energy is

$$\mathrm{E}_{\mathrm{deloc}} = E_{\pi e}(C_4H_6) - E_{\pi e}(2C = C) = 0.48\beta < 0$$

Electron delocalization (π-conjugation) enhances the stability!

After-class Problem

For 1,3-butadiene, the two occupied HMO′s (ψ_1 & ψ_2) are delocalized in nature and expressed as

$$\boxed{\begin{array}{ll}\psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 & E_1 = \alpha + 1.618\beta \\ \psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 & E_2 = \alpha + 0.618\beta\end{array}}$$

Let us consider the linear combinations of these two delocalized HMO′s, which can be expressed as

$$\boxed{\begin{array}{l}\Phi_1 = (\psi_1 + \psi_2)/\sqrt{2} = [0.974(\phi_1 + \phi_2) + 0.23(\phi_3 - \phi_4)]/\sqrt{2} \\ \Phi_2 = (\psi_1 - \psi_2)/\sqrt{2} = [0.23(\phi_2 - \phi_1) + 0.974(\phi_3 + \phi_4)]/\sqrt{2}\end{array}}$$

Please prove the two wavefunctions, Φ_1 and Φ_2, have equal energy. Please figure out what they represent.

- ***Is the C1=C2 bond stronger than a normal C=C bond?***

$CH_2CHCHCH_2 + H_2 \rightarrow CH_3CHCHCH_3 + \Delta H_1$

$CH_3CHCHCH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_3 + \Delta H_2$

Stable

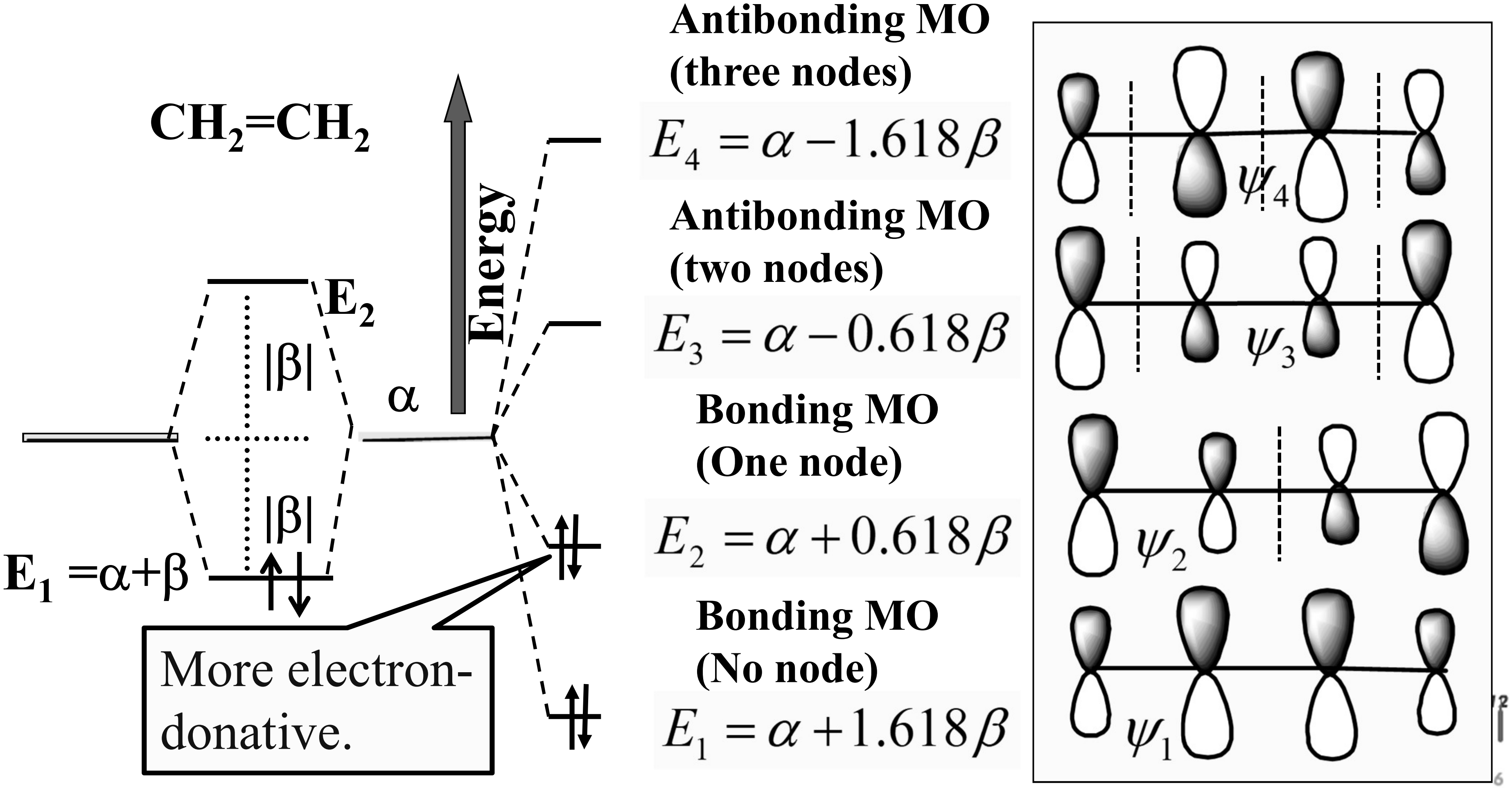
$\Delta H_2 < \Delta H_1 < 0$

$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$ (a)

$CH_2CHCHCH_2 + Br_2 \rightarrow CH_2BrCHCHCH_2Br$ (b)

Reactive!

$k_a < k_b$



Antibonding MO (three nodes)

$E_4 = \alpha - 1.618\beta$

Antibonding MO (two nodes)

$E_3 = \alpha - 0.618\beta$

Bonding MO (One node)

$E_2 = \alpha + 0.618\beta$

Bonding MO (No node)

$E_1 = \alpha + 1.618\beta$

More electron-donative.

5.4.3 Population analysis and molecular diagrams of conjugated system

i. Charge density --- the total π-electron density on the ***i***th atom

$$\rho_i = \sum_k n_k c_i^2(k)$$

The probability of an electron in the ***k***th MO to appear on the ***i***th atom

$\boldsymbol{n_k}$: number of electrons in the ***k***th MO.

$$\because \psi(k) = \sum_i c_i(k)\phi_i$$

→

$$1 = \int \psi^2(k)d\tau = \sum_i c_i^2(k)$$

→

The total π-electron density on the ***i***th atom is:

$$\rho_i = \sum_k n_k c_i^2(k)$$

- For 1,3-butadiene, the two doubly occupied MO′s are

$$\psi_{\pi 1} = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$
$$\psi_{\pi 2} = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$

→

$$\rho_1 = 2\times 0.372^2 + 2\times 0.602^2 = 1.000$$
$$\rho_2 = 2\times 0.602^2 + 2\times 0.372^2 = 1.000$$
$$\rho_3 = \rho_4 = 1.000$$

5.4.3 Population analysis and molecular diagrams of conjugated system

ii. Bond order --- the strength of the π-bond between atoms ***i*** and ***j***

$$p_{ij} = \sum_{k} n_k c_i(k) c_j(k)$$

Sum over all occupied MO′s.

n**_**k**_*: number of electrons in the ***kth occupied MO.

For 1,3-butadiene, the two occupied MO′s are

$$\begin{aligned}\psi_{\pi 1} &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\ \psi_{\pi 2} &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4\end{aligned}$$

$$\boxed{p_{12} = 2\times 0.372\times 0.602 + 2\times 0.602\times 0.372 = 0.896 = p_{34}}$$

$$\boxed{p_{23} = 2\times 0.602^2 - 2\times 0.372^2 = 0.448}$$

$$\therefore p_{12} = p_{34} = 2p_{23}$$

- The π-bond order of C1=C2 or C3=C4 is twice of the C2-C3 π-bond order.

iii. Free valence index --- the relative magnitude of the residue bonding ability of the ith atom

$$F_i = P_{max} - \sum_{j=i\pm1} P_{ij}; \qquad P_{max} = \sqrt{3}$$

$$F_1 = \sqrt{3} - P_{12} = \sqrt{3} - 0.896 = 0.836 = F_4$$

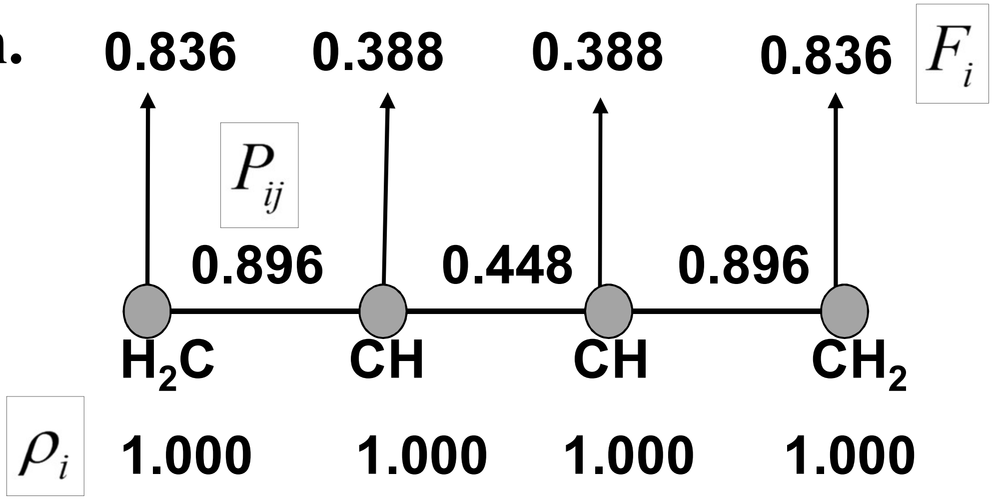
$$F_2 = \sqrt{3} - P_{12} - P_{23} = \sqrt{3} - 0.448 - 0.896 = 0.388 = F_3$$

In butadiene, the 1,4-sites are more reactive than the 2,3-sites!

Example: 1,4 addition reaction of butadiene

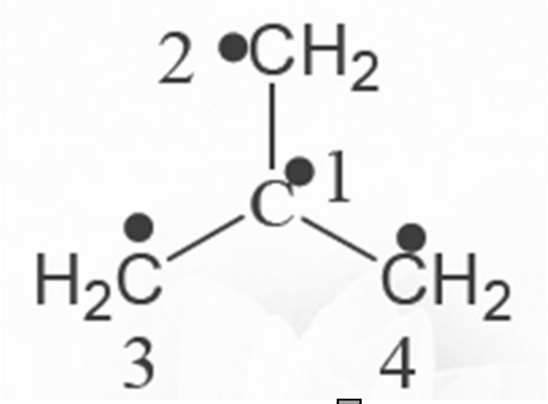
$H_2C{=}CH{-}CH{=}CH_2 + Br_2 \rightarrow BrH_2C{-}CH{=}CH{-}CH_2Br$

iv. Molecular diagram.



Another example:

Please derive the secular determinant of trimethylenemethane.



π-MO

$$\psi = \sum_i c_i \phi_i$$

Variation theorem

$$\begin{pmatrix} \alpha - E & \beta & \boxed{\beta} & \boxed{\beta} \\ \beta & \alpha - E & 0 & 0 \\ \boxed{\beta} & 0 & \alpha - E & 0 \\ \boxed{\beta} & 0 & 0 & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

Then the secular determinant is

$$\begin{vmatrix} \alpha - E & \beta & \beta & \beta \\ \beta & \alpha - E & 0 & 0 \\ \beta & 0 & \alpha - E & 0 \\ \beta & 0 & 0 & \alpha - E \end{vmatrix} = 0$$

$$x = \frac{(\alpha - E)}{\beta}$$

$$\begin{vmatrix} x & 1 & 1 & 1 \\ 1 & x & 0 & 0 \\ 1 & 0 & x & 0 \\ 1 & 0 & 0 & x \end{vmatrix} = 0$$

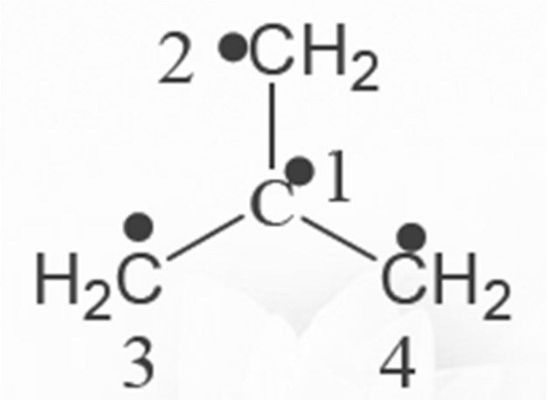
$$x^2(x^2 - 3) = 0 \Rightarrow x_{1,4} = \pm\sqrt{3}, x_{2,3} = 0$$

After-class assignment

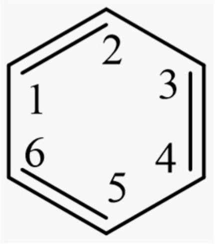
- Please construct the π-MOs of trimethylenemethane by using symmetry and then quickly obtain the eigenvalue of each π-MO as well as the C-C π-bond order by using the HMO approximation !

C1 : ϕ_1 A; ***C2-4: {ϕ_2, ϕ_3, ϕ_4}***

C_3	E	C_3	C_3^2		$\epsilon = e^{2\pi i/3}$
A	1	1	1	z, R_z	$x^2 + y^2, z^2$
E	1	ϵ	ϵ^*	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (yz, xz)$
	1	ϵ^*	ϵ		



5.4.4 HMO treatments of cyclic conjugated polyenes (C_nH_n)
e.g., π-conjugation in Benzene



$$\psi = \sum_{i=1}^{6} c_i \phi_i$$

Variation Theorem

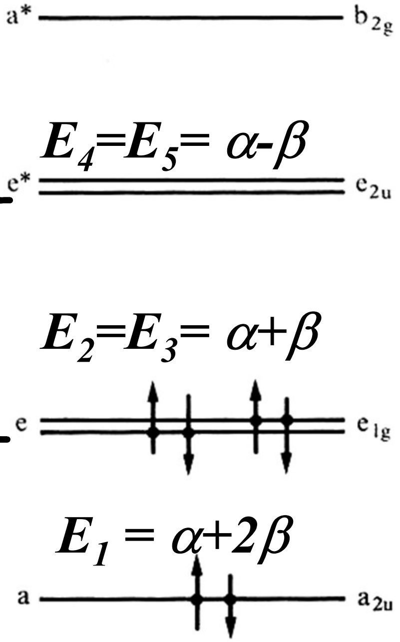
$$\begin{pmatrix} \alpha-E & \beta & 0 & 0 & 0 & \boxed{\beta} \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \boxed{\beta} & 0 & 0 & 0 & \beta & \alpha-E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix} = 0$$

$$\psi_6(b_{2g}) = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

$$\left.\begin{aligned} \psi_5(e_{2u}) &= \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6) \\ \psi_4(e_{2u}) &= \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) \end{aligned}\right\}$$

$$\left.\begin{aligned} \psi_3(e_{1g}) &= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6) \\ \psi_2(e_{1g}) &= \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) \end{aligned}\right\}$$

$$\psi_1(a_{2u}) = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

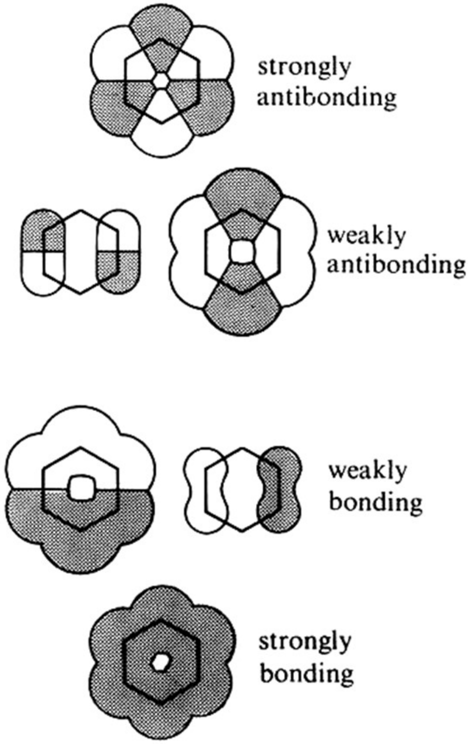


$E_6 = \alpha - 2\beta$

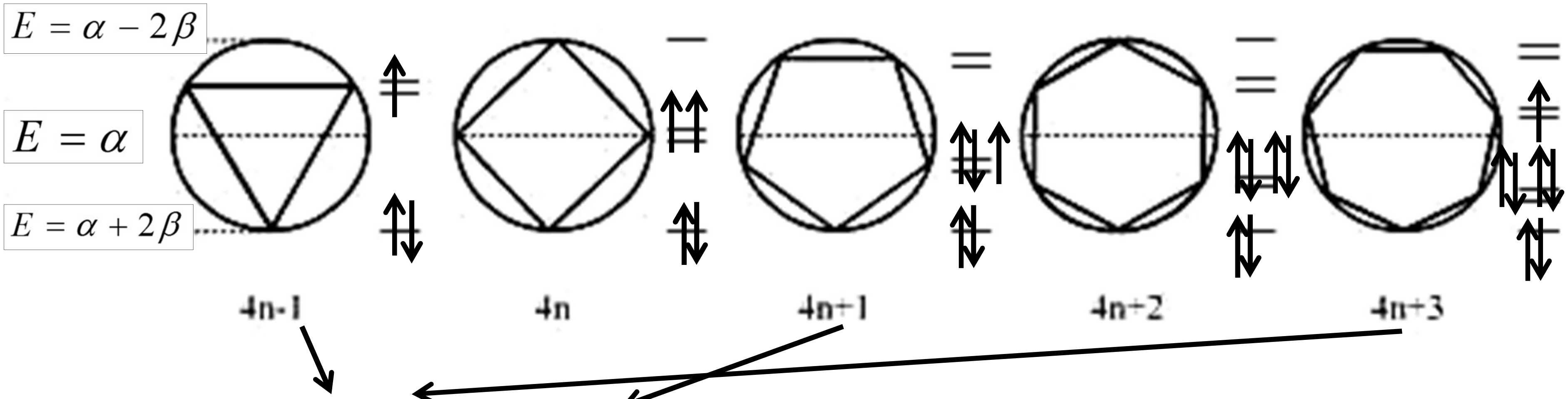
$E_4 = E_5 = \alpha - \beta$

$E_2 = E_3 = \alpha + \beta$

$E_1 = \alpha + 2\beta$



General HMO solutions for cyclic conjugated polyenes (C_nH_n)



- When *n=4m+1* or *4m+3*, the system has a singly occupied HOMO, being radicaloid.

- When *n=4m*, the system has two degenerate singly-occupied HOMOs (non-bonding), thus being diradicaloid.

- Only when *n= 4m+2* can a cyclically conjugated system has fully occupied HOMOs and be chemically stable. (fulfilling the Hückel rule of aromaticity!)

§ 5.5 Graphical method to predefine the coefficients of HMOs for conjugated systems

Background

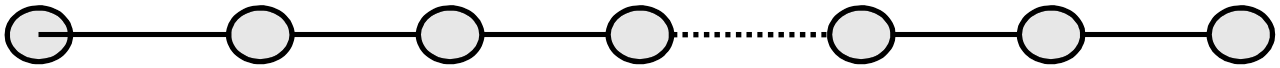
- The AO coefficients of HMO′s for π-conjugated organic systems correlate with their geometries, displaying "***quasi-periodicity***".

  e.g., 1,3-butadiene

$$\begin{aligned}
\psi_1 &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\
\psi_2 &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 \\
\psi_3 &= 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 \\
\psi_4 &= 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4
\end{aligned}$$

- Accordingly, a graphical method was developed by ***Q.E. Zhang*** et al. to predefine the AO coefficients of HMOs for such type of systems.

5.5.1 Principle for linear conjugated [n]polyenes.



$$\psi_\pi = \sum_{i=1}^{n} C_i \phi_i$$

For a linear [n]polyene, we have ***n*** secular equations:

$$C_1(\alpha-E) + C_2\beta=0; \qquad C_1\beta + C_2(\alpha-E) + C_3\beta = 0$$

$$C_2\beta + C_3(\alpha-E) + C_4\beta = 0; \qquad \ldots\ldots$$

$$C_{k-1}\beta + C_k(\alpha-E) + C_{k+1}\beta = 0\ ; \quad \ldots\ldots; \quad C_{n-1}\beta + C_n(\alpha-E) = 0$$

Or in the matrix form,

$$\begin{pmatrix} \alpha-E & \beta & \ldots & 0 & 0 \\ \beta & \alpha-E & \ldots & 0 & 0 \\ 0 & \beta & \ldots & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & \ldots & \beta & \alpha-E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \\ C_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

Define $x = (\alpha - E)/\beta$

$$\sin\alpha_1 + \sin\alpha_2 = 2\sin\frac{\alpha_1+\alpha_2}{2}\cos\frac{\alpha_1-\alpha_2}{2}$$

$$C_2 = -xC_1 + 0$$

$$C_3 = -xC_2 - C_1$$

$$C_4 = -xC_3 - C_2$$

……

$$C_{k+1} = -xC_k - C_{k-1}$$

……

$$C_n = -xC_{n-1} - C_{n-2}$$

$$0 = -xC_n - C_{n-1}$$

$$C_{k+1} + C_{k-1} = -xC_k$$

(cyclic formula)

Now define

$$x = -2\cos\theta$$

$$C_k = \sin k\theta$$

$$C_{k+1} + C_{k-1} = 2\cos\theta C_k$$

naturally with

$$C_{k-1} = \sin(k-1)\theta$$

$$C_{k+1} = \sin(k+1)\theta$$

$$C_1 = \sin\theta$$

$$C_2 = 2\cos\theta C_1 = \sin 2\theta$$

$$C_3 = 2\cos\theta C_2 - C_1 = \sin 3\theta$$

$$C_4 = 2\cos\theta C_3 - C_2 = \sin 4\theta$$

……

$$C_{k+1} = \sin(k+1)\theta$$

……

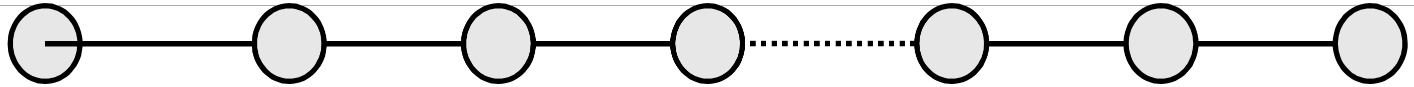
$$C_n = \sin n\theta$$

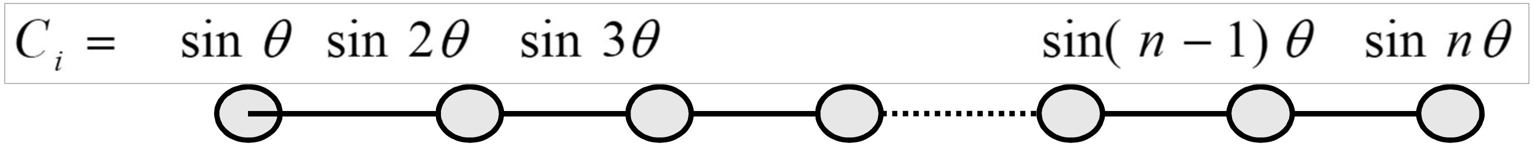
$$C_{n+1} = \sin(n+1)\theta = 0$$

Boundary Condition!

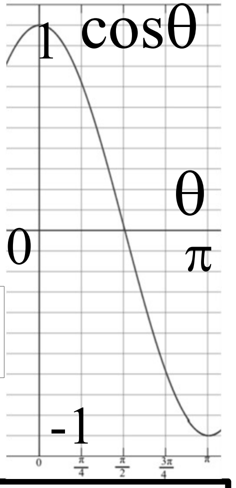
Now we get θ, and then $E=\alpha+2\beta\cos\theta$ and $\{C_k\}$ simultaneously!

C_i $\sin\theta$ $\sin 2\theta$ $\sin 3\theta$ $\sin(n-1)\theta$ $\sin n\theta$





$C_i = \quad \sin\theta \quad \sin 2\theta \quad \sin 3\theta \quad \cdots \quad \sin(n-1)\theta \quad \sin n\theta$



Boundary condition: $\boldsymbol{sin(}n+1\boldsymbol{)}\theta = 0 \;\; \& \;\; \boldsymbol{sin}\, n\theta \neq 0$

$\therefore \boldsymbol{(}n+1\boldsymbol{)}\theta = m\pi$ $\Rightarrow \theta = m\pi/\boldsymbol{(}n+1\boldsymbol{)} < \pi \quad (m = 1,2,3,\ldots,\mathrm{n})$

$$\therefore \; E_m = \alpha + 2\beta\cos\frac{m\pi}{n+1} \qquad (\mathrm{m} = 1,2,3,\ldots,\mathrm{n})$$

Higher ***m***, higher ***E***.

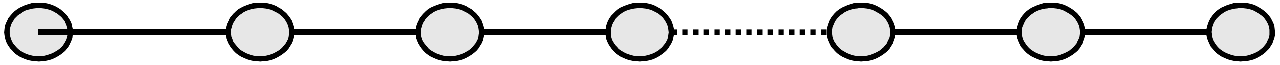
$$\psi_m = A\sum_{k=1}^{n}\phi_k sin(\frac{km\pi}{n+1}) = \sqrt{\frac{2}{n+1}}\sum_{k=1}^{n}\phi_k sin\boldsymbol{(}\frac{km\pi}{n+1}) \quad (\mathrm{m} = 1,2,3,\ldots,\mathrm{n})$$

Normalization coefficient

- For linear [***n***]polyenes with ***n***=***even***， there are ***n/2*** bonding π-MO′s and ***n/2*** antibonding π-MO′s.

- For linear [***n***]polyenes with ***n***=***odd***， there are ***(n-1)/2*** bonding π-MO′s, ***(n-1)/2*** antibonding π-MO′s and **a non-bonding** π-MO.

Frontier MO′s of [n]polyene: C_nH_{n+2}

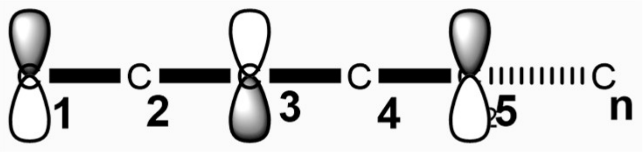


$$E_m = \alpha + 2\beta\cos\frac{m\pi}{n+1}, \quad \psi_m = \sqrt{\frac{2}{n+1}}\sum_{k=1}^{n}\phi_k sin(\frac{km\pi}{n+1}) \quad (\mathrm{m} = 1,2,3,\ldots,\mathrm{n})$$

---

a) When *n=odd*, SOMO, *m = (n+1)/2*, $\theta_{SOMO} = \pi/2, \quad E_{SOMO} = \alpha$

$\psi_{SOMO} = A(\phi_1 - \phi_3 + \phi_5 - \ldots)$ Non-bonding!



b) When *n=even*, HOMO, *m= n/2*; LUMO, *m=(n+2)/2*.

$$\theta_{HOMO} = \frac{n\pi}{2(\mathrm{n}+1)} = \frac{\pi}{2} - \frac{\pi}{2(n+1)}$$

$$\theta_{LUMO} = \frac{(n+2)\pi}{2(n+1)} = \frac{\pi}{2} + \frac{\pi}{2(n+1)}$$

Coefficients of AO’s:	**HOMO**	**LUMO**
n = 4l+2:	$C_n = C_1, \quad C_{n-1} = C_2, \ldots$	$C_n = -C_1, C_{n-1} = -C_2, \ldots$
n = 4l:	$C_n = -C_1, C_{n-1} = -C_2, \ldots$	$C_n = C_1, \quad C_{n-1} = C_2, \ldots$

Example: butadiene (n=4)

$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \quad \sin 4\theta$

$$\pi - MOs: \qquad \psi = A\sum_{i=1}^{4} c_i\phi_i$$

$$\because \sin 5\theta = 0 \;\&\; \sin\theta \neq 0, \qquad \therefore \theta = m\pi/5 \quad (m = 1,2,3,4)$$

m	1	2	3	4
θ	$\pi/5$	$2\pi/5$	$3\pi/5$	$4\pi/5$
$2\cos\theta$	1.618	0.618	-0.618	-1.618
E	$\alpha + 1.618\beta$	$\alpha + 0.618\beta$	$\alpha - 0.618\beta$	$\alpha - 1.618\beta$

$$\psi_m = \sqrt{\frac{2}{5}}\left(\sin\frac{m\pi}{5}\phi_1 + \sin\frac{2m\pi}{5}\phi_2 + \sin\frac{3m\pi}{5}\phi_3 + \sin\frac{4m\pi}{5}\phi_4\right)$$

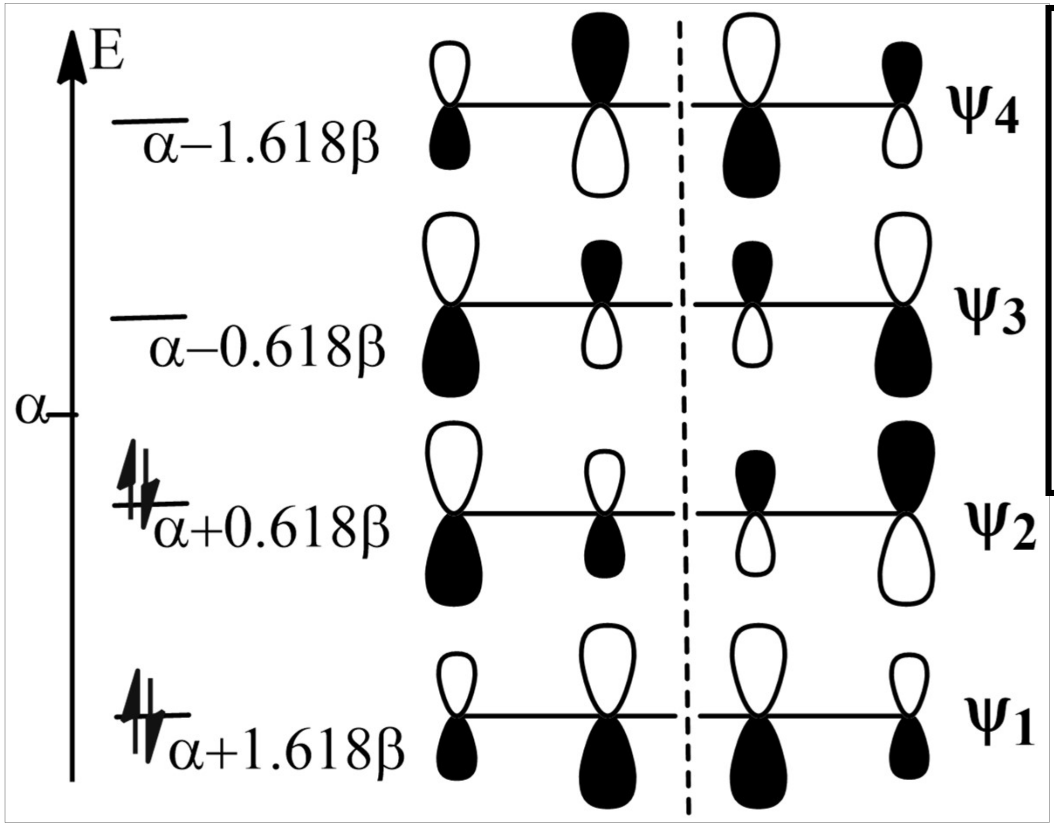
$$\begin{aligned}
\psi_1 &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\
\psi_2 &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 && \text{HOMO} \\
\psi_3 &= 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 && \text{LUMO} \\
\psi_4 &= 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4
\end{aligned}$$

$$E_1 = \alpha + 1.618\beta,\ \psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \ \text{symmetric}$$

$$E_2 = \alpha + 0.618\beta, \psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 \ \text{asymmetric}$$

$$E_3 = \alpha - 0.618\beta, \psi_3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 \ \text{symmetric}$$

$$E_4 = \alpha - 1.618\beta, \psi_4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4 \ \text{asymmetric}$$

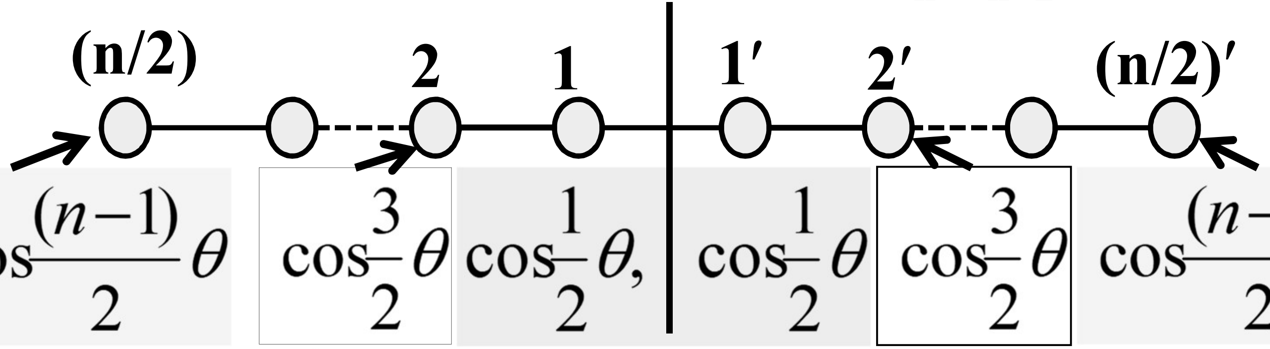


The MOs of a [n]polyene can be classified into two categories, symmetric and asymmetric ones, in terms of their AO coefficients.

5.5.2 Symmetry classification

a. [n]polyenes with even-number carbon atoms: C_nH_{n+2} (n=even)

Symmetric MOs:



$$\cos\frac{(n-1)}{2}\theta \quad \cos\frac{3}{2}\theta \quad \cos\frac{1}{2}\theta, \quad \cos\frac{1}{2}\theta \quad \cos\frac{3}{2}\theta \quad \cos\frac{(n-1)}{2}\theta$$

$$\because C_1 = C_{1'}$$
$$C_2 = C_{2'} \;\;\ldots,$$
$$C_{n/2} = C_{(n/2)'}$$

Note : $cos\,\alpha + cos\,\beta = 2\,cos\frac{\alpha+\beta}{2}\,cos\frac{\alpha-\beta}{2}$

$$\& \, C_{k-1} + C_{k+1} = 2C_k \cos\theta$$ （*Cyclic formula*）

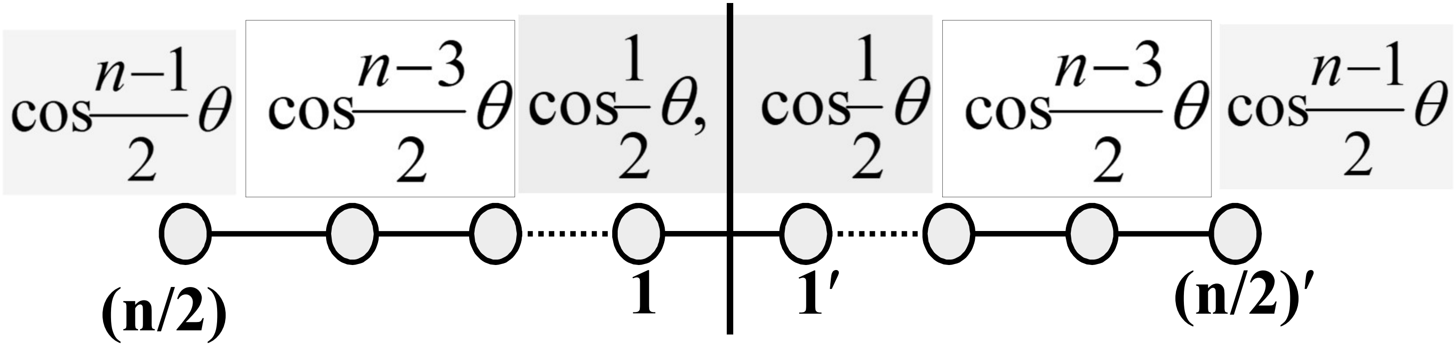
Let coefficients of central atoms (**1** & **1′**) be $cos(\theta/2)$

$$\Rightarrow C_2 = C_{2'} = 2\,cos\frac{\theta}{2}\,cos\,\theta - cos\frac{\theta}{2} = (cos\frac{3\theta}{2} + cos\frac{\theta}{2}) - cos\frac{\theta}{2} = cos\frac{3\theta}{2}$$

$$C_3 = C_{3'} = 2\cos\frac{3\theta}{2}\cos\theta - \cos\frac{\theta}{2} = (\cos\frac{5\theta}{2} + \cos\frac{\theta}{2}) - \cos\frac{\theta}{2} = \cos\frac{5\theta}{2}$$

$$\ldots, C_{(n/2)} = C_{(n/2)'} = \cos\frac{(n-1)\theta}{2}$$

Symmetric MOs:



$\cos\frac{n-1}{2}\theta$ $\cos\frac{n-3}{2}\theta$ $\cos\frac{1}{2}\theta,$ $\cos\frac{1}{2}\theta$ $\cos\frac{n-3}{2}\theta$ $\cos\frac{n-1}{2}\theta$

Boundary condition: $\cos\frac{n+1}{2}\theta = 0$

$$\Rightarrow \frac{n+1}{2}\theta = \frac{2m+1}{2}\pi \qquad \Rightarrow \theta = \frac{2\mathrm{m}+1}{\mathrm{n}+1}\pi \quad (\mathrm{m} = 0,1,\ldots,< \mathrm{n}/2)$$

$$\therefore\ \mathrm{E}_{\mathrm{m}}^{\mathrm{sym}} = \alpha + 2\beta\cos\frac{2\mathrm{m}+1}{\mathrm{n}+1}\pi \quad (m = 0,1,2,\ldots,< \frac{n}{2})$$

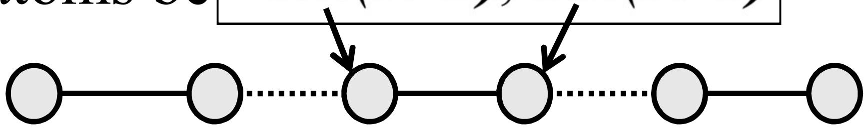
A total of n/2 values

Asymmetric MOs:

$$\& \, C_{k-1} + C_{k+1} = 2C_k \, \boldsymbol{\cos\theta}$$

$$\because C_1 = -C_{1'}, C_2 = -C_{2'}, \ldots,$$

Let coefficients for central atoms be $-\boldsymbol{\sin(\theta/2)}, \; \boldsymbol{\sin(\theta/2)}$



$\boldsymbol{C_i}$ $\quad -\sin\frac{n-1}{2}\theta, \; -\sin\frac{n-3}{2}\theta \qquad \sin\frac{n-3}{2}\theta, \; \sin\frac{n-1}{2}\theta$

Then coefficients for terminal atoms are $-\sin\frac{n-1}{2}\theta$ and $\sin\frac{n-1}{2}\theta$

The boundary condition:

$$\sin\frac{n+1}{2}\theta = 0 \;\; \Rightarrow \;\; \frac{n+1}{2}\theta = m\pi$$

$$\therefore \theta = \frac{2m\pi}{n+1} \qquad (m = 1,2,\ldots,\frac{n}{2})$$

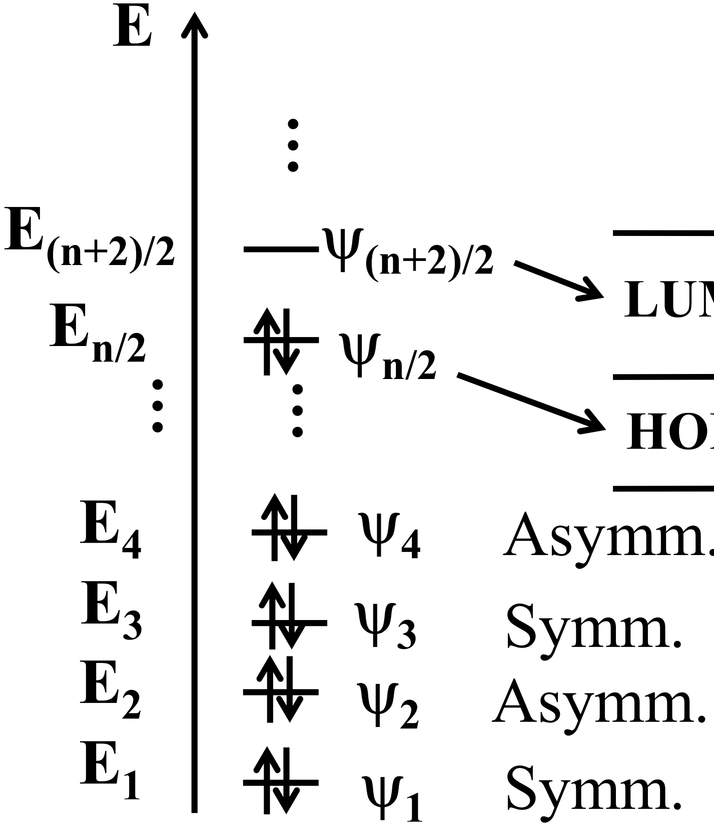
$$\therefore E = \alpha + 2\beta\cos\frac{2m\pi}{n+1} \qquad (m = 1,2,\ldots,\frac{n}{2})$$

A total of n/2 values.

Symmetric MO′s $$E_{sym} = \alpha + 2\beta\cos\frac{2m+1}{n+1}\pi \quad (m = 0,1,2,\ldots,< \frac{n}{2})$$

Asymmetric MO′s $$E_{asym} = \alpha + 2\beta\cos\frac{2m}{n+1}\pi \quad (m = 1,2,\ldots,\frac{n}{2})$$

Thus, the lowest ***n/2*** MO′s ($\theta<\pi/2$) are bonding and doubly occupied!



	n= 4k n/2= 2k (n+2)/2= 2k+1	n= 4k+2 n/2= 2k+1 (n+2)/2= 2k+2
LUMO	Symm.	Asymm.
HOMO	Asymm.	Symm.

- Even-numbered MO’s are asymmetric.
- Odd-numbered MO’s are symmetric.

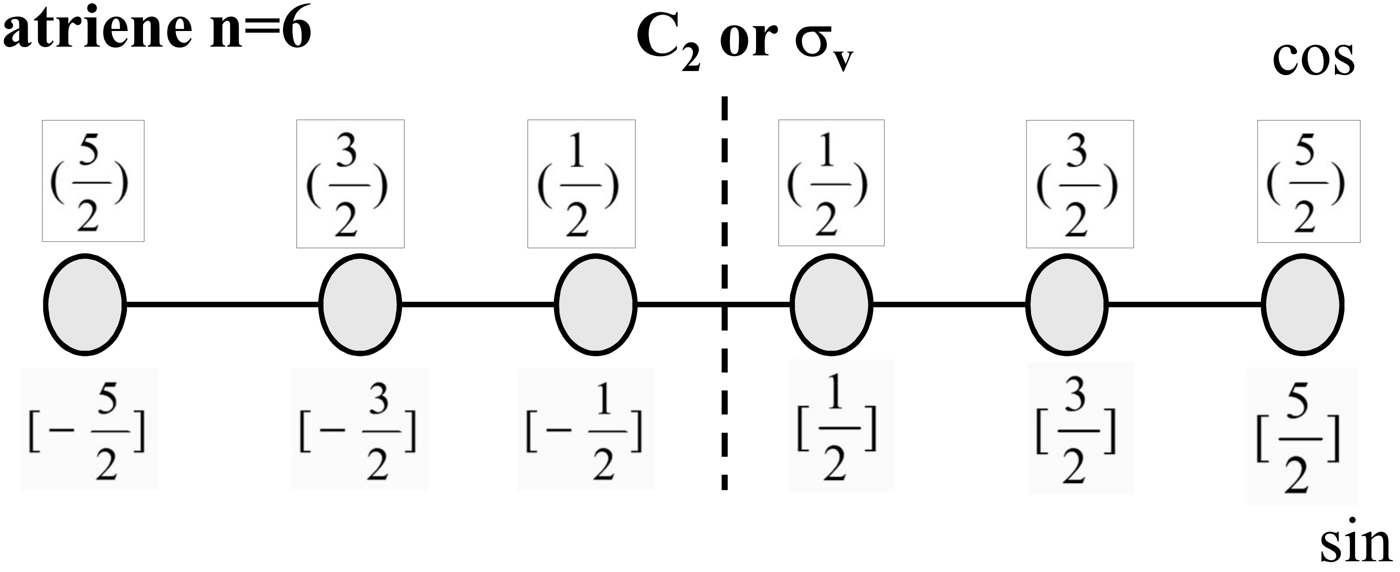
Symmetric MO′s $$E_{\text{sym}} = \alpha + 2\beta\cos\frac{2m+1}{n+1}\pi \quad (m = 0,1,2,\ldots,< \frac{n}{2})$$

Asymmetric MO′s $$E_{\text{asym}} = \alpha + 2\beta\cos\frac{2m}{n+1}\pi \quad (m = 1,2,\ldots,\frac{n}{2})$$

Thus, the lowest ***n/2*** MO′s (*θ<π/2*) are bonding and doubly occupied!

n = 4k	**FMO symmetry**		θ	**E**
HOMO	Asymm.	$m = \frac{n}{4}$	$\frac{n}{2(n+1)}\pi$	$E_{\text{asym}} = \alpha + 2\beta\cos\frac{n}{2(n+1)}\pi$
LUMO	Symm.	$m = \frac{n}{4}$	$\frac{n+2}{2(n+1)}\pi$	$E_{\text{sym}} = \alpha + 2\beta\cos\frac{n+2}{2(n+1)}\pi$
n = 4k+2				
HOMO	Symm.	$m = \frac{n-2}{4}$	$\frac{n}{2(n+1)}\pi$	$E_{\text{sym}} = \alpha + 2\beta\cos\frac{n}{2(n+1)}\pi$
LUMO	Asymm.	$m = \frac{n+2}{4}$	$\frac{n+2}{2(n+1)}\pi$	$E_{\text{asym}} = \alpha + 2\beta\cos\frac{n+2}{2(n+1)}\pi$

Example: hexatriene n=6



Symmetric MO $(\frac{5}{2})$ $(\frac{3}{2})$ $(\frac{1}{2})$ $(\frac{1}{2})$ $(\frac{3}{2})$ $(\frac{5}{2})$

Asymmetric $[-\frac{5}{2}]$ $[-\frac{3}{2}]$ $[-\frac{1}{2}]$ $[\frac{1}{2}]$ $[\frac{3}{2}]$ $[\frac{5}{2}]$

Symmetric MO: $$\cos\frac{7}{2}\theta = 0 \qquad \Rightarrow \theta = \frac{2m+1}{7}\pi \quad (m = 0,1,2)$$

$$\mathrm{E} = \alpha + 2\beta\cos\frac{2\mathrm{m}+1}{7}\pi \quad (m = 0,1,2)$$

$m = 0,1$ $(\because \mathrm{E} < \alpha, \ \therefore$ bonding$)$

$m = 2$ $(\because \mathrm{E} > \alpha, \ \therefore$ anti - bonding$)$

Asymmetric MO: $$\sin\frac{7}{2}\theta = 0 \quad \Rightarrow \quad \theta = \frac{2m}{7}\pi \quad (m = 1,2,3)$$

$$\mathrm{E} = \alpha + 2\beta\cos\frac{2\mathrm{m}}{7}\pi \quad (m = 1,2,3)$$

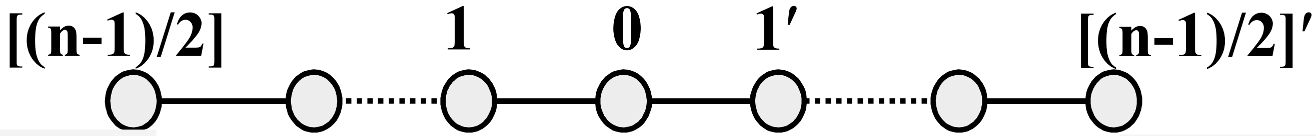
$m = 1$ bonding

$m = 2,3$ anti - bonding

Three doubly occupied MOs, two sym. + one asym.

b. [n]polyenes with odd-number carbon atoms: (n=odd)

Symmetric MO′s:



$$\cos\frac{n-1}{2}\theta \quad \cos\frac{n-3}{2}\theta \quad \cos\theta,\ 1,\ \cos\theta \quad \cos\frac{n-3}{2}\theta \quad \cos\frac{n-1}{2}\theta$$

$$\because C_{k-1} + C_{k+1} = 2C_k\cos\theta \qquad \& \, C_0 = 1, C_1 = C_{1'}, \ldots, C_{[(n-1)/2]} = C_{[(n-1)/2]'}$$

$$\Rightarrow C_1 = C_{1'} = \cos\theta \qquad \Rightarrow C_2 = 2C_1\cos\theta - 1 = \cos 2\theta$$

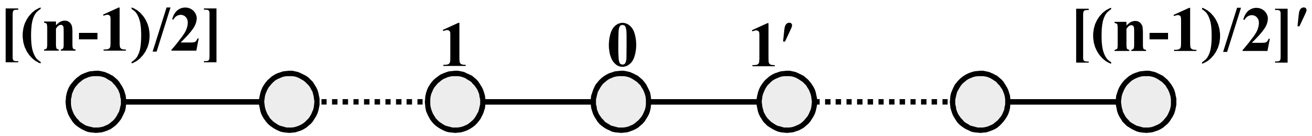
$$\Rightarrow \ldots, C_{(n-3)/2} = \cos\frac{n-3}{2}\theta \qquad \Rightarrow C_{(n-1)/2} = \cos\frac{n-1}{2}\theta$$

Boundary conditions:

$$\cos\frac{n+1}{2}\theta = 0 \ \Rightarrow \ \frac{n+1}{2}\theta = \frac{2\mathrm{m}+1}{2}\pi \qquad \Rightarrow \theta = \frac{2\mathrm{m}+1}{\mathrm{n}+1}\pi \quad \left(m = 0,1,2,\ldots,\frac{n-1}{2}\right)$$

$$\therefore \mathrm{E}_{\mathrm{sym}} = \alpha + 2\beta\cos\theta = \alpha + 2\beta\cos\frac{2\mathrm{m}+1}{\mathrm{n}+1}\pi \quad \left(m = 0,1,2,\ldots,\frac{n-1}{2}\right)$$

Asymmetric MO′s:



$$\boldsymbol{sin}\frac{n-1}{2}\theta \quad \boldsymbol{sin}\frac{n-3}{2}\theta \quad \boldsymbol{sin}\theta, \boxed{0}, \text{-}\,\boldsymbol{sin}\theta \quad -\boldsymbol{sin}\frac{n-3}{2}\theta \quad -\boldsymbol{sin}\frac{n-1}{2}\theta$$

$$\because C_{k-1} + C_{k+1} = 2C_k \cos\theta \quad \boldsymbol{\&}\, C_0 = 0, C_1 = \text{-}C_{1'}, \ldots, C_{[(n-1)/2]} = \text{-}C_{[(n-1)/2]'}$$

$$\text{Let } C_1 = \text{-}C_{1'} = \sin\theta \quad \Rightarrow C_2 = 2C_1\, \boldsymbol{cos}\,\theta = \sin 2\theta$$

$$\ldots \Rightarrow C_{[(n-3)/2]} = \sin[(\mathrm{n}-3)\theta/2] = \text{-}C_{[(n-3)/2]'}$$

$$\Rightarrow C_{[(n-1)/2]} = \sin[(\mathrm{n}-1)\theta/2] = \text{-}C_{[(n-1)/2]'}$$

Boundary condition: $\boldsymbol{sin}\frac{n+1}{2}\theta = 0$ $\quad \Rightarrow \theta = \frac{2\mathrm{m}}{\mathrm{n}+1}\pi \quad (m = 1,2,\ldots,\frac{n-1}{2})$

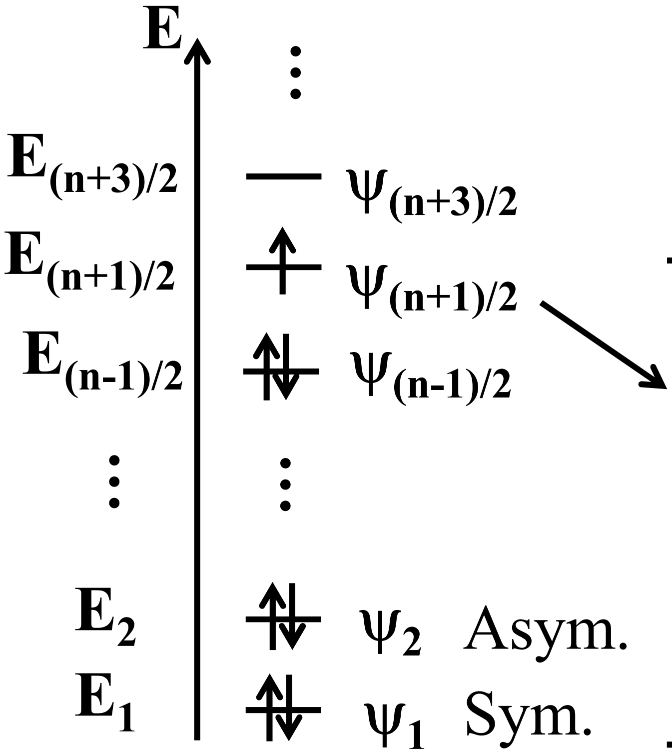
$$\mathrm{E}_{\mathrm{asym}} = \alpha + 2\beta\, \boldsymbol{cos}\,\theta = \alpha + 2\beta\cos\frac{2\mathrm{m}}{\mathrm{n}+1}\pi \quad (m = 1,2,\ldots,\frac{n-1}{2})$$

MOs of [n]polyenes with odd-number carbon atoms

Asymmetric MO's: $$E_{\text{asym}} = \alpha + 2\beta\cos\frac{2m}{n+1}\pi \quad (m = 1,2,\ldots,\frac{n-1}{2})$$

Symmetric MO's: $$E_{\text{sym}} = \alpha + 2\beta\cos\frac{2m+1}{n+1}\pi \quad (m = 0,1,2,\ldots,\frac{n-1}{2})$$

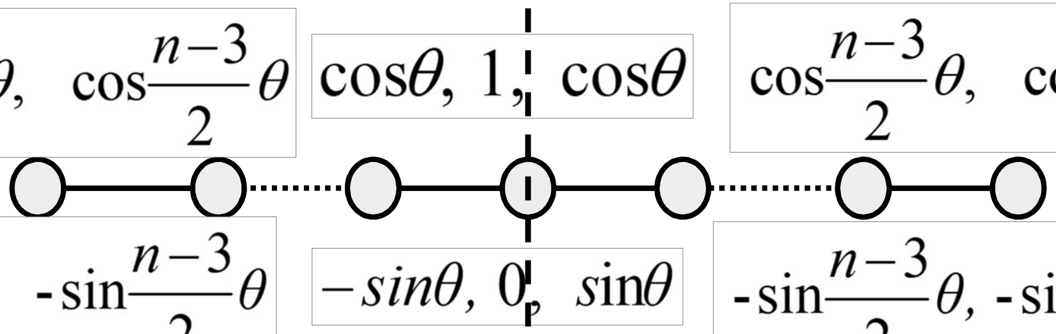
ne_π, → (n-1)/2 MOs doubly occupied, and one non-bonding SOMO!



- Even-numbered MO's are asymmetric.
- Odd-numbered MO's are symmetric.

SOMO	$\theta = \pi/2$ $E_{SOMO} = \alpha$	
	n = 4k+1 (n+1)/2= 2k+1 Sym.	n = 4k+3 (n+1)/2= 2k+2 Asym.

FMOs of [n]polyenes with odd-number carbon atoms



Symmetric:

$\cos\frac{n-1}{2}\theta,\ \ \cos\frac{n-3}{2}\theta$ $\cos\theta,\ 1,\ \cos\theta$ $\cos\frac{n-3}{2}\theta,\ \ \cos\frac{n-1}{2}\theta$

Asymmetric:

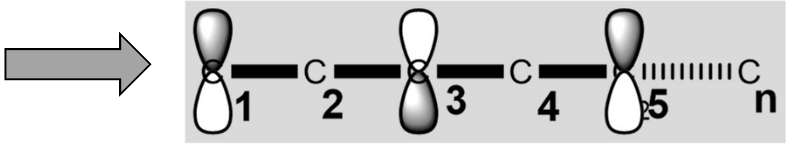
$-sin\frac{n-1}{2}\theta,\ \ \text{-}\sin\frac{n-3}{2}\theta$ $-sin\theta,\ 0,\ \ \sin\theta$ $\text{-}\sin\frac{n-3}{2}\theta,\ \text{-}\sin\frac{n-1}{2}\theta$

	SOMO
n = 4k+1	**symmetric**
n = 4k+3	**asymmetric**

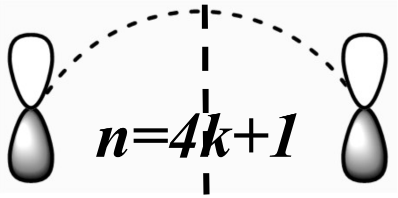
$$E = \alpha + 2\beta \boldsymbol{\cos}\theta$$

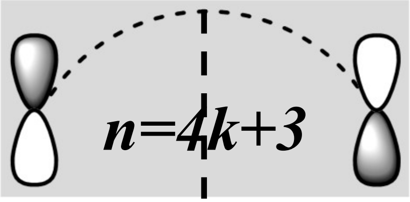
$$\theta = \pi / 2,\ \ E = \alpha$$

$$\psi_{SOMO} = A\sum_{k=1}^{n}(\varphi_1 - \varphi_3 + \varphi_5 - \ldots)$$



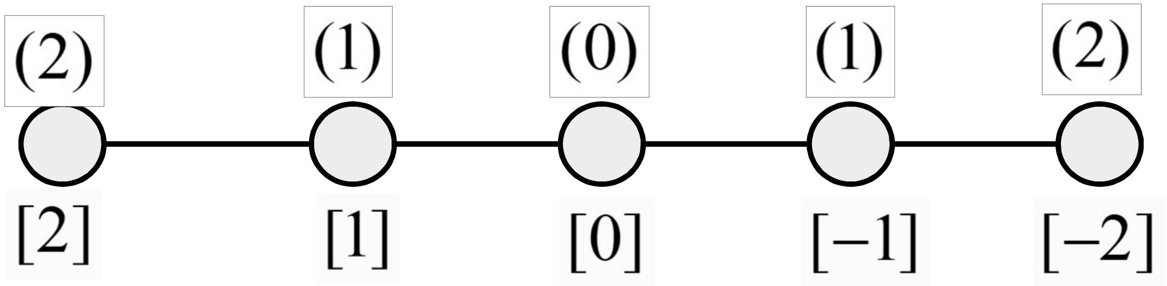
Simplified diagram of SOMO:





Example:

n=5



symmetric

asymmetric

Symmetric MO′s:

$$\cos 3\theta = 0 \Rightarrow \theta = \frac{2m+1}{6}\pi \quad (m=0,1,2)$$

➡
$$E = \alpha + 2\beta\cos\frac{2m+1}{6}\pi$$
$$(m=0,1,2)$$

$$\mathrm{m}=0,\quad \theta=\pi/6,\quad E_{s1}=\alpha+1.732\beta$$
$$\mathrm{m}=1,\quad \theta=3\pi/6,\quad E_{s2}=\alpha$$
$$\mathrm{m}=2,\quad \theta=5\pi/6,\quad E_{s3}=\alpha-1.732\beta$$

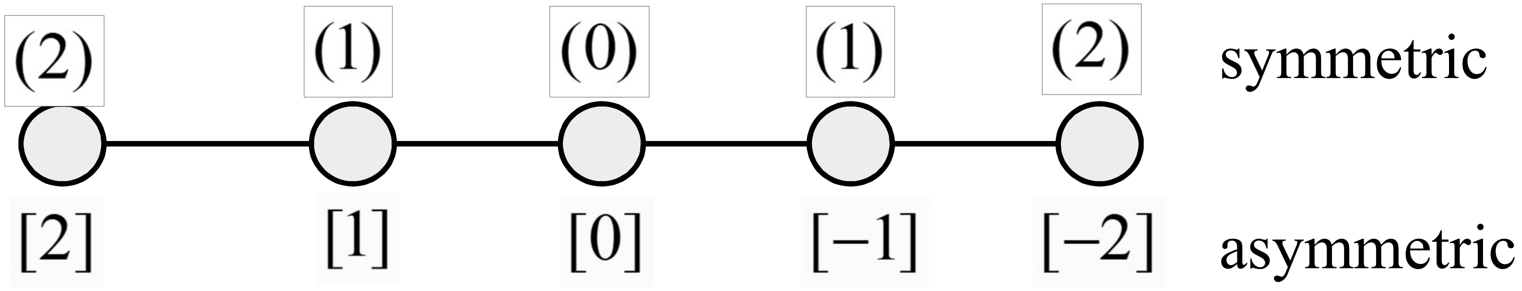
$$\Psi_{s1}=\sqrt{\frac{1}{3}}\left(\frac{1}{2}\varphi_1+\frac{\sqrt{3}}{2}\varphi_2+\varphi_3+\frac{\sqrt{3}}{2}\varphi_4+\frac{1}{2}\varphi_5\right)$$ Bonding

$$\Psi_{s2}=\sqrt{\frac{1}{3}}(\varphi_1-\varphi_3+\varphi_5)$$ Non-bonding

$$\Psi_{s3}=\sqrt{\frac{1}{3}}\left(\frac{1}{2}\varphi_1-\frac{\sqrt{3}}{2}\varphi_2+\varphi_3-\frac{\sqrt{3}}{2}\varphi_4+\frac{1}{2}\varphi_5\right)$$ anti-bonding

Example:

n=5



Asymmetric MO′s:

$$\sin 3\theta = 0 \;\&\; \sin\theta \neq 0 \Rightarrow \theta \;=\frac{m\pi}{3}\,(m=1,2)$$

$$\mathrm{E} = \alpha + 2\beta\cos\frac{m}{3}\pi \quad (m=1,2)$$

$$m=1, \theta=\pi/3, \quad E_{as1}=\alpha+\beta \quad \text{bonding}$$

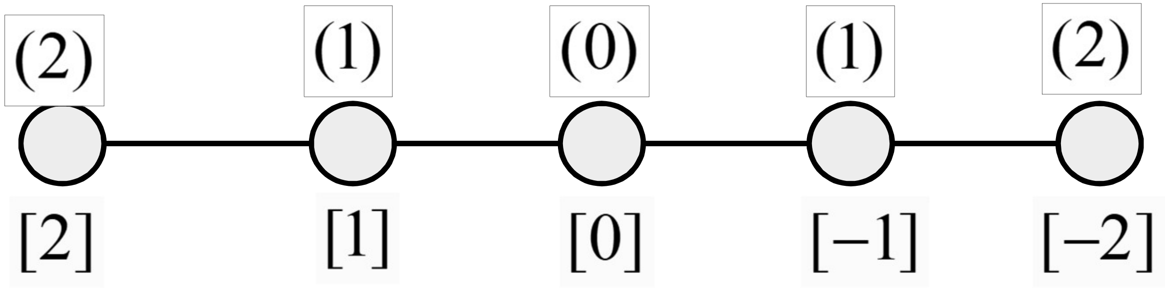
$$m=2, \theta=2\pi/3, E_{as2}=\alpha-\beta \;\; \text{anti - bonding}$$

$$\Psi_{as1}=\frac{1}{2}(\varphi_1+\varphi_2-\varphi_4-\varphi_5) \quad \text{Bonding}$$

$$\Psi_{as2}=\frac{1}{2}(\varphi_1-\varphi_2+\varphi_4-\varphi_5) \quad \text{Anti-bonding}$$

Example:

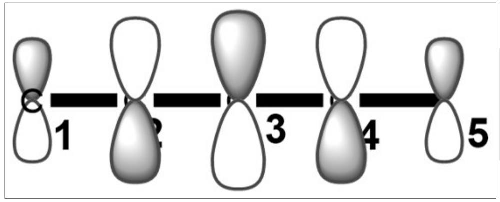
n=5



symmetric

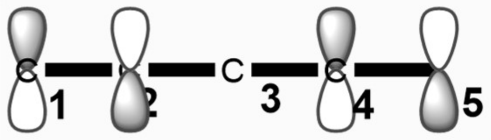
asymmetric

$$\Psi_{s3} = \sqrt{\frac{1}{3}}\left(\frac{1}{2}\phi_1 - \frac{\sqrt{3}}{2}\phi_2 + \phi_3 - \frac{\sqrt{3}}{2}\phi_4 + \frac{1}{2}\phi_5\right)$$



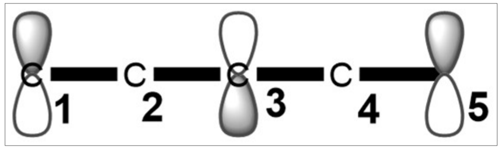
$\alpha - \sqrt{3}\beta$

$$\Psi_{as2} = \frac{1}{2}\left(\phi_1 - \phi_2 + \phi_4 - \phi_5\right)$$



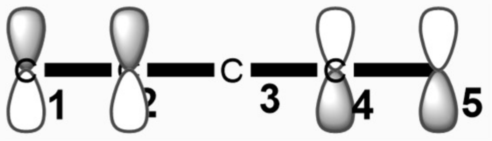
α - β

$$\Psi_{s2} = \sqrt{\frac{1}{3}}\left(\phi_1 - \phi_3 + \phi_5\right)$$



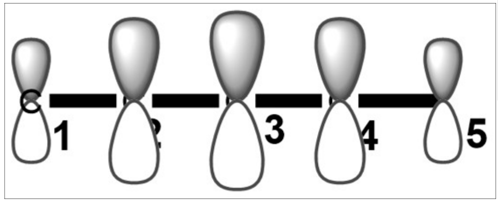
α

$$\Psi_{as1} = \frac{1}{2}\left(\phi_1 + \phi_2 - \phi_4 - \phi_5\right)$$



$\alpha + \beta$

$$\Psi_{s1} = \sqrt{\frac{1}{3}}\left(\frac{1}{2}\phi_1 + \frac{\sqrt{3}}{2}\phi_2 + \phi_3 + \frac{\sqrt{3}}{2}\phi_4 + \frac{1}{2}\phi_5\right)$$

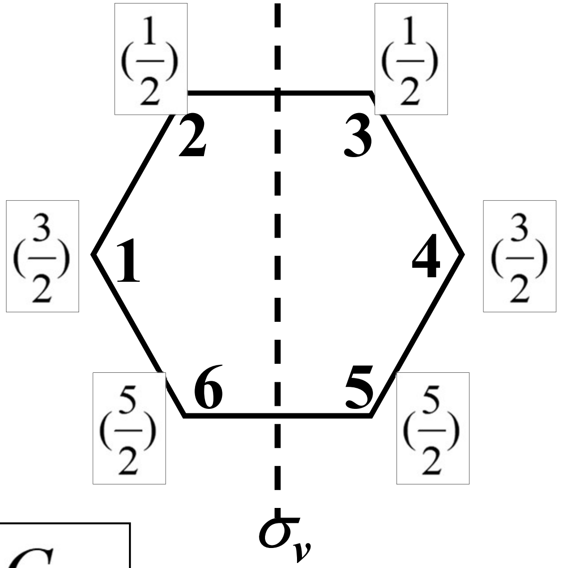


$\alpha + \sqrt{3}\beta$

c. Cyclic conjugated molecules

Example 1： benzene ---solution I (**n=6 !**)

i) Symmetric MO′s



$$\boxed{C_k = C_k' = \cos\frac{2k-1}{2}\theta \quad (k = 1,2,..\frac{n}{2})}$$

Boundary condition: $\boxed{2\cos\theta C_k = C_{k+1} + C_{k-1}}$

$$\Rightarrow \quad \boxed{2\cos\theta C_6 = C_5 + C_1}$$

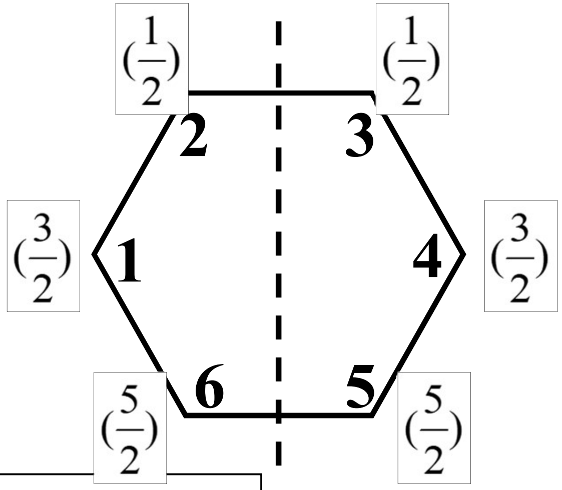
$$\Rightarrow \quad 2\cos\theta\cos\frac{5}{2}\theta = \cos\frac{5}{2}\theta + \cos\frac{3}{2}\theta \quad \Rightarrow$$

$$\cos\frac{7}{2}\theta - \cos\frac{5}{2}\theta = 0 \quad \Rightarrow \quad -2\sin 3\theta \sin\frac{\theta}{2} = 0$$

$$\Rightarrow \sin 3\theta = 0 \quad \Rightarrow \quad \theta = m\pi/3 \quad (m = 0,1,2)$$

$$\therefore 2\cos\theta = 2, \;\; 1, \;\; -1$$

θ	0°,	60°,	120°
$\cos\theta$	1	1/2	-1/2
$2\cos\theta$	2	1	-1
E	$\alpha+2\beta$	$\alpha+\beta$	$\alpha-\beta$



θ	E
0°	$\alpha+2\beta$
60°	$\alpha+\beta$
120°	$\alpha-\beta$

$$\psi_1 = N(\varphi_1+\varphi_2+\varphi_3+\varphi_4+\varphi_5+\varphi_6)$$

$$=\frac{1}{\sqrt{6}}(\varphi_1+\varphi_2+\varphi_3+\varphi_4+\varphi_5+\varphi_6)$$

Bonding

$$\psi_2 = N(0+\frac{\sqrt{3}}{2}\varphi_2+\frac{\sqrt{3}}{2}\varphi_3+0-\frac{\sqrt{3}}{2}\varphi_5-\frac{\sqrt{3}}{2}\varphi_6)$$

$$=\frac{1}{2}(\varphi_2+\varphi_3-\varphi_5-\varphi_6)$$

Bonding

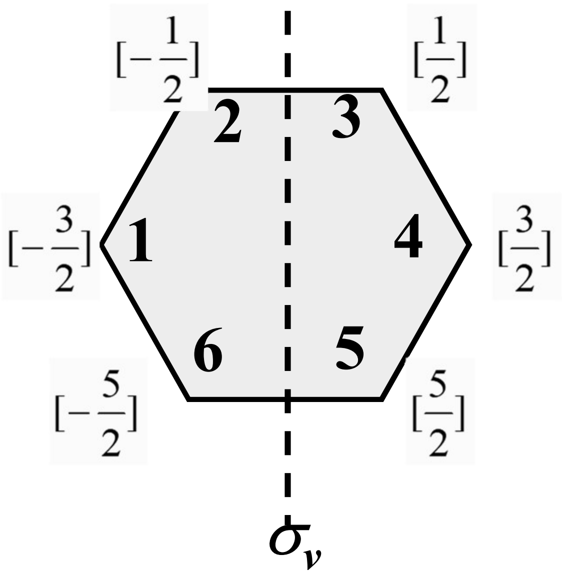
$$\psi_3 = N(-\varphi_1+\frac{1}{2}\varphi_2+\frac{1}{2}\varphi_3-\varphi_4+\frac{1}{2}\varphi_5+\frac{1}{2}\varphi_6)$$

Antibonding

$$=\frac{1}{\sqrt{6}}(2\varphi_1-\varphi_2-\varphi_3+2\varphi_4-\varphi_5-\varphi_6)$$

ii) Asymmetric MO′s

Boundary condition： $\boxed{2\cos\theta C_k = C_{k+1}+C_{k-1}}$



$$\boxed{2\cos\theta\sin\frac{5}{2}\theta = \sin\frac{3}{2}\theta - \sin\frac{5}{2}\theta}$$

$$\sin\frac{7}{2}\theta + \sin\frac{3}{2}\theta = \sin\frac{3}{2}\theta - \sin\frac{5}{2}\theta$$

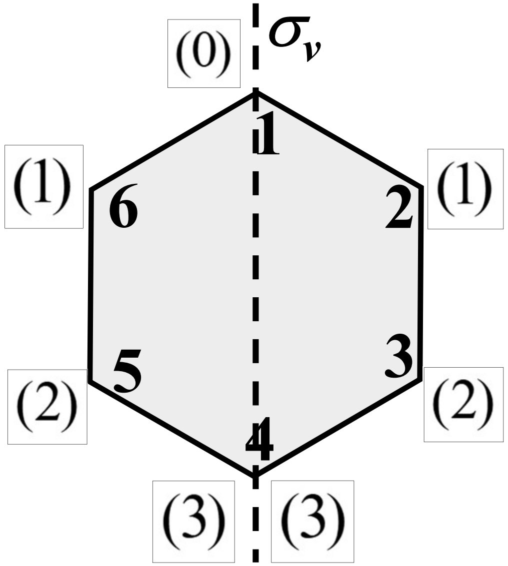
$$\sin\frac{7}{2}\theta + \sin\frac{5}{2}\theta = 0 \quad \Rightarrow \sin 3\theta\cos\frac{\theta}{2} = 0$$

$$\Rightarrow \ \sin 3\theta = 0 \ \Rightarrow \ \theta = \frac{\mathrm{m}}{3}\pi \quad (m=1,2,3)$$

θ	60°,	120°,	180°
$\cos\theta$	1/2	-1/2	-1
$2\cos\theta$	1	-1	-2
E	$\alpha+\beta$	$\alpha-\beta$	$\alpha-2\beta$
	ψ_4	ψ_5	ψ_6

Example 2： benzene ---solution II (**n= 7!**)

i) Symmetric MO′s



Boundary condition: $\boxed{2\cos\theta C_k = C_{k+1} + C_{k-1}}$

$$\Rightarrow 2\cos\theta\cos 3\theta = \cos 2\theta + \cos 2\theta$$

$$\cos 4\theta + \cos 2\theta = 2\cos 2\theta \quad \Rightarrow \cos 4\theta - \cos 2\theta = 0$$

$$\Rightarrow -\sin 3\theta \sin\theta = 0 \Rightarrow \sin 3\theta = 0$$

$$\Rightarrow \quad \theta = \frac{m}{3}\pi \; (m = 0,1,2,3 < \frac{7}{2})$$

⇩

θ	0°,	60°	120°	180°
$\cos\theta$	1	1/2	-1/2	-1
$2\cos\theta$	2	1	-1	-2
E	$\alpha + 2\beta$	$\alpha + \beta$	$\alpha - \beta$	$\alpha - 2\beta$
	ψ_1	ψ_2	ψ_3	ψ_4
	bonding		anti - bonding	

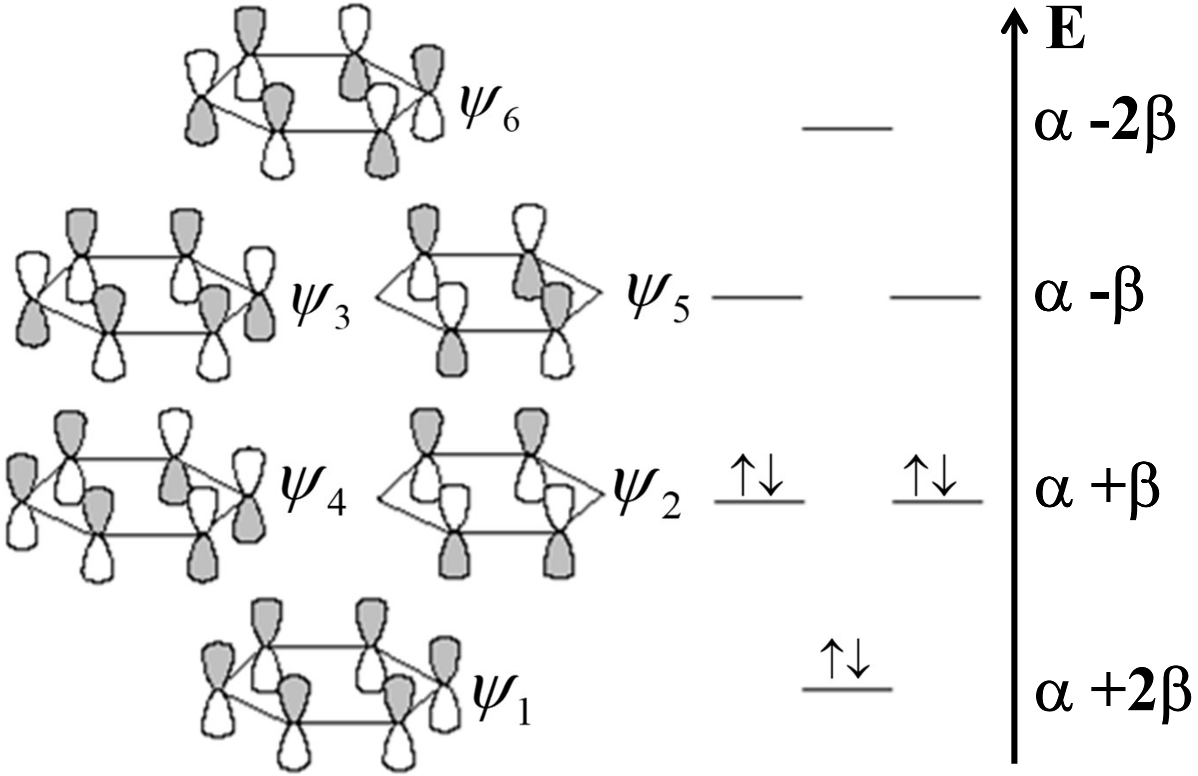
Similar to the linear polyene (n=7) case by supposing the two terminal atoms overlapping!

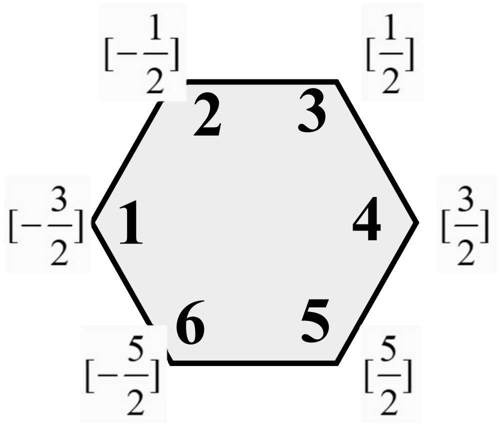
θ	E
60°	$\alpha+\beta$
120°	$\alpha-\beta$
180°	$\alpha-2\beta$

$$\psi_4=\frac{1}{\sqrt{6}}(2\phi_1+\phi_2-\phi_3-2\phi_4-\phi_5+\phi_6)$$ Bonding

$$\psi_5=\frac{1}{2}(\phi_2-\phi_3+\phi_5-\phi_6)$$ Anti-bonding

$$\psi_6=\frac{1}{\sqrt{6}}(\phi_1-\phi_2+\phi_3-\phi_4+\phi_5-\phi_6)$$ Anti-bonding





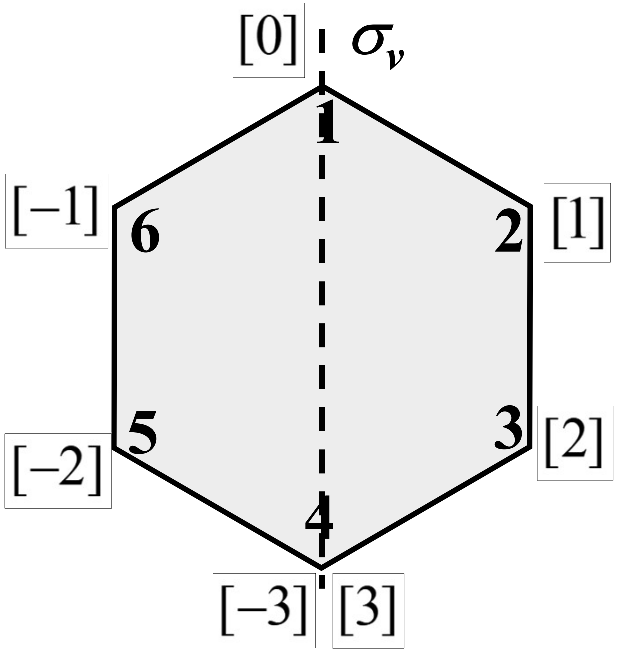
ii) Asymmetric MO′s

$$\because \sin 3\theta = -\sin 3\theta \ \text{ and } \ \sin\theta \neq 0$$

$$\therefore \sin 3\theta = 0 \quad \Rightarrow \quad \theta = \frac{\mathrm{m}}{3}\pi \quad (m = 1,2 < 7/2)$$

Question: Why do we exclude the case of ***m* = *3***?

θ	60°,	120°
$\cos\theta$	1/2	-1/2
$2\cos\theta$	1	-1
E	$\alpha+\beta$	$\alpha - \beta$
	ψ_1	ψ_2
	bonding	anti-bonding



Please derive the MO′s after class!

Complicated π-conjugation: e.g., benzyl radical

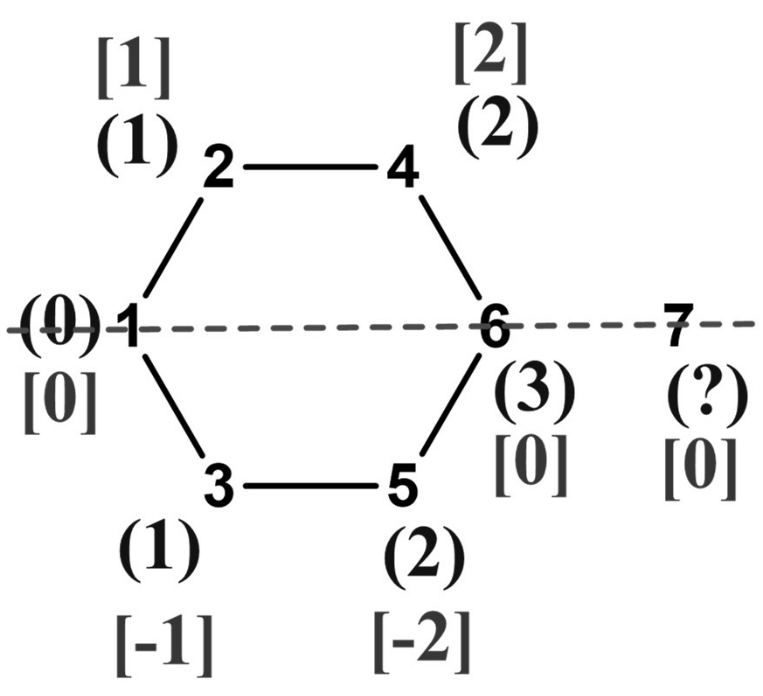
How to get the coefficient of atom **7**?

1) Symmetric MOs:

$$\boxed{\begin{array}{l} \textit{The}\text{ secular equation centred at atom 6}: \\ C_6(\alpha - E) + C_4\beta + C_5\beta + C_7\beta = 0 \end{array}}$$

$$\boxed{\begin{array}{l} let \quad -2\cos\theta = (\alpha - E)/\beta \\ \therefore C_7 = 2\boldsymbol{cos}\,\theta C_6 - C_4 - C_5 \end{array}}$$

$$\boxed{\begin{array}{l} = 2\boldsymbol{cos}\,\theta\,\boldsymbol{cos}\,3\theta - 2\boldsymbol{cos}\,2\theta \\ = \boldsymbol{cos}\,4\theta - \boldsymbol{cos}\,2\theta \end{array}}$$



Boundary condition: $\boxed{2\cos\theta C_7 = C_6 \Rightarrow}$

$$\boxed{2\cos\theta(\cos 4\theta - \cos 2\theta) = \cos 3\theta \quad \Rightarrow 2\cos\theta = 0,\ \pm(3 \mp \sqrt{2})^{1/2}}$$

2) Asymmetric MOs:

The coefficients of atoms 1,6 and 7 that are located in the reflection plane should be 0. Then

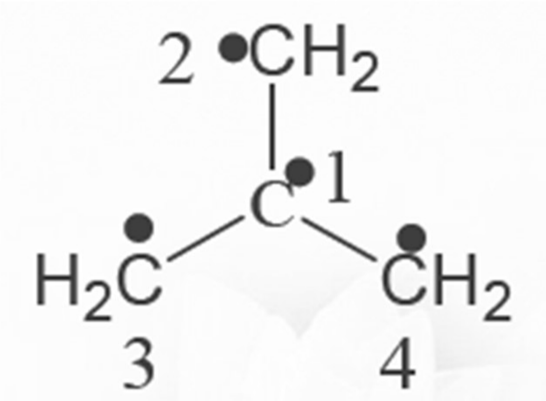
$$\begin{array}{l} \boldsymbol{sin}\,3\theta = 0 \Rightarrow \theta = m\pi/3 \quad (\mathrm{m} = 1{,}2) \\ \Rightarrow 2\boldsymbol{cos}\,\theta = \pm 1 \Rightarrow E = \alpha \mp \beta \end{array}$$

Remarks on HMO treatment of system with complicated π-conjugation,

1) The use of symmetry can simplify the process. e.g., naphthalene

2) Secular equations pertaining to the multiply connected atoms should be carefully considered!

Example: Please derive the HMO′s of trimethylenemethane (Π_4^4) without directly solving its secular determinant.



Question:

1. Can HMO theory be used to deal with other multicenter-multielectron bonds (e.g., 3c2e bond in H_3^+, 3c4e bond in PF5 etc) than the aforementioned Π_n^m bonds?

2. Please try to perform HMO treatment on H_3^+ and figure out whether this cation is triangular or linear!

§ 5.6 Symmetry of molecular orbital and symmetry rules for molecular reactions

Brief introduction:

- Frontier Molecular orbital (FMO) Theory proposed by K. Fukui in early 1950s. (*J. Chem. Phys.* 1952, 20, 722.)
- The Principle of Orbital Symmetry Conservation proposed by R.B. Woodward and R. Hoffmann in 1965. (*JACS*, 1965, 87, 395.)
- Owing to their aforementioned contributions, Fukui and Hoffmann were awarded Nobel Prize in Chemistry in 1981.

5.6.1 Frontier molecular orbitals Theory (1951)

- A deeper understanding of chemical reactivity can be gained by focusing on the *frontier orbitals* of the reactants.

- We need to consider only two frontier molecular orbitals (FMO′s), the HOMO and LUMO, to predict the structure of the product.

Highest occupied molecular orbital (HOMO)

Lowest unoccupied molecular orbital (LUMO)

•The FMO theory can be regarded as a natural extension of MO theory that facilitates us to obtain qualitative understanding of chemical reactivity.

Reaction condition

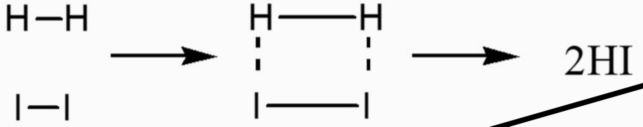
1. During the course of a chemical reaction, the orbitals that are most readily accessible for interaction are the frontier orbitals.

2. When two molecules approach each other, **the symmetry of the HOMO of one molecule must be compatible with that of the LUMO of the other molecule, i.e. orbitals with the same sign will overlap.** This forms a transition state which is relatively stable and is a symmetry-allowed state.

3. **The energy levels of the interacting HOMO and LUMO must be comparable** (**< 6 eV**).

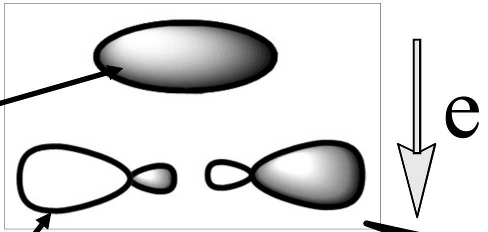
4. When the HOMO and LUMO of two molecules overlap, electrons are transferred from the HOMO of one molecule to the LUMO of the other molecule. **The direction of the transfer should be in line with the electronegativities** and be consistent with the weakening of the original bond.

example **A :** $\mathbf{H_2 + I_2 \Leftrightarrow 2HI}$



$H_2 : \underline{(\sigma_{1s})}^2 \underline{(\sigma_{1s}}*)^0$

$I_2 : (\sigma_{5p})^2 (\pi_{5p})^4 \underline{(\pi_{5p}}*)^4 \underline{(\sigma_{5p}}*)^0$



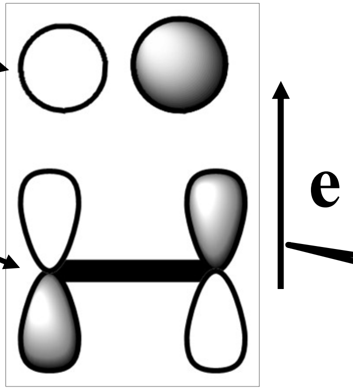
HOMO(H_2)

LUMO(I_2)

（a）

overlap=0!!

Symmetry-incompatible



LUMO(H_2)

HOMO(I_2)

（b）

Electronegativity-incompatible

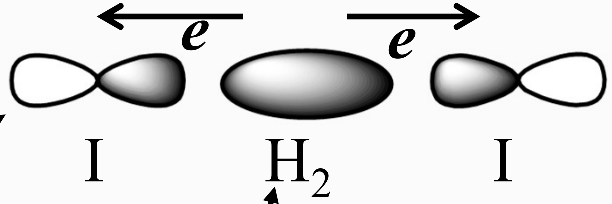
Real mechanism

$I_2 \rightarrow \mathbf{2}I$

$I + H_2 \rightarrow HI + H$

$H + I \rightarrow HI$

$H_2 + I_2 \rightarrow \mathbf{2}HI$



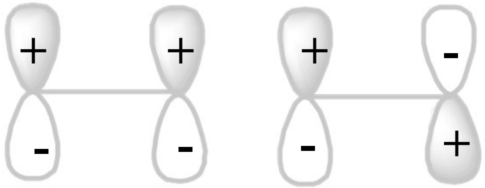
$H_2 : (\sigma_{1s})^2 (\sigma_{1s}*)^0$

$I_2 : (\sigma_{5p})^2 (\pi_{5p})^4 (\pi_{5p}*)^4 (\sigma_{5p}*)^0$

Such a three-step mechanism meets all requirements!

Example B: $C_2H_4 + H_2 \rightarrow C_2H_6$

C_2H_4



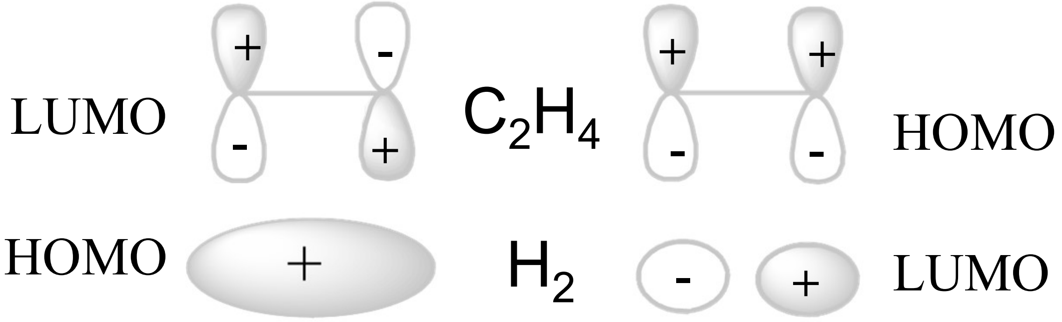
π
HOMO

π*
LUMO

$$H_2 : (\sigma_{1g})^2 (\sigma_{1u})^0$$

HOMO LUMO

Without catalyst

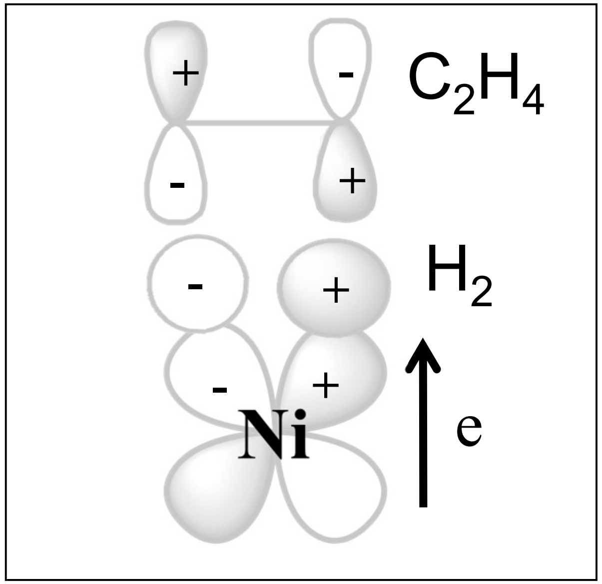


Overlap=0

incompatible in symmetry

not allowed thermally!

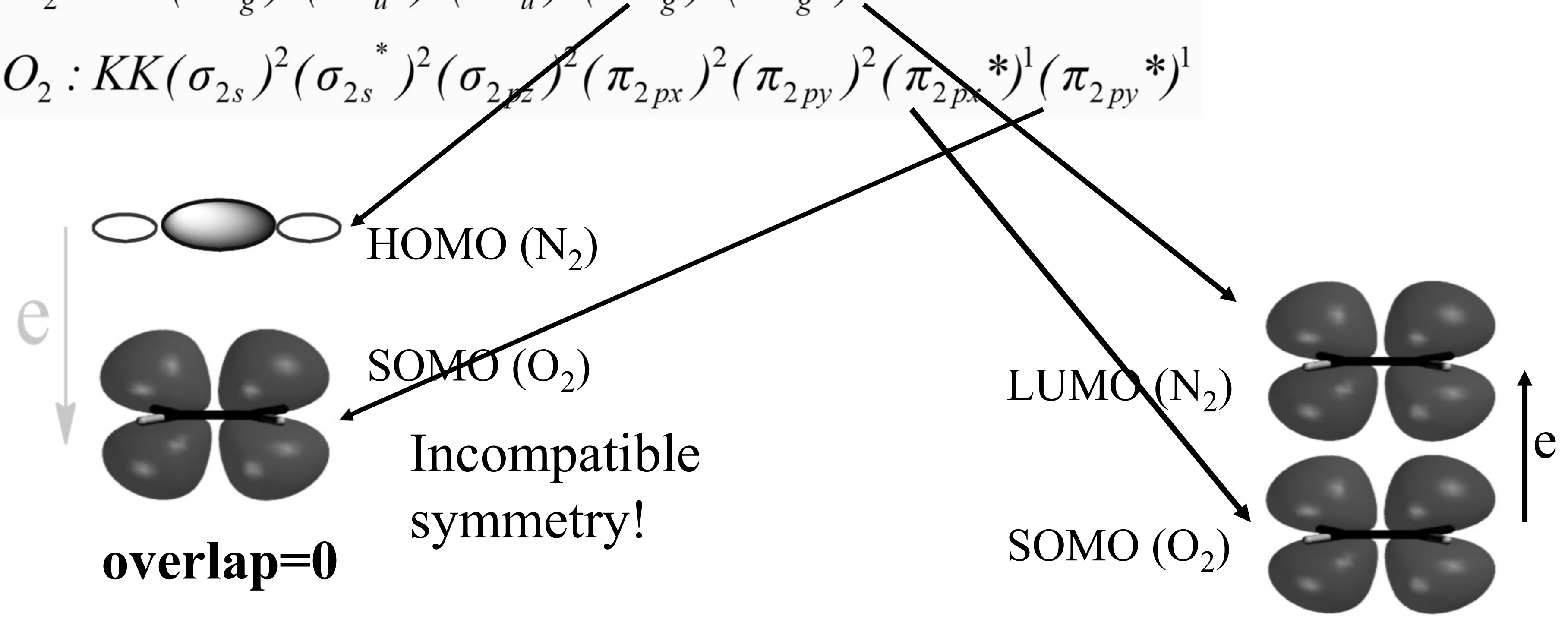
With TM catalyst



Example C, $N_2 + O_2 \not\rightarrow 2NO$

$$N_2 : KK(1\sigma_g)^2(1\sigma_u^{\ *})^2(1\pi_u)^4(2\sigma_g)^2(1\pi_g{}^*)^0$$

$$O_2 : KK(\sigma_{2s})^2(\sigma_{2s}^{\ *})^2(\sigma_{2pz})^2(\pi_{2px})^2(\pi_{2py})^2(\pi_{2px}{}^*)^1(\pi_{2py}{}^*)^1$$



Incompatible symmetry!

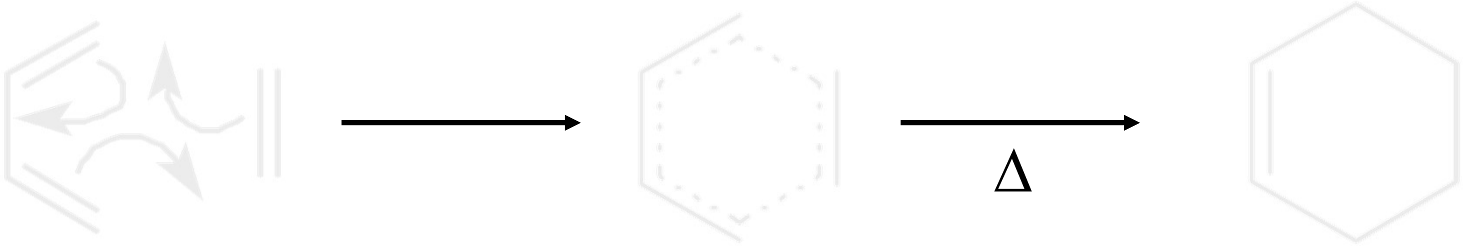
overlap=0

Unreasonable electron transfer!

Though both N_2 and O_2 are abundant in the atmosphere of the Earth, no such reaction can occur without catalyst!

Example D: $C_4H_6 + C_2H_4$ A Nobel-prize-wining Rxn!

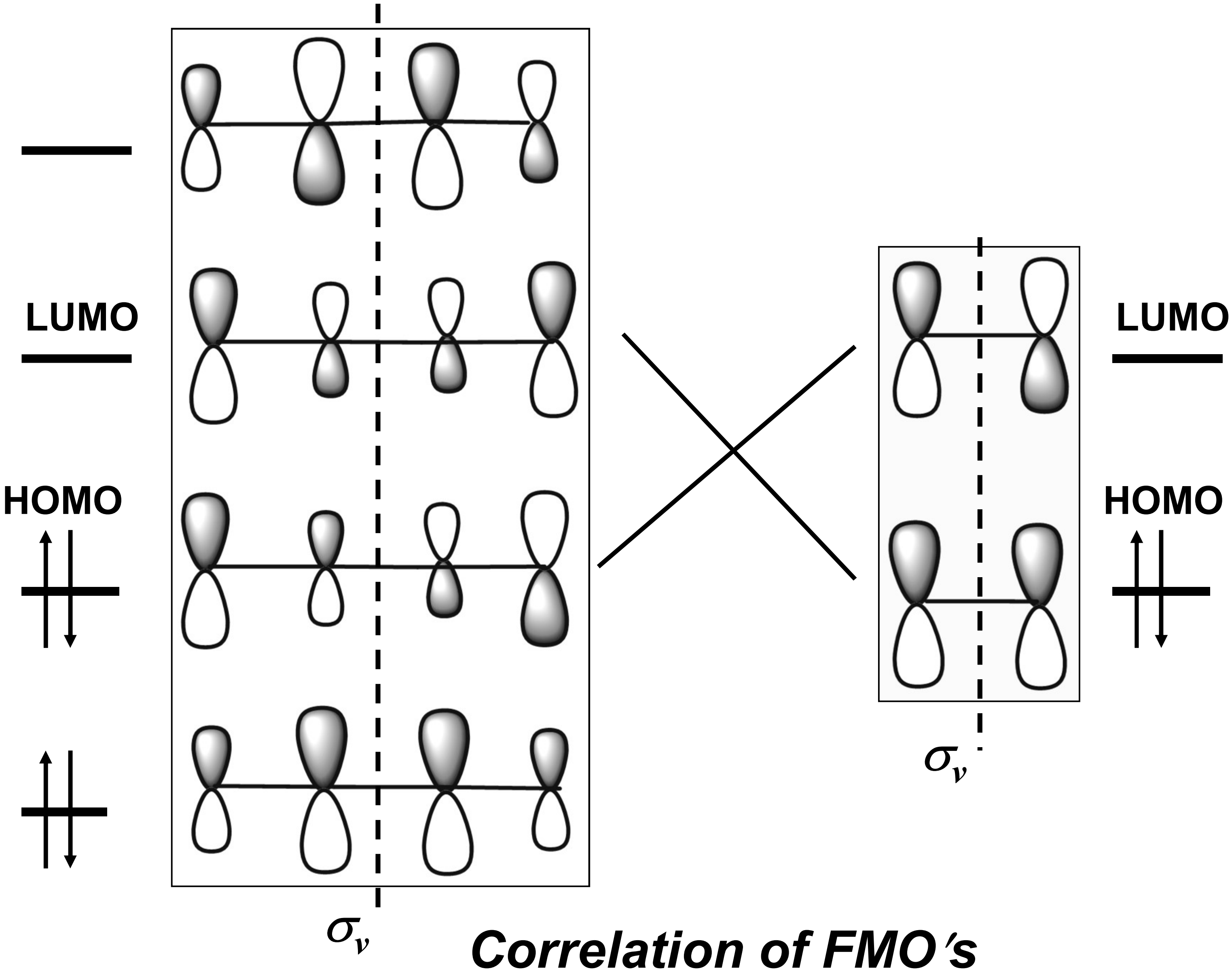
Diels-Alder Reaction [4+2]-π-electrons



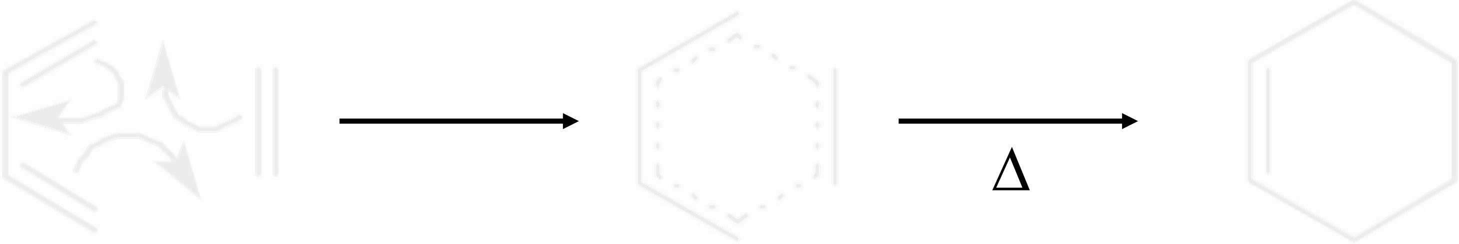
Transition state

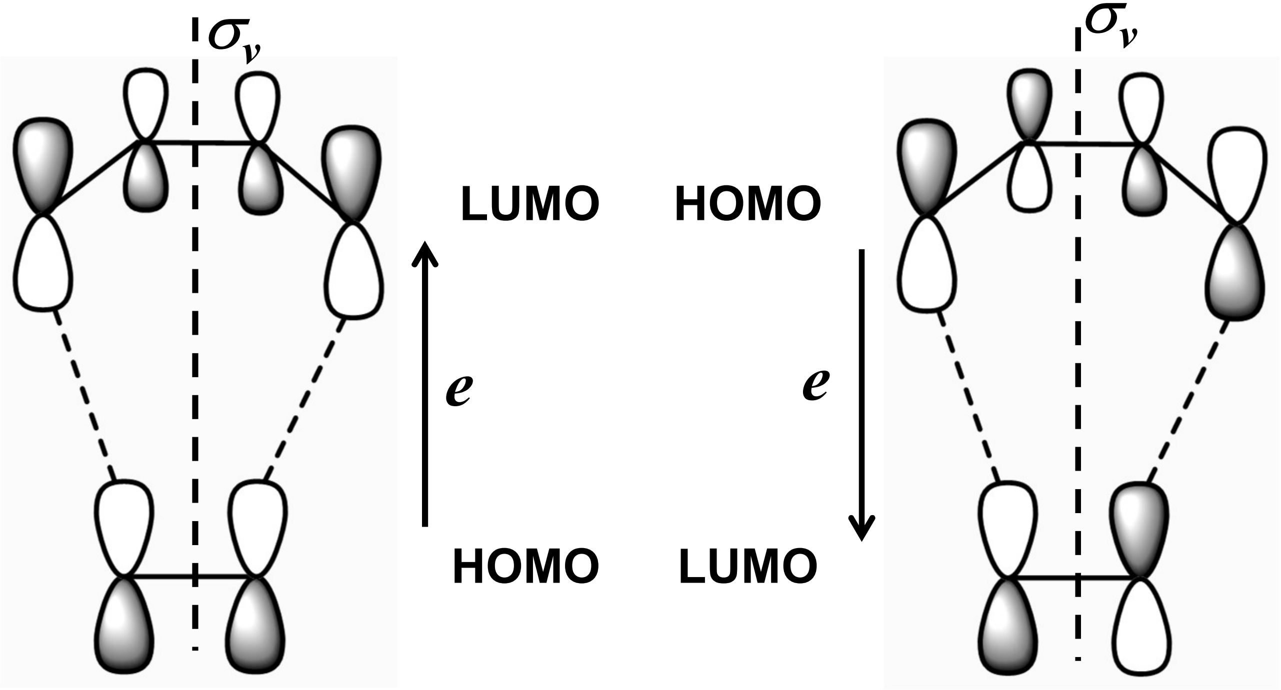
- We can illustrate the HOMO-LUMO interactions by way of the Diels-Alder reaction between ethylene and 1,3-butadiene.
- We need consider only the π electrons of ethylene and 1,3-butadiene, and ignore the framework of σ bonds in each reactants.

π-MO′s of 1,3-Butadiene π-MO′s of ethylene



Correlation of FMO′s

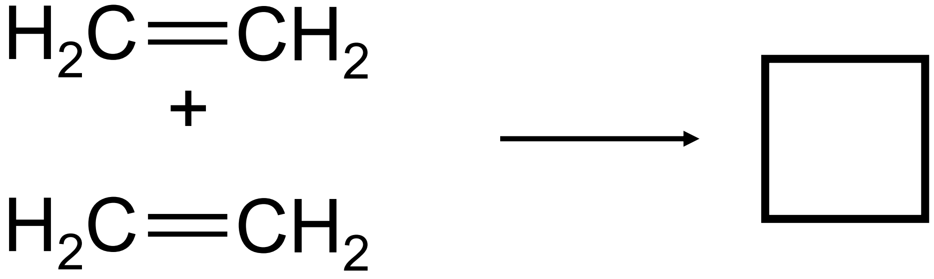




FMO′s of two reactants can overlap effectively!

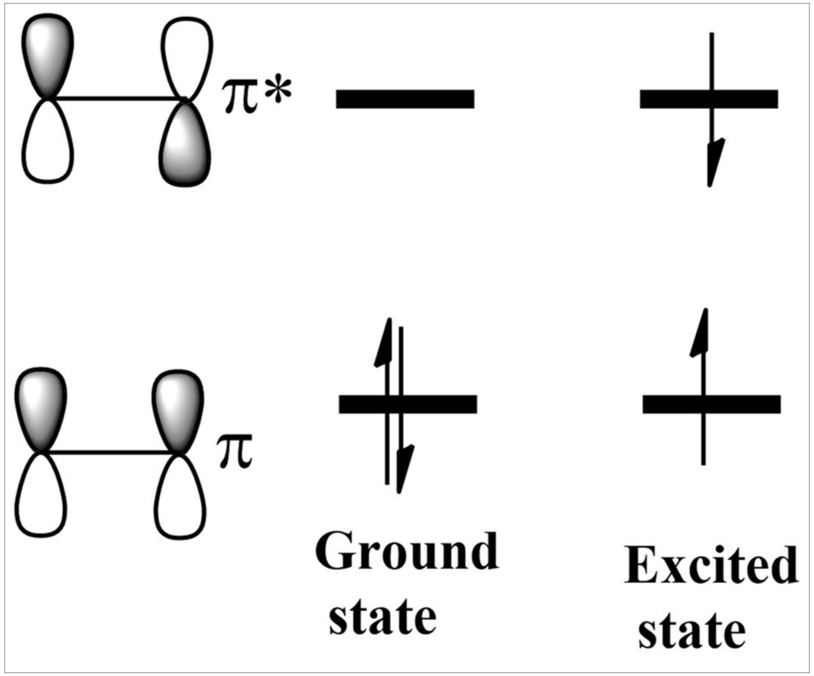
- Symmetry-allowed and thermally activated.

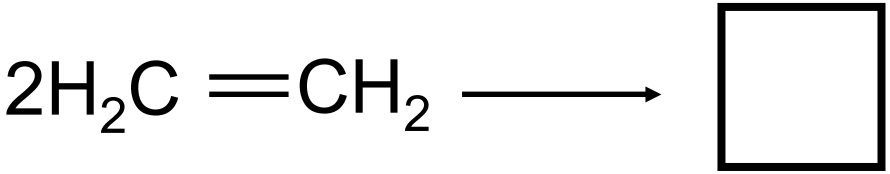
Example E: ***A thermally "forbidden" reaction***



- The dimerization of ethylene to give cyclobutane does not occur under conditions of typical Diels-Alder reactions(heating). i.e., it’s thermally forbidden.
- Why?

A thermally "forbidden" reaction





$2H_2C{=}CH_2 \longrightarrow$

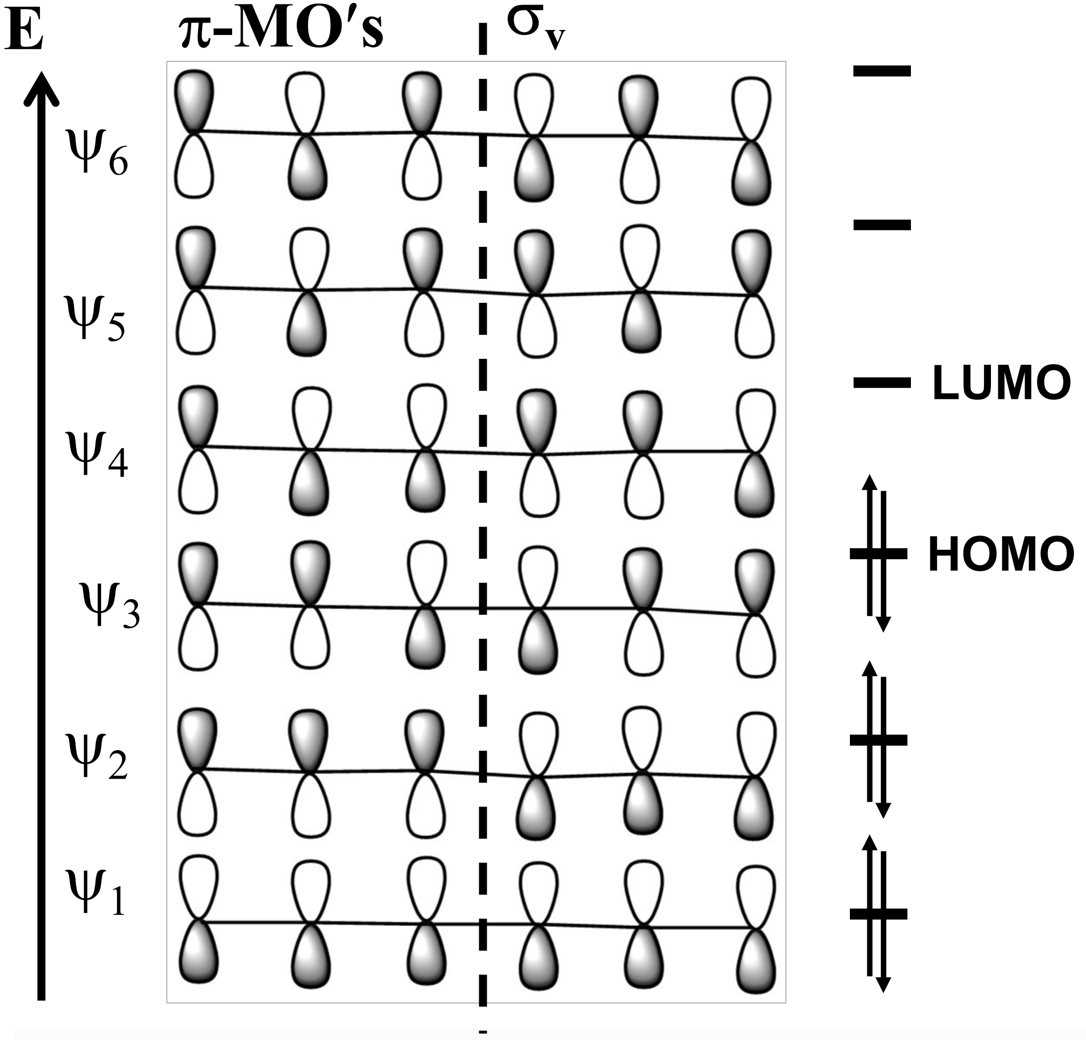
- HOMO-LUMO mismatch of two ethylene molecules in their ground state precludes single-step formation of two new σ bonds!

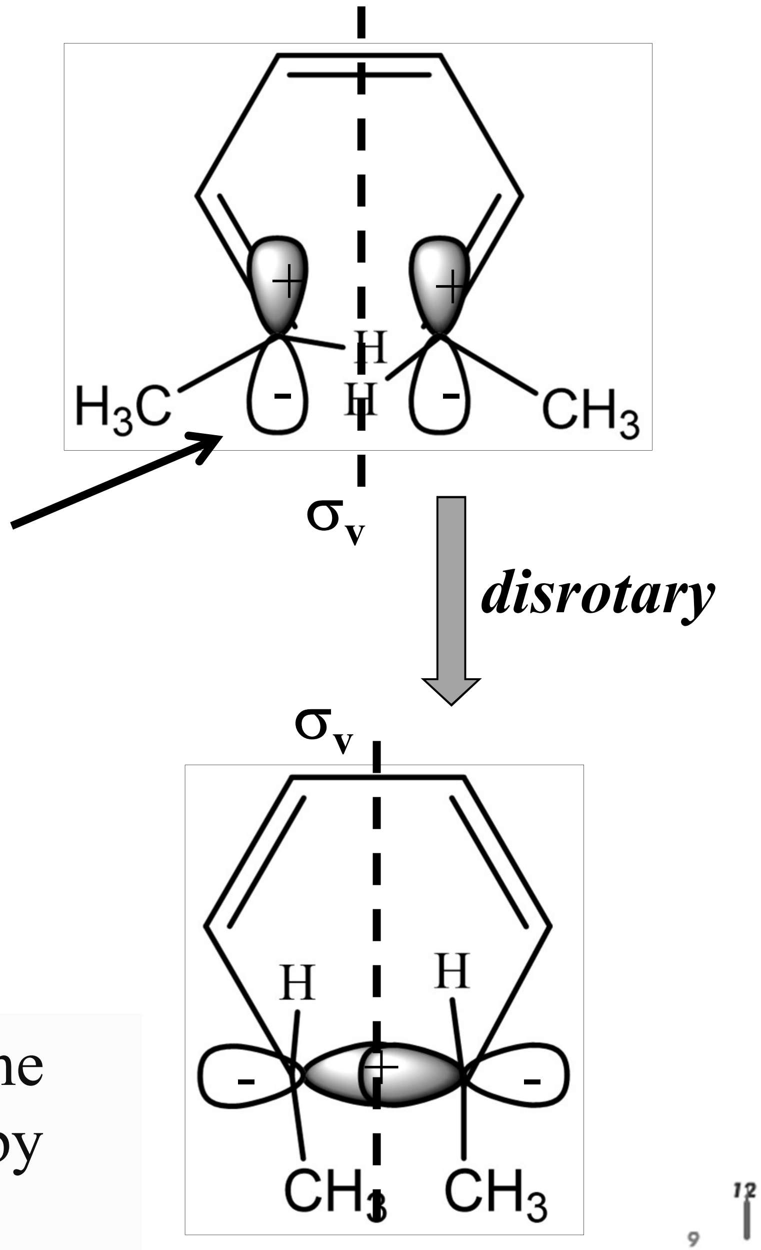
- The addition reaction is thermally forbidden, but allowed between two photo-excited ethenes.
- A catalyst-free photochemical reaction involves the LUMO orbitals of reactants, i.e., excited state of reactants.

Can the [2+2]-cycloaddition occur catalytically?

Example F: 2,4,6-Octatriene

Thermal Electrocyclic Reactions

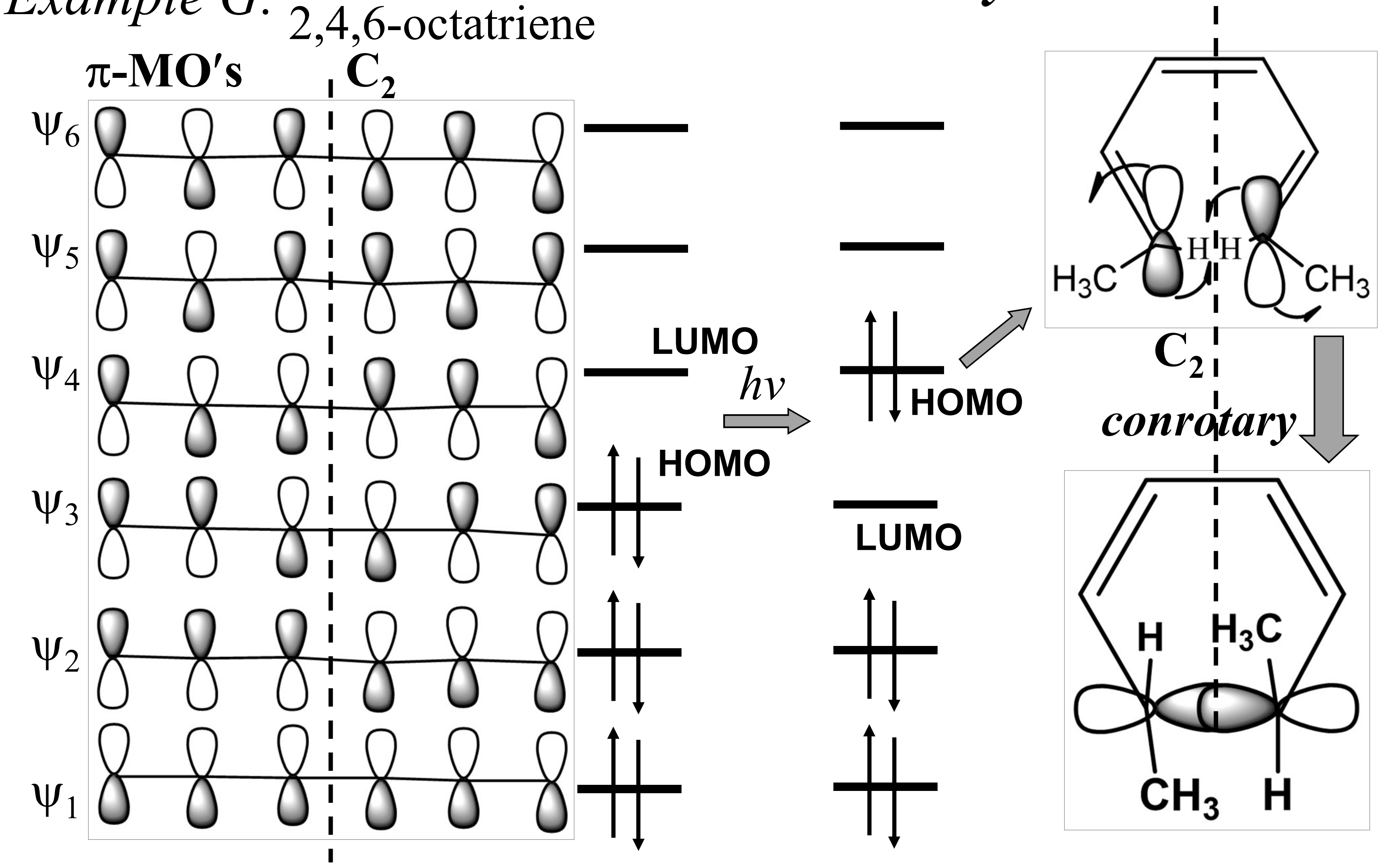




This reaction is thermally allowed with the stereochemistry of its product governed by the symmetry-allowed disrotary.

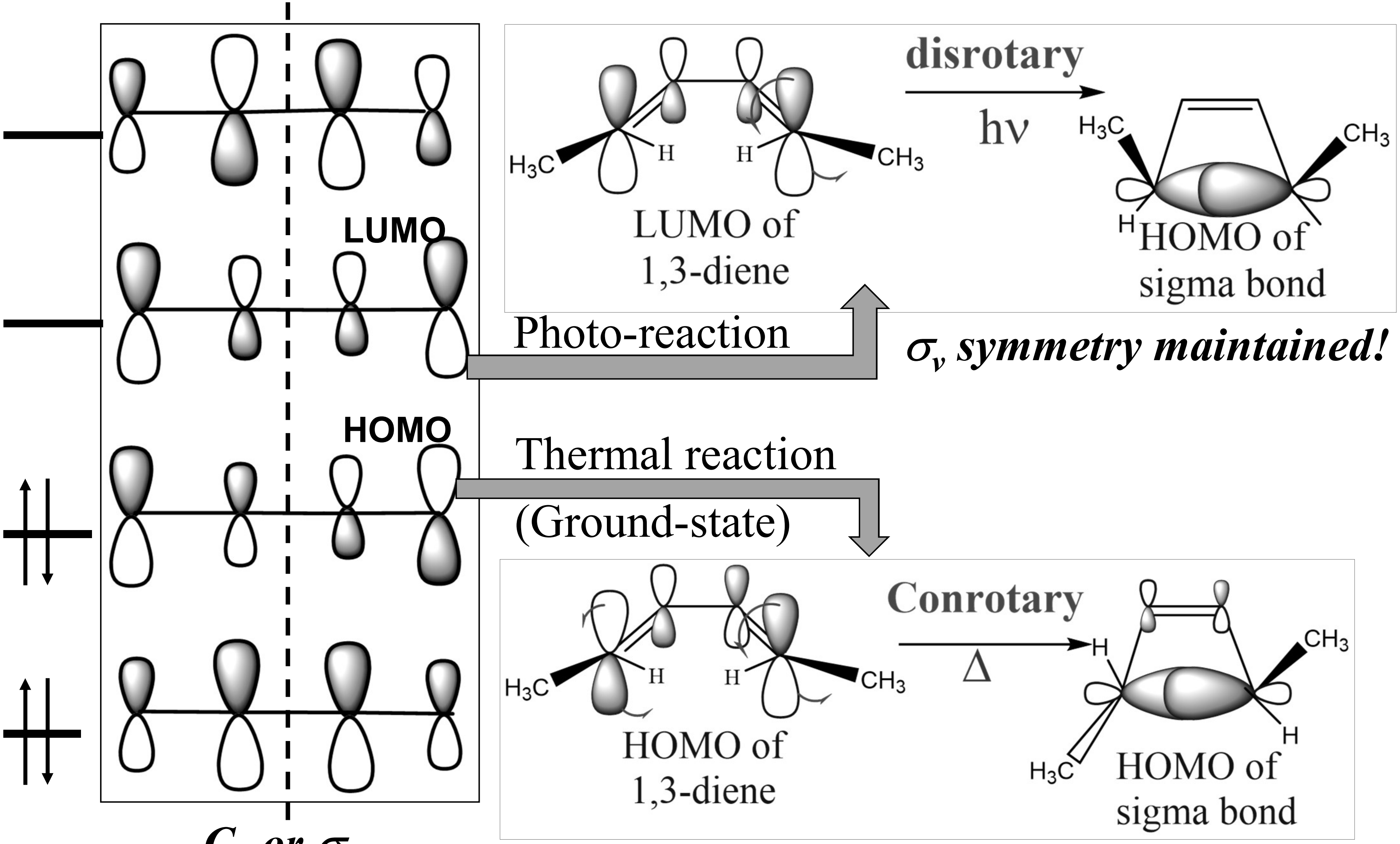
Photochemical Electrocyclic Reactions

Example G: 2,4,6-octatriene



This photochemical cyclic reaction occurs with the stereochemistry of its product being governed by the symmetry-allowed conrotary.

Example H: **Electrocyclic reaction of 1,3-diene**



***σ_v* symmetry maintained!**

***C_2* symmetry maintained!**

Stereochemical Rules for the Electrocyclic Reactions of [n]polyenes (n =even)

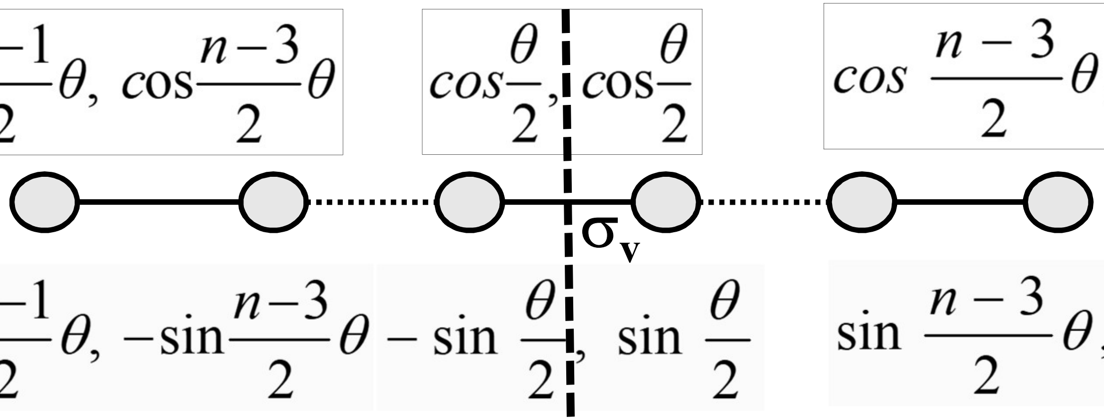
Number of Electron pairs (double bonds)	Thermal Reaction	Photochemical Reaction
Even (i.e., $n = 4k$)	conrotatory	disrotatory
Odd (i.e., $n = 4k+2$)	disrotatory	conrotatory

Why ?

[n]Polyenes with even-number p_π-orbitals.

Symm. $\cos\frac{n-1}{2}\theta,\ \cos\frac{n-3}{2}\theta$ $\cos\frac{\theta}{2},\ \cos\frac{\theta}{2}$ $\cos\frac{n-3}{2}\theta,\ \cos\frac{n-1}{2}\theta$

Upon σ_v



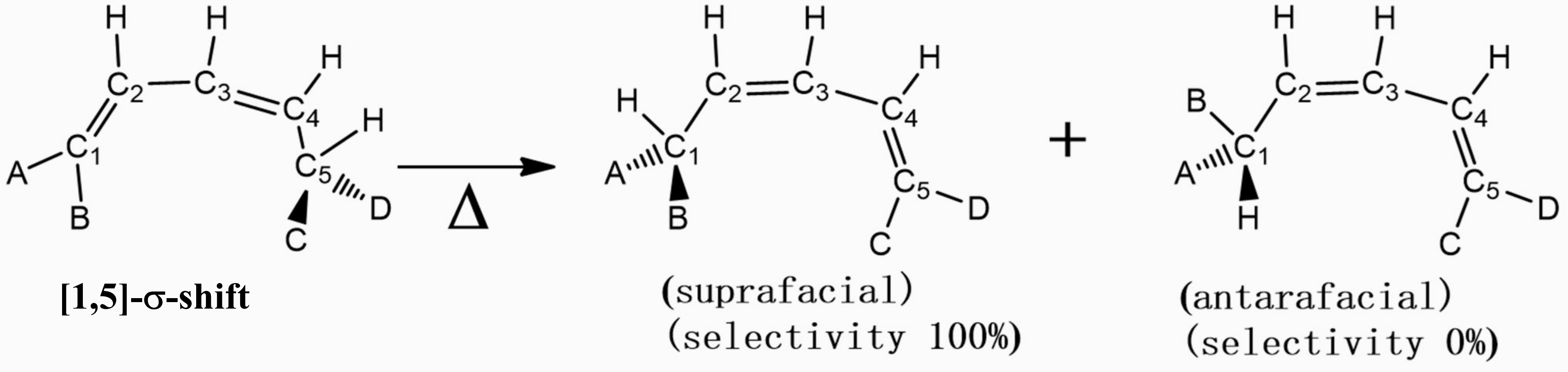
Asym. $-\sin\frac{n-1}{2}\theta,\ -\sin\frac{n-3}{2}\theta$ $-\sin\frac{\theta}{2},\ \sin\frac{\theta}{2}$ $\sin\frac{n-3}{2}\theta,\ \sin\frac{n-1}{2}\theta$

Nature of FMO′s	**HOMO** σ_v / C_2		**LUMO** σ_v / C_2	
n=4k (k=1,2,,..):	**Asym / Sym**		**Sym / Asym**	
n=4k+2 (k=1,..):	**Sym / Asym**		**Asym / Sym**	

	Thermal reaction (HOMO-based)	**Photo-reaction (LUMO-based)**
n=4k	**Conrotary (C_2)**	**Disrotary (σ_v)**
n=4k+2	**Disrotary (σ_v)**	**Conrotary (C_2)**

Stereochemical rules for electrocyclic reactions

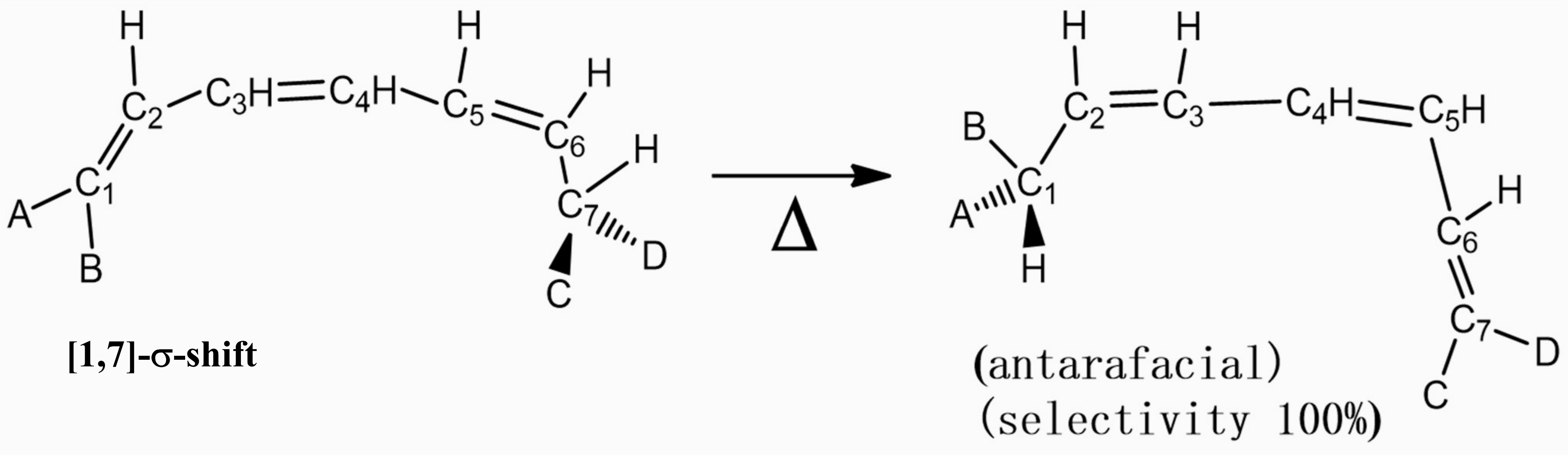
[1,n] sigmatropic shift : stereochemical rules



[1,5]-σ-shift

(suprafacial)
(selectivity 100%)

(antarafacial)
(selectivity 0%)



[1,7]-σ-shift

(antarafacial)
(selectivity 100%)

Strategy: Suppose the transition state is a combination of a H atom and a [n]polyene with odd-number p_π orbitals.

[n]Polyenes: *n=odd*

$$\psi = \sum_i c_i \phi_i$$

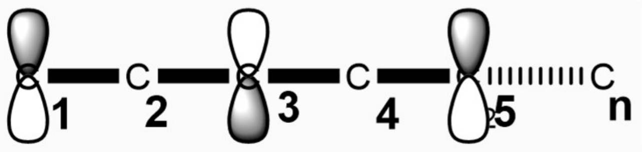
c_i $\sin\theta, \sin 2\theta \ldots.$ $\sin(n-1)\theta,\ \sin n\theta$

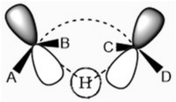
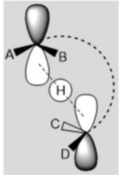
$$\theta = m\pi/(n+1);\quad E = \alpha + 2\beta\cos\theta \quad (m = 1,2,\ldots.n)$$

If n =odd, **SOMO, m = (n+1)/2,** $\theta_{somo} = \pi/2,\ E_{somo} = \alpha$

$$c_1 = \sin(\pi/2) = 1;\ c_2 = 0;\ c_3 = -1;\ldots, c_n = \sin(n\pi/2)$$

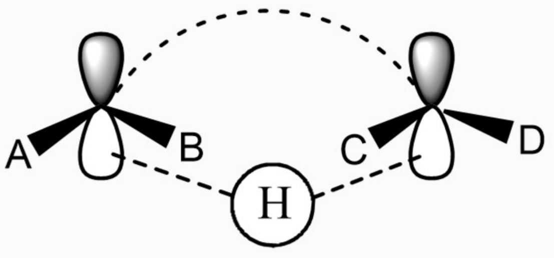
$$\Rightarrow \psi_{SOMO} = A\sum_{k=1}^{n}(\phi_1 - \phi_3 + \phi_5 - \ldots) \Rightarrow$$



	Symmetry of SOMO			**Sigmatropic shift**		
	σ_v	C_2		**TS symmetry**		**Mode**
n= 4k+1	**Sym.**	**Asym.**		$\sigma_v \rightarrow$ 		**Suprafacial**
n= 4k+3	**Asym.**	**Sym.**		$C_2 \longrightarrow$		**Antarafacial**

Note that the H-shift demands both ends of SOMO of [n]polyene (***n=odd***) to overlap effectively with the H 1s orbital.

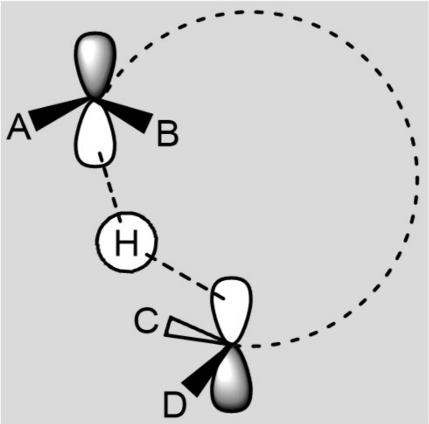
- The sigmatropic H-transfer demands both ends of SOMO of such [n]polyene (***n=odd***) can overlap with the H 1s orbital. i.e.,



n=4k+1

Suprafacial mode

TS requires C_S-symmetry!

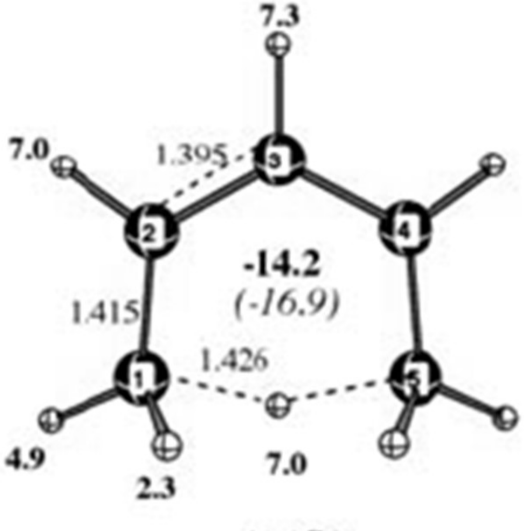


n=4k+3

antarafacial mode

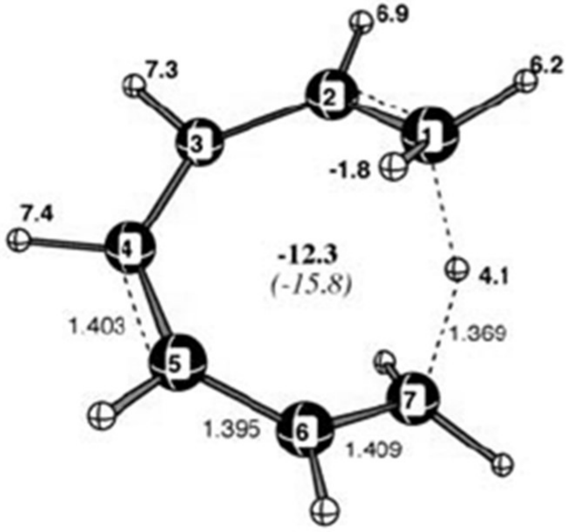
TS requires C_2-symmetry!

QM-predicted transition states of [1,n]-sigmatropic shift



41 (C_s)

[1,5]-sigmatropic shift



53 (C_2)

[1,7]-sigmatropic shift

2. Woodward-Hoffmann rules --- principle of orbital symmetry conservation （ 分子轨道对称性守恒原理）

Proposed originally to predict the stereochemistry of pericyclic reactions based on orbital symmetry.

i. There is a one to one correspondence between the MO’s of the reactant and the product.

ii. The symmetry of the correlated orbitals is the same.

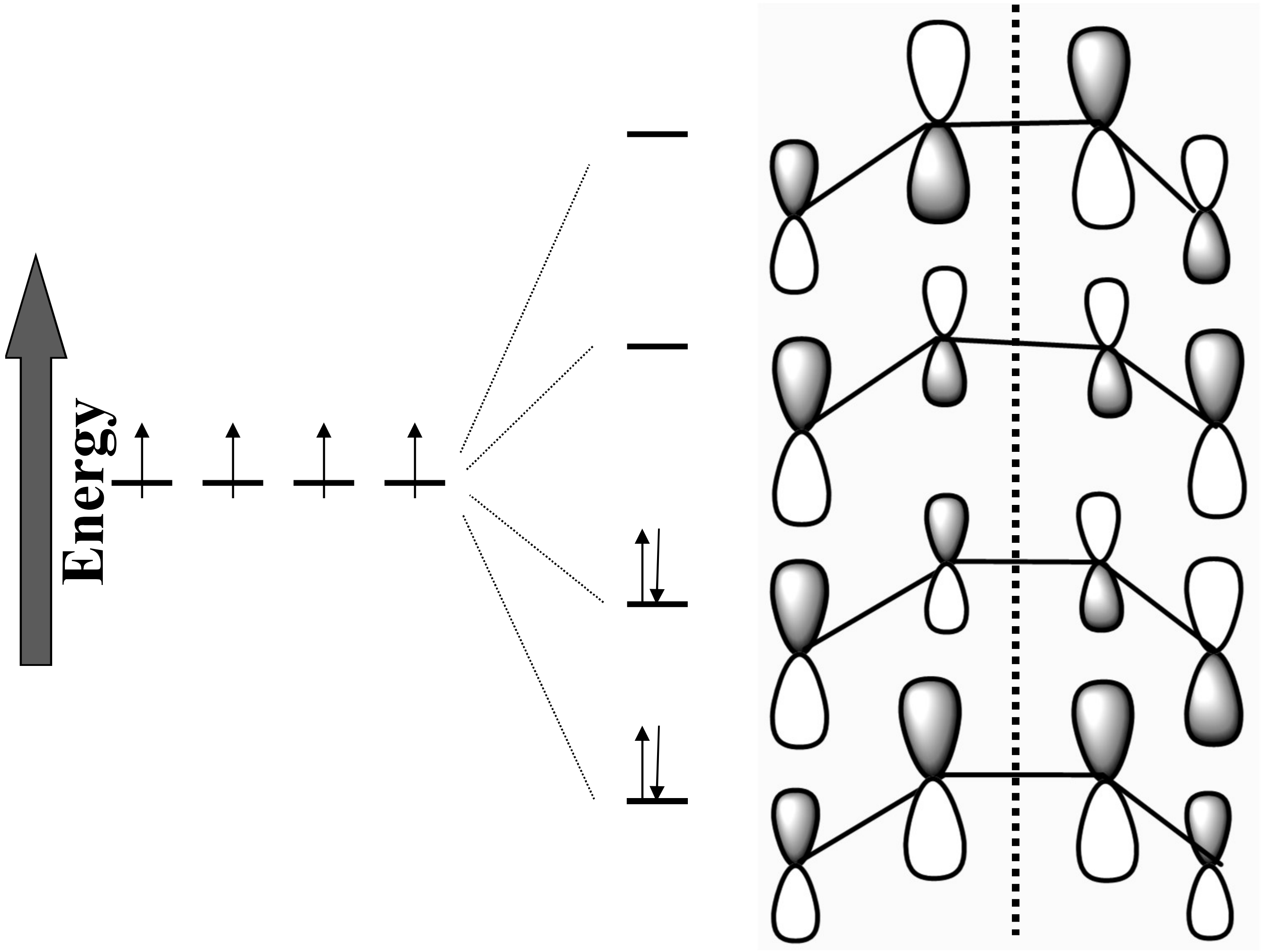
iii. The correlated orbitals should have comparable energies.

iv. The correlation lines for orbitals with the same symmetry do not intersect.

Orbital Symmetry Conservation

Example A: ***Electrocyclic Reactions of butadiene***

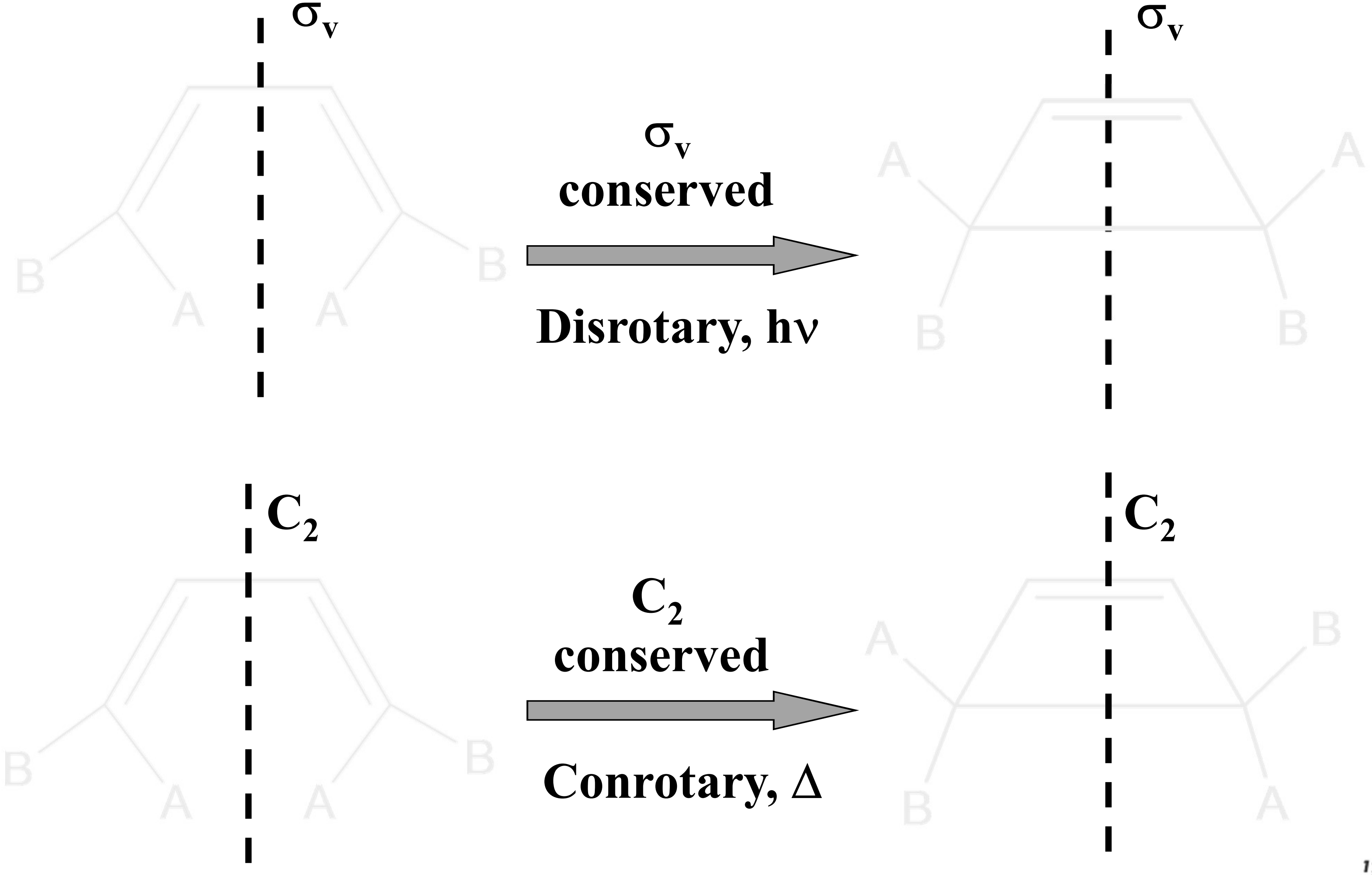
π MOs of butadiene



σ_v	C_2	
A	**S**	
S	**A**	LUMO
A	**S**	HOMO
S	**A**	

Orbital Symmetry Conservation

Orbital Symmetry Conservation

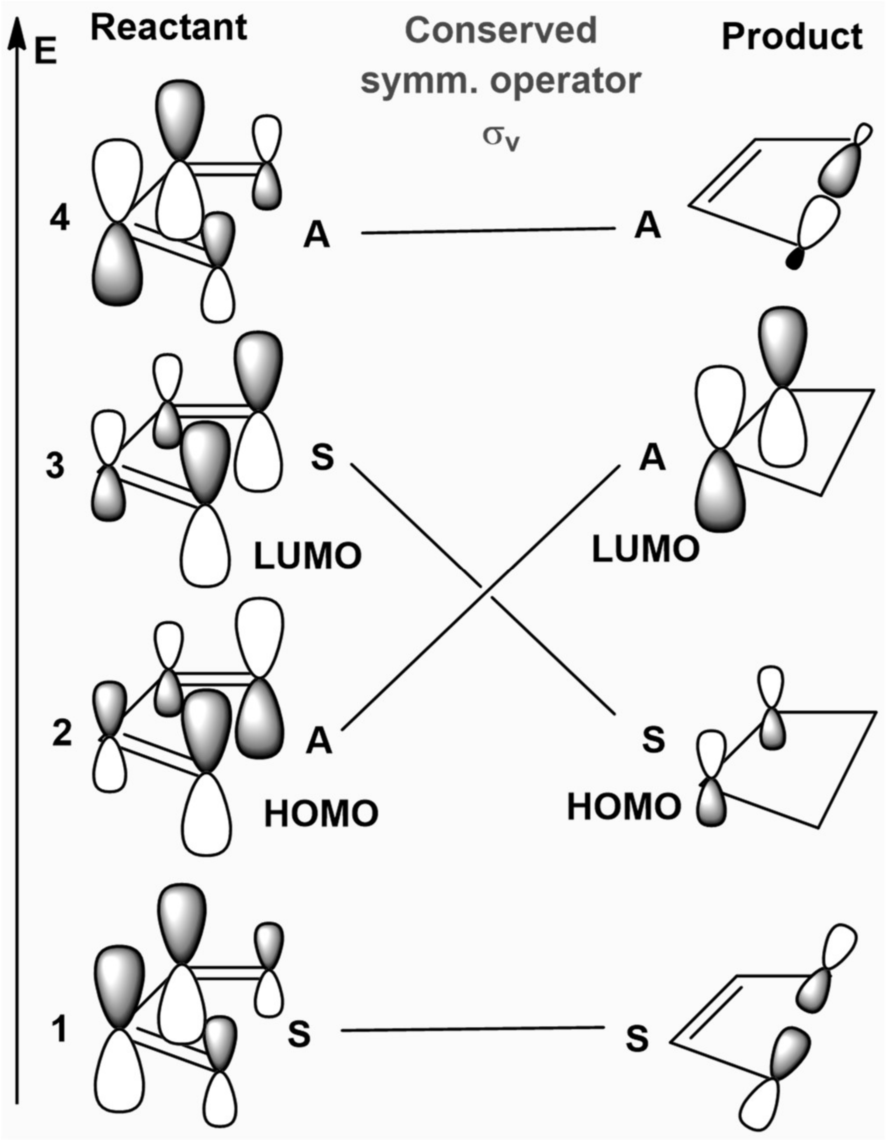


σ_v conserved

Disrotary, hν

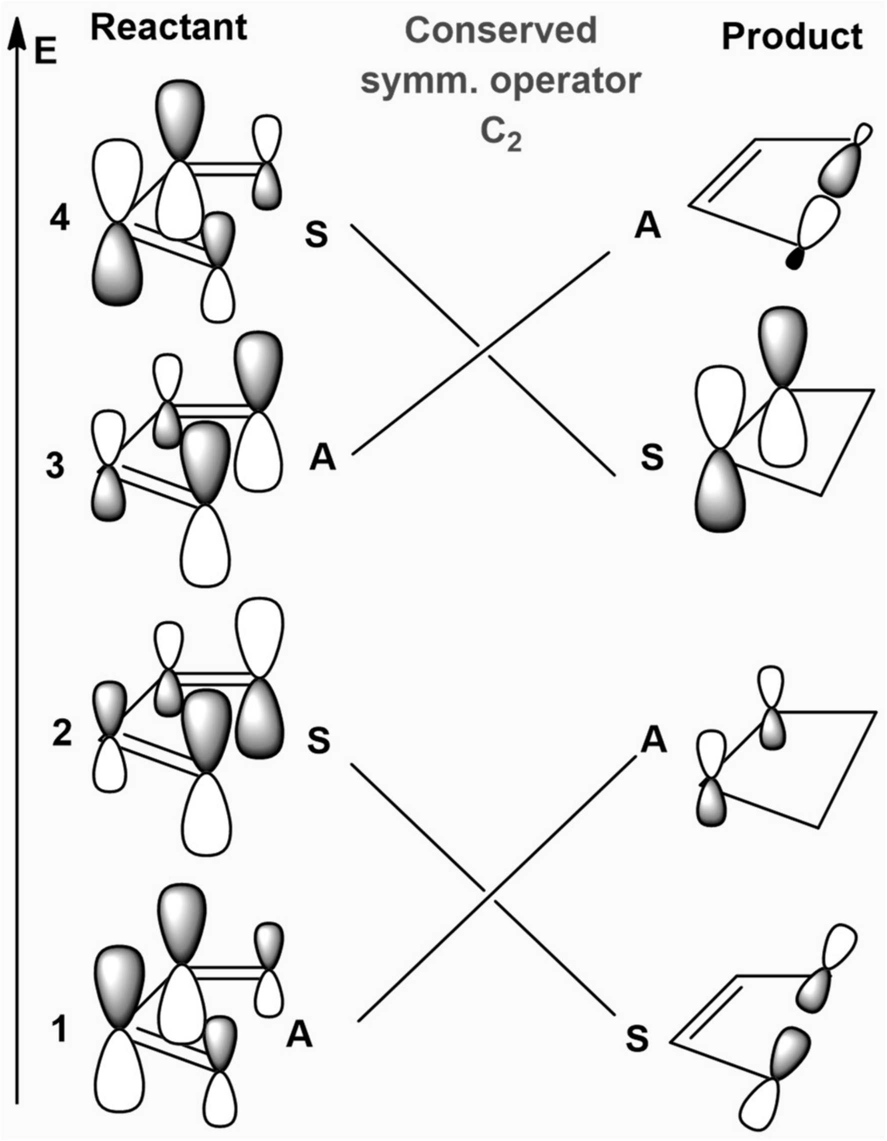
C_2 conserved

Conrotary, Δ



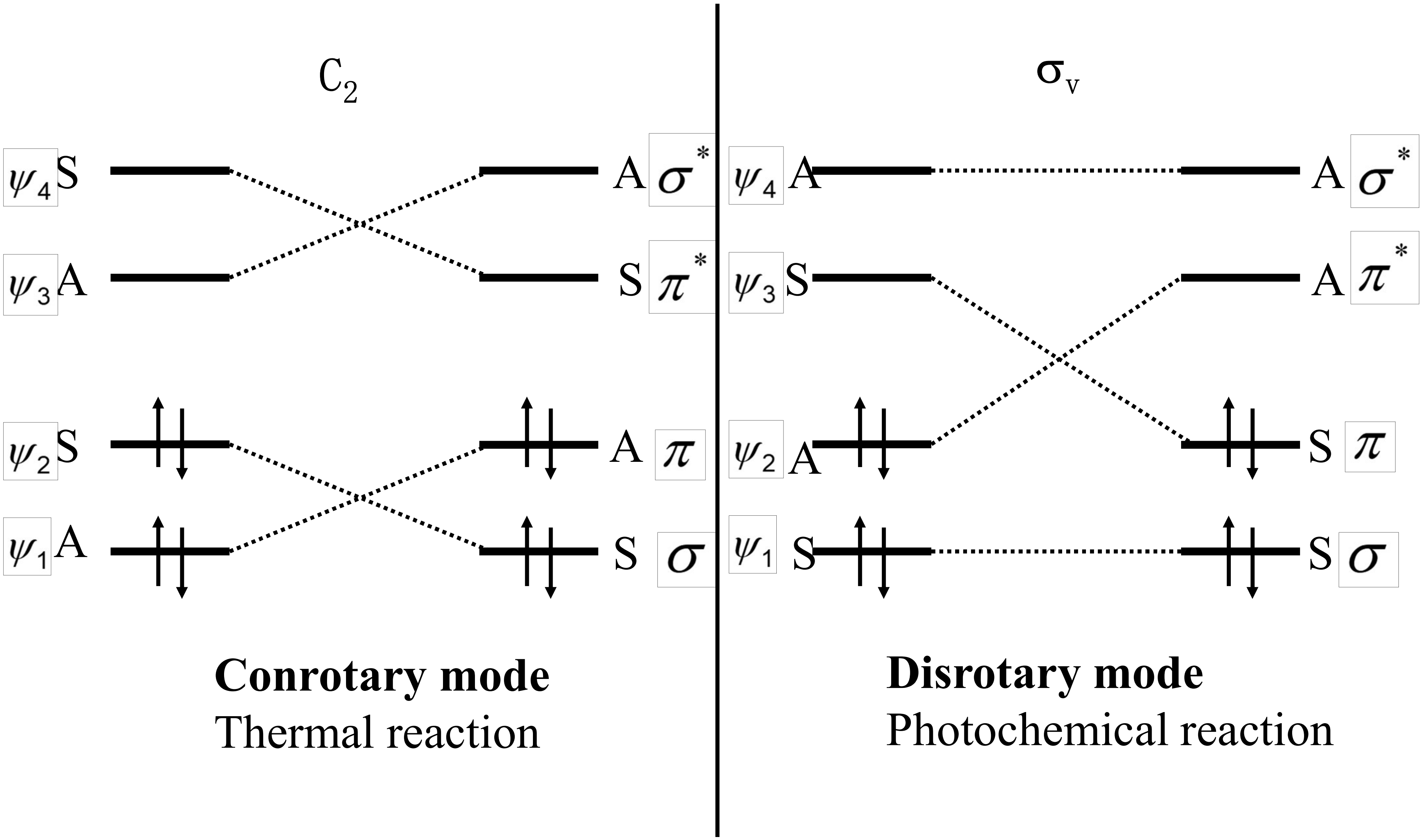
Energy/orbital correlation diagram

1. During the disrotatory cyclic reaction, the systems have a common σ_v symmetry.
2. Thus the symmetries of all involved molecular orbitals subject to this operation should be maintained before/after the reaction.
3. In this regard, the HOMO and LUMO of the reactant are correlated with the LUMO and HOMO of the product by conservation of orbital symmetry.
4. Thus the reaction should be photo-promoted.



Energy correlation diagram

1. During the conrotatory cyclic reaction, the C_2 symmetry is conserved.
2. The symmetries of all involved molecular orbitals subject to this operator should be maintained before/after the reaction.
3. The HOMO and HOMO-1 of the reactant are correlated with the HOMO-1 and HOMO of the product. So do the unoccupied MO's.
4. Thus the reaction occurs for the reactant at its ground state.



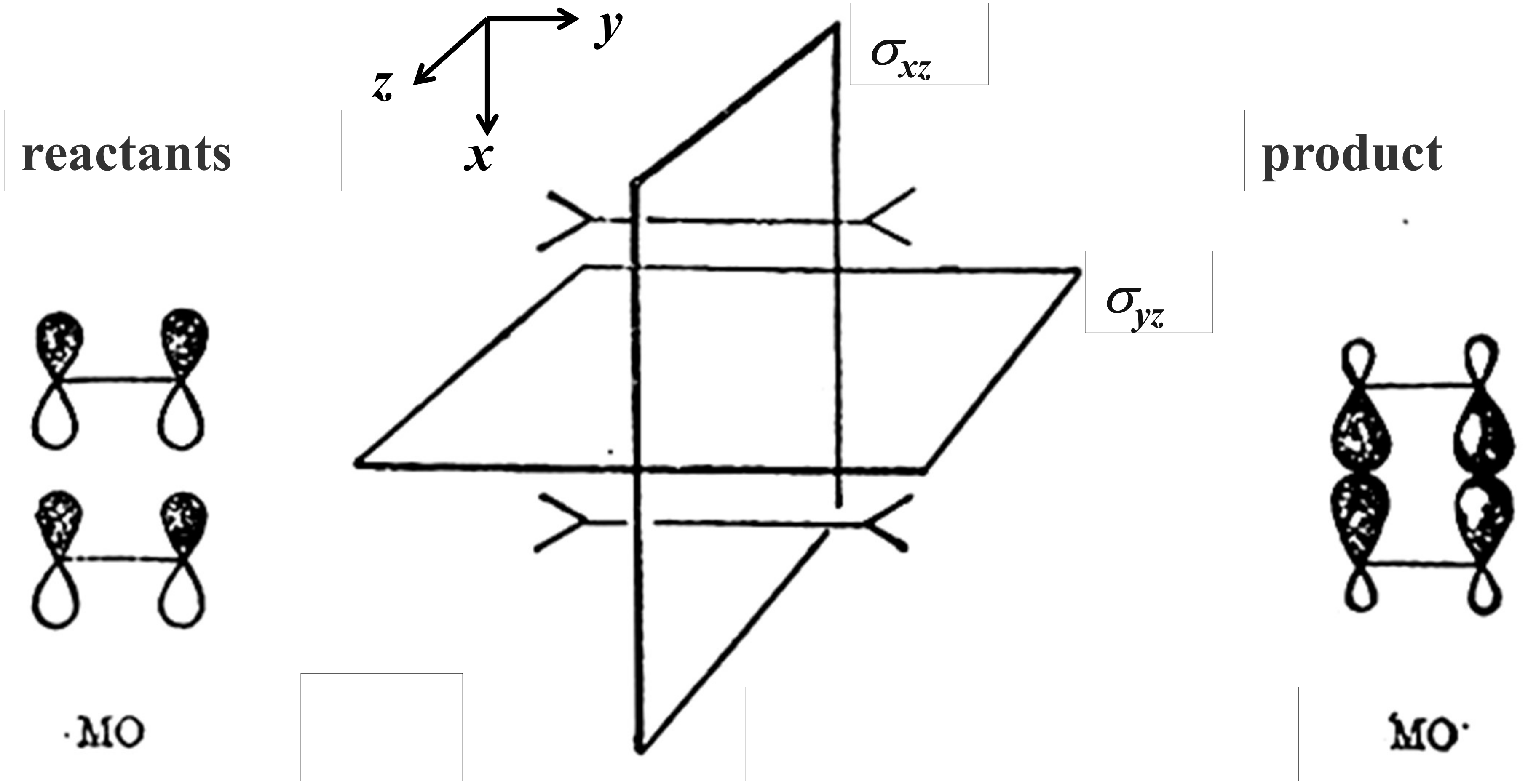
Conrotary mode
Thermal reaction

Disrotary mode
Photochemical reaction

The MO correlation diagrams of (a) conrotary and (b) disrotary cyclic reactions of butadiene to cyclobutene

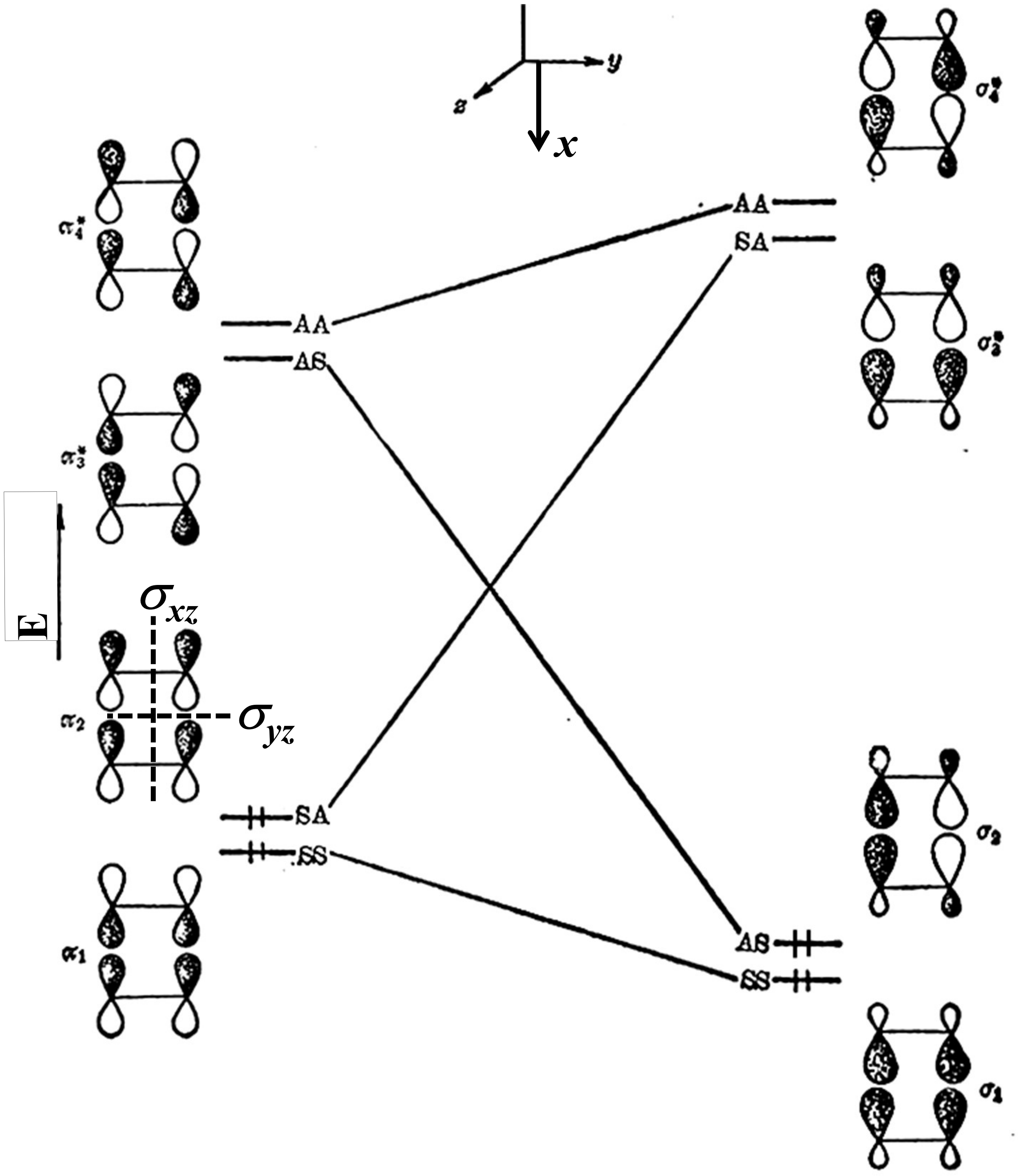
Example B: ***Cycloaddition of ethylene: a photochemical reaction***

$2H_2C{=}CH_2 \longrightarrow$



reactants

product



In photochemical reaction mode

- Conserved symm. Operators: σ_{xz} and σ_{yz}.
- The HOMO and LUMO of reactants are correlated with the LUMO and HOMO of the product, respectively.
- Thus excited states of the reactants should be involved for the reaction to occur.

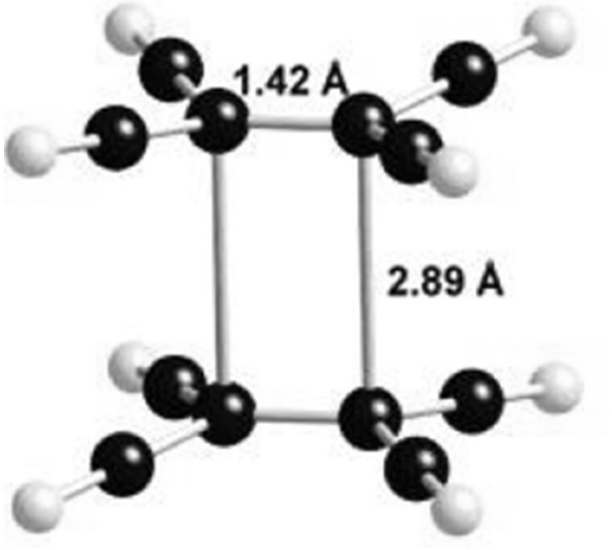
FMO theory vs. Orbital symmetry conservation principle

Symmetry of MO′s ⇔

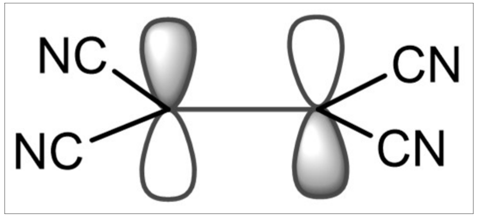
- Viability of reactions
- Stereochemical rules of reactions.

FMO theory	Orbital symmetry conservation principle
• FMO′s of reactants	• All correlated valence MO′s of reactants and products
• Symmetry of the FMO′s determines everything.	• Need to figure out the symmetry operators conserved in the reactions.
• Simple, and widely applicable	• Useful, yet a bit complicated

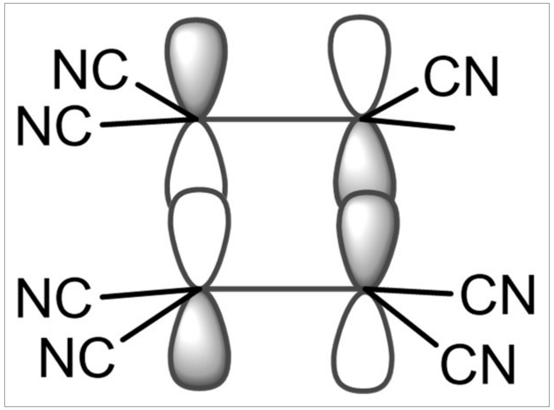
The reaction of [Et$_4$N]I and tetracyanoethylene (TCNE) forms [Et$_4$N]$_2$[TCNE]$_2$, which possesses [TCNE]$_2^{2-}$ with an intradimer C-C bond distance of 2.827(3) Å (CrystEngComm, 2001, 47,1). Please analyze the unusual intradimer bonding.



- The LUMO of neutral TCNE is the π* MO of the C=C moiety.
- The SOMO of [TCNE]$^-$:



- So the SOMOs of two [TCNE]$^-$ are symmetry-compatible and can effectively interact with each other!



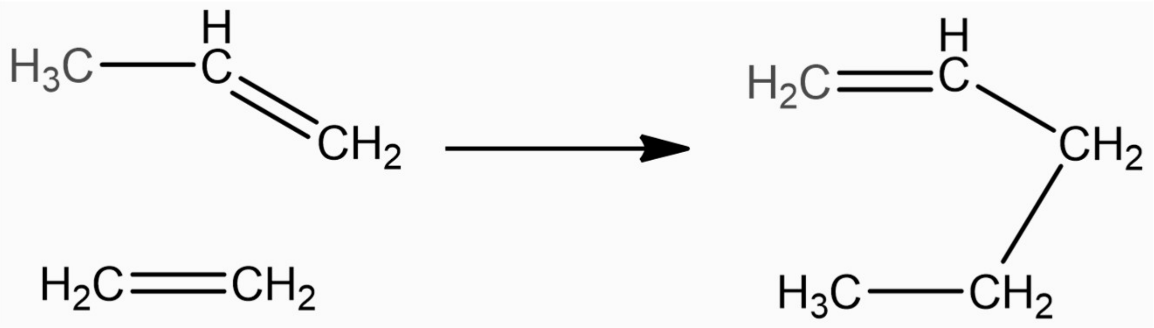
Spin conservation

- A chemical reaction occurs with conservation of spin.

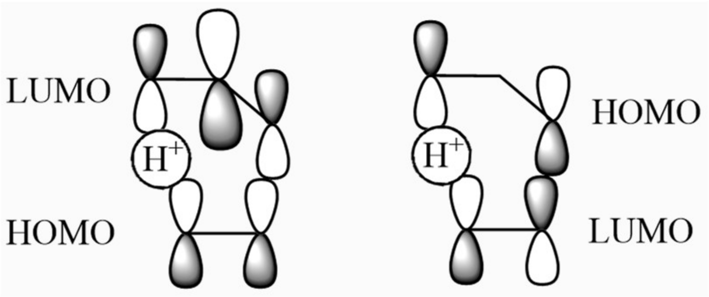
$$2H_2({}^1\Sigma_g^+) + O_2({}^3\Sigma_g^-) \xcancel{\xrightarrow[\Delta]{}} 2H_2O({}^1A_1)$$

$$C_2H_4(s=0) + C_4H_6(s=0) \xrightarrow[\Delta]{} C_6H_{10}(s=0)$$

- Please make use of the FMO theory to assess whether the ene reaction can occur thermally?



Hint: In the transition state of this reaction, the propene can be regarded as an allylic anion and a proton.



Symmetry allowed!

Summary of Chapter 5

Key points/concepts

1. Hybrid orbital theory and VSEPR

   (Mostly Qualitative Theory/model!)

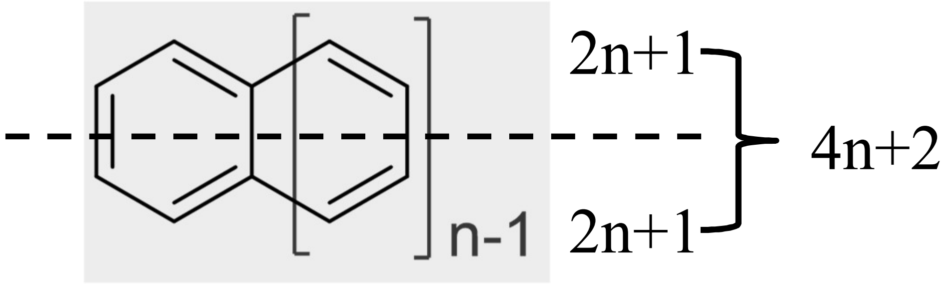
2. HMO, HMO treatment of π-conjugated systems

3. Graphical method to predefine coefficients of HMO of π-conjugated systems. (Semi-quantitative Theory)

4. Symmetry rules for molecular reactions.

   (Qualitative Theory)

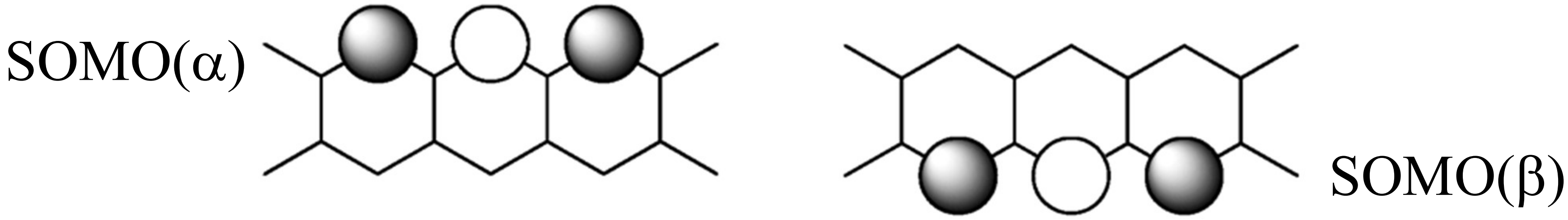
[n]Polyacene: laterally fused benzene rings



$$\Pi_{4n+2}^{4n+2}$$

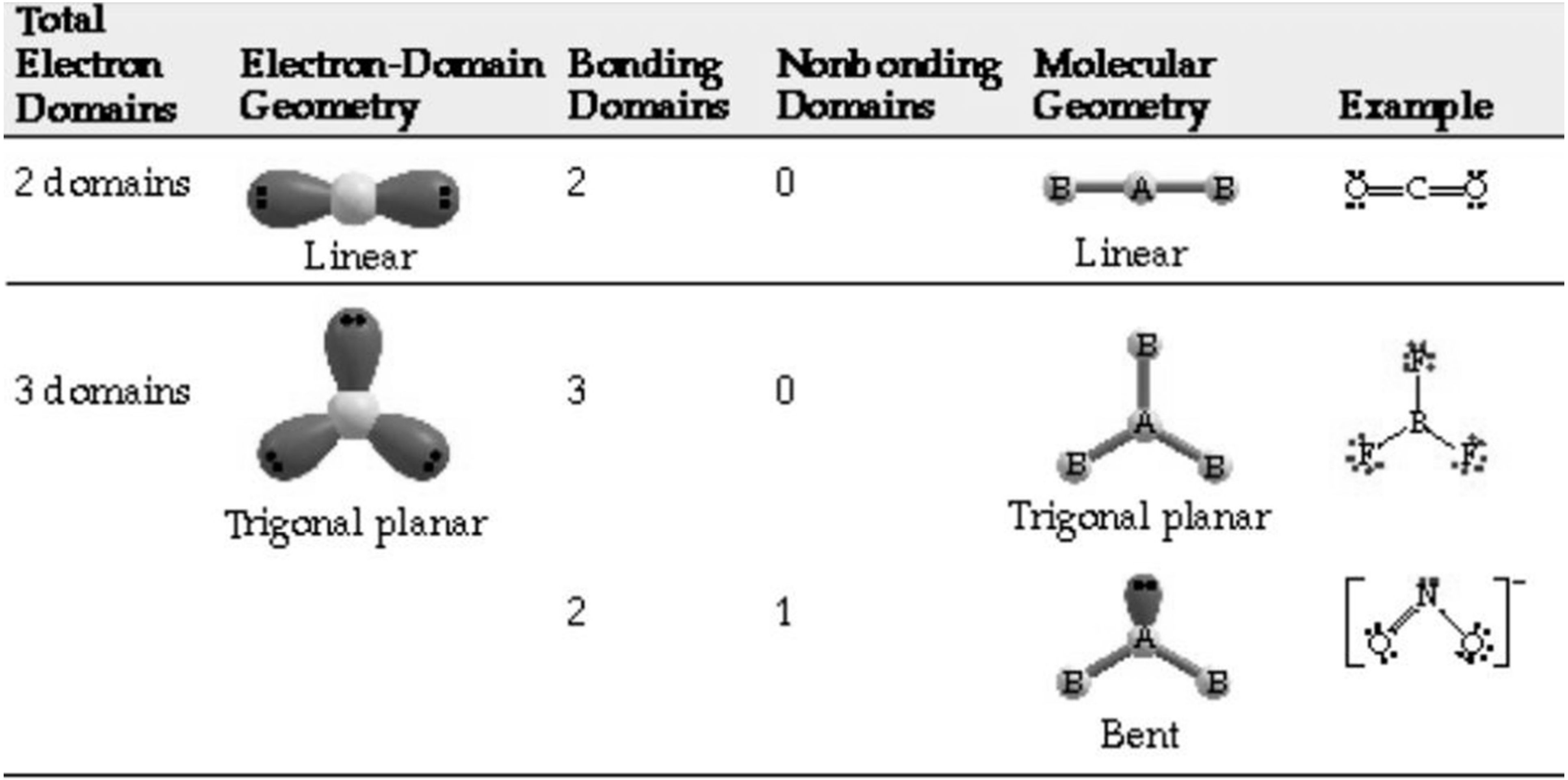
Benzene, naphthalene, anthracene,.., pentacene, hexacene,…

1) HOMO-LUMO gap of oligoacene decreases with increasing of n.
2) Pristine oligoacene becomes instable with n > 5.
3) When n > 6, pristine oligoacene adopts an open-shell singlet ground state, i.e., biradical. (*J. Am. Chem. Soc., 2004, 126, 7416*)

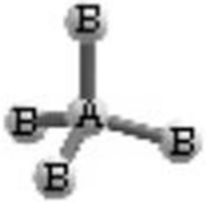
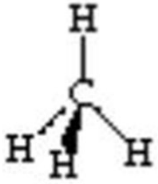
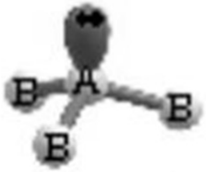
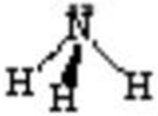
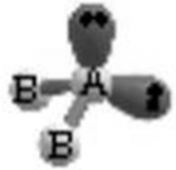


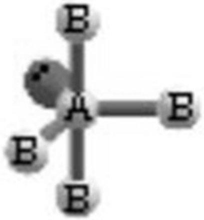
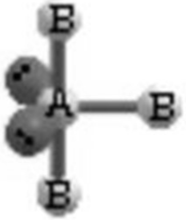
Two degenerate disjoint non-bonding orbitals of [n]polyacene. (n>6)

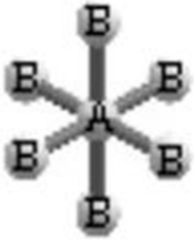
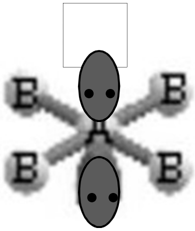
Spatial Arrangements of Electron Pairs in Terminal Atoms in AB_n



Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2 domains	Linear	2	0	B—A—B Linear	$O=C=O$
3 domains	Trigonal planar	3	0	Trigonal planar	
		2	1	Bent	

4 domains	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

5 domains	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

6 domains	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

$$\cos(\alpha \pm \beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$

$$\cos\alpha + \cos\beta = 2\cos\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2}$$

$$\cos\alpha - \cos\beta = -2\sin\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2}$$

$$\sin\alpha + \sin\beta = 2\sin\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2}$$

$$\sin\alpha - \sin\beta = 2\cos\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2}$$

[n]Polyenes: Nature of their FMOs

C_i $\sin\theta, \sin 2\theta ....$ $\sin(n-1)\theta,\ \sin n\theta$

$$\theta = m\pi/(n+1); \quad E = \alpha + 2\beta\cos\theta \quad (m = 1,2,....n)$$

ne_π, bonding MOs, $\theta \le \pi/2$; *If n being an even number,*

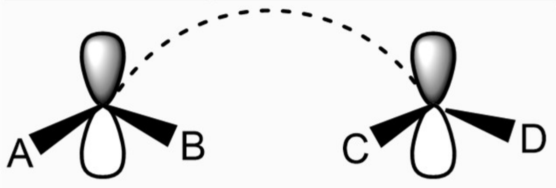
HOMO: m = n/2 $\theta = n\pi/2(n+1)$ **LUMO: m = (n/2)+1** $\theta = (n+2)\pi/2(n+1)$

Nature of HOMO $c_1 = \sin\theta = \sin[n\pi/2(n+1)] = \cos[\pi/2(n+1)]$

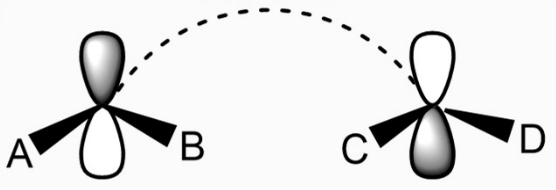
$$c_n = \sin n\theta = \sin\frac{n^2}{2(n+1)}\pi = \sin\left\{\frac{n}{2}\pi - [\frac{\pi}{2} - \frac{\pi}{2(n+1)}]\right\}$$

If n= 4k $c_n = \sin\left\{\frac{n}{2}\pi - [\frac{\pi}{2} - \frac{\pi}{2(n+1)}]\right\} = -\cos\frac{\pi}{2(n+1)} = -c_1$ **Asymmetric**

If n= 4k+2 $c_n = \sin\left\{\frac{n}{2}\pi - [\frac{\pi}{2} - \frac{\pi}{2(n+1)}]\right\} = \cos\frac{\pi}{2(n+1)} = c_1$ **symmetric**



symmetric



asymmetric

[n]Polyenes: Nature of their FMOs

C_i

$\sin\theta, \sin 2\theta....$ $\quad$ $\sin(n-1)\theta,\ \sin n\theta$

$$\theta = \mathrm{m}\pi/(\mathrm{n}+1);\quad \mathrm{E} = \alpha + 2\beta\cos\theta\quad (\mathrm{m} = 1,2,....\mathrm{n})$$

LUMO **m = (n/2)+1** $\theta = (n+2)\pi/2(n+1)$

Nature of LUMO

$$c_1 = \sin\theta = \sin[(n+2)\pi/2(n+1)] = \cos[\pi/2(n+1)]$$

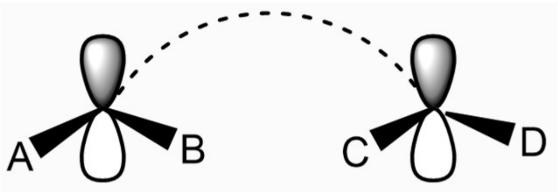
$$c_n = \sin n\theta = \sin\frac{\mathrm{n(n+2)}}{2(n+1)}\pi = \sin\left\{\frac{n}{2}\pi + [\frac{\pi}{2} - \frac{\pi}{2(n+1)}]\right\}$$

If n= 4k

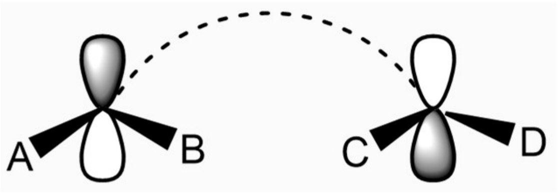
$$c_n = \sin\left\{\frac{n\pi}{2} + [\frac{\pi}{2} - \frac{\pi}{2(n+1)}]\right\} = \cos\frac{\pi}{2(n+1)} = c_1$$ **symmetric**

If n= 4k+2

$$c_n = \sin\left\{\frac{n}{2}\pi + [\frac{\pi}{2} - \frac{\pi}{2(n+1)}]\right\} = -\cos\frac{\pi}{2(n+1)} = -c_1$$ **asymmetric**



symmetric



asymmetric

[n]Polyenes: Nature of their FMOs

C_i

$\sin\theta, \sin 2\theta ....$ $\sin(n-1)\theta,\ \sin n\theta$

$$\theta = m\pi/(n+1); \quad E = \alpha + 2\beta\cos\theta \quad (m = 1,2,....n)$$

ne_π, bonding MOs, $\theta \le \pi/2$; *If n being an odd number,*

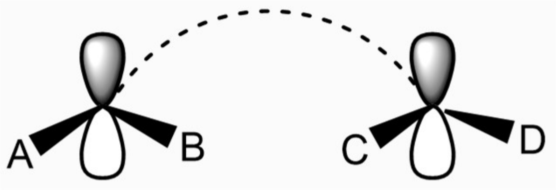
SOMO **m = (n+1)/2** $\theta = \pi/2$

Nature of SOMO $c_1 = \sin\theta = \sin(\pi/2) = 1;\ c_2 = 0;\ c_3 = -1;$

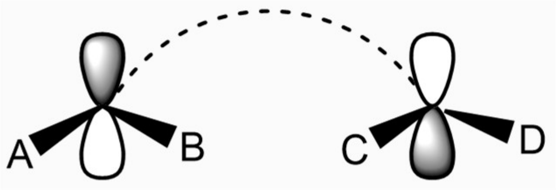
$$..., c_n = \sin n\theta = \sin\frac{n}{2}\pi$$

If n= 4k+1 $c_n = \sin\dfrac{n\pi}{2} = \sin(2k\pi + \pi/2) = 1 = c_1$ **symmetric**

If n= 4k+3 $c_n = \sin\dfrac{n\pi}{2} = \sin(2k\pi + 3\pi/2) = -1 = -c_1$ **asymmetric**



symmetric



asymmetric

HMO Treatment: Linear [n]polyenes (C_nH_{n+2})

$$\Pi_n^n$$

$$\psi = \sum_{i=1}^{n} c_i \phi_i$$

Trial π-MO

Variation Theorem

$$\begin{pmatrix} \alpha - E & \beta & \dots & 0 \\ \beta & \alpha - E & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & \dots & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_n \end{pmatrix} = 0$$

$\{E_j\}$, $\{c_i(j)\}$
(j =1, 2, …, n)

$$\psi(j) = \sum_{i=1}^{n} c_i(j)\phi_i$$

- The ***n*** MO′s differ from each other in energy (non-degenerate MO′s!).
- The lowest ***n/2*** (***n*** = even) or **(n+1)/2** (***n***= odd) MO′s are occupied.

- For linear polyenes having ***even*** orbitals， there are ***n/2*** bonding orbitals and ***n/2*** antibonding orbitals.
- For linear polyenes having ***odd*** orbitals， there are ***(n-1)/2*** bonding orbitals, ***(n-1)/2*** antibonding orbitals and **a non-bonding** orbital.

e.g., Hexatriene - Π_6^6

$$\psi = A\sum_{i=1}^{4} c_i\phi_i$$

$$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \quad \sin 4\theta \quad \sin 5\theta \quad \sin 6\theta$$

$$\because \sin 7\theta = 0 \;\&\; \sin\theta \neq 0; \quad \therefore \theta = \frac{\mathrm{m}\pi}{7} \quad (\mathrm{m} = 1,2,\ldots,6)$$

$$E_m = \alpha + 2\beta\cos\frac{m\pi}{7} \quad (m = 1,2,\ldots,6)$$

$$\psi_m = \sqrt{\frac{2}{7}}\sum_{K=1}^{6}(\sin\frac{Km\pi}{7})\phi_K$$

m= 3, HOMO, bonding!

m=4, LUMO, antibonding!

In light of the superposition principle, each LMO of CH_4 can be expressed by a linear combination of its CMOs, or verse visa.

LMO CMOs HO of C, H 1s

$$
\begin{aligned}
\Phi_a &= \Psi_s + \Psi_x + \Psi_y + \Psi_z = (s + p_x + p_y + p_z)/2 + 1s_a \\
\Phi_b &= \Psi_s + \Psi_x - \Psi_y - \Psi_z = (s + p_x - p_y - p_z)/2 + 1s_b \\
\Phi_c &= \Psi_s - \Psi_x - \Psi_y + \Psi_z = (s - p_x - p_y + p_z)/2 + 1s_c \\
\Phi_d &= \Psi_s - \Psi_x + \Psi_y - \Psi_z = (s - p_x + p_y - p_z)/2 + 1s_d
\end{aligned}
$$

Yet to be normalized!

- It is provable that the four LMOs have the same energy!

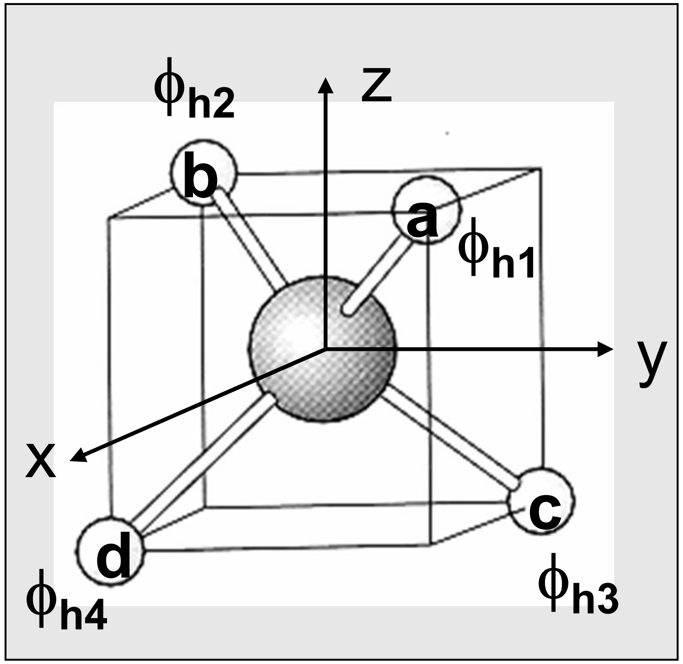
As CMOs are eigenfunctions of one-particle eigenequations, we have

$$\hat{h}\,\Psi_i^{CMO} = \varepsilon_i \Psi_i^{CMO} \;\&\; \int (\Psi_j^{CMO})^* \Psi_i^{CMO} d\tau = \delta_{ij}$$

$$\because \phi_j^{LMO} = \sum_{i=1}^{4} c_i^{\,j} \Psi_i^{CMO} \;\&\; c_i^j = +/-1 \Rightarrow E_j^{LMO} = \int (\phi_j^{LMO})^* \hat{h}\,\phi_j^{LMO} d\tau \Big/ \int (\phi_j^{LMO})^* \phi_j^{LMO} d\tau$$

$$= \sum_{i=1}^{4} (c_i^j)^2 \varepsilon_i \Big/ \sum_{i=1}^{4} (c_i^j)^2 = \Big(\sum_{i=1}^{4} \varepsilon_i\Big)/4 = (\varepsilon_1 + 3\varepsilon_2)/4 \qquad \text{(for } j = 1,\ldots,4)$$

Formation of four localized MO′s of CH_4:



LMO	HO of C	H 1s
$\Phi_a =$	$(s+p_x+p_y+p_z)/2$	$+\ 1s_a$
$\Phi_b =$	$(s+p_x-p_y-p_z)/2$	$+\ 1s_b$
$\Phi_c =$	$(s-p_x-p_y+p_z)/2$	$+\ 1s_c$
$\Phi_d =$	$(s-p_x+p_y-p_z)/2$	$+\ 1s_d$

ε_i^{CMO}	*CMO*	AO_C	AO's of H atoms
ε_1	a_1: $\Psi_s =$	s	$+(1s_a+1s_b+1s_c+1s_d)/2$
	$\Psi_x =$	p_x	$+(1s_a+1s_b-1s_c-1s_d)/2$
ε_2	t_2 $\Psi_y =$	p_y	$+(1s_a-1s_b-1s_c+1s_d)/2$
	$\Psi_z =$	p_z	$+(1s_a-1s_b+1s_c-1s_d)/2$

SALC′s of CH_4

$$\Psi_i^{CMO} = \sum_m c_{im}\varphi_m^{AO}$$

In light of the superposition principle, each LMO of CH_4 can be expressed by a linear combination of its CMOs, or verse visa.

LMO	CMOs	HO of C,	H 1s
Φ_a	$= \Psi_s + \Psi_x + \Psi_y + \Psi_z$	$= (s + p_x + p_y + p_z)/2$	$+ 1s_a$
Φ_b	$= \Psi_s + \Psi_x - \Psi_y - \Psi_z$	$= (s + p_x - p_y - p_z)/2$	$+ 1s_b$
Φ_c	$= \Psi_s - \Psi_x - \Psi_y + \Psi_z$	$= (s - p_x - p_y + p_z)/2$	$+ 1s_c$
Φ_d	$= \Psi_s - \Psi_x + \Psi_y - \Psi_z$	$= (s - p_x + p_y - p_z)/2$	$+ 1s_d$

Yet to be normalized!

- It is provable that the four LMOs have the same energy!

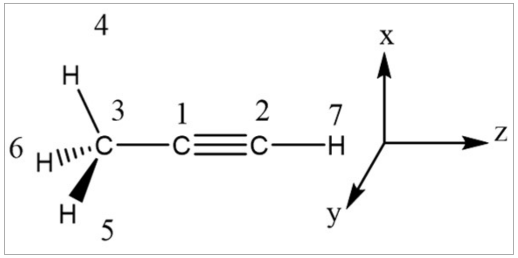
As CMOs are eigenfunctions of one-particle eigenequations, we have

$$\hat{h}\,\Psi_i^{CMO} = \varepsilon_i \Psi_i^{CMO} \ \& \int (\Psi_j^{CMO})^* \Psi_i^{CMO} d\tau = \delta_{ij}$$

$$\because \phi_j^{LMO} = \sum_{i=1}^{4} c_i^{\,j} \Psi_i^{CMO} \ \& \ c_i^j = +/-1 \Rightarrow E_j^{LMO} = \int (\phi_j^{LMO})^* \,\hat{h}\, \phi_j^{LMO} d\tau \Big/ \int (\phi_j^{LMO})^* \phi_j^{LMO} d\tau$$

$$= \sum_{i=1}^{4} (c_i^j)^2 \varepsilon_i \Big/ \sum_{i=1}^{4} (c_i^j)^2 = (\sum_{i=1}^{4} \varepsilon_i)/4 = (\varepsilon_1 + 3\varepsilon_2)/4 \qquad (\text{for } j = 1,\ldots,4)$$

3H 1s: {ϕ_4, ϕ_5, ϕ_6}; C3 2s-A; 2p{ϕ_{3x}, ϕ_{3y}}-E,



C1,2 p_{xz}, p_{yz} : ϕ_{1x} , ϕ_{1y} ; ϕ_{2x} , ϕ_{2y}

C_3	E	C_3	C_3^2		$\epsilon = e^{2\pi i/3}$
A	1	1	1	z, R_z	$x^2 + y^2$, z^2
E	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\left.\begin{matrix}\epsilon^*\\\epsilon\end{matrix}\right\}$	(x, y), (R_x, R_y)	$(x^2 - y^2, xy)$, (yz, xz)
Γ_{H1s}	3	0	0		$\Gamma_\pi = A \oplus E$

$$\mathrm{SALC}^{\mathrm{A}} = \phi_4 + \phi_5 + \phi_6$$

$$\mathrm{SALC}^{E}_{\mathrm{y}} = \phi_5 - \phi_6$$

$$\mathrm{SALC}^{E}_{\mathrm{x}} = 2\phi_4 - \phi_5 - \phi_6$$

+ 2s (C3)

+ 2p$_y$ (C3)

+ 2p$_x$ (C3)

$$\Psi^{\mathrm{A}}_{1,4}(CH_3) = A(\phi_4 + \phi_5 + \phi_6) \pm B\phi_{3(2s)}$$

$$\Psi^{E}_{2,5}(CH_3) = A(\phi_4 - \phi_5) \pm B\phi_{3y}$$

$$\Psi^{E}_{3,6}(CH_3) = A(2\phi_4 - \phi_5 - \phi_6) \pm \mathrm{B}\phi_{3x}$$


12
9
3
6