

Chapter 5

The structure of polyatomic molecules (A)

§ 5.1 Theory of hybrid orbital and atomic orbital hybridization

1. Hybrid orbital theory ---Proposed by Pauling in 1928

Chemical bonding theories

MOLECULAR ORBITAL THEORY

- Valence electrons are **delocalized**
- Valence electrons spread over entire molecule.

VALENCE BOND THEORY

- Valence electrons are **localized** between atoms (or are lone pairs).
- Half-filled atomic orbitals overlap to form bonds.

Simplified MO diagram of diatomic molecules

$$\sigma_g(2s) = (\phi_{2sA} + \phi_{2sB})$$

$$\sigma_g(2p_z) = (\phi_{2p_zA} - \phi_{2p_zB})$$

$$\sigma_g(2sp) =$$

$$c_1(\phi_{2sA} + \phi_{2sB}) \pm c_2(\phi_{2p_zA} - \phi_{2p_zB})$$

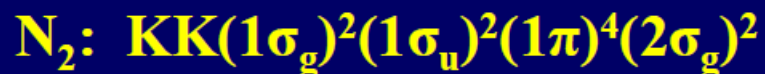
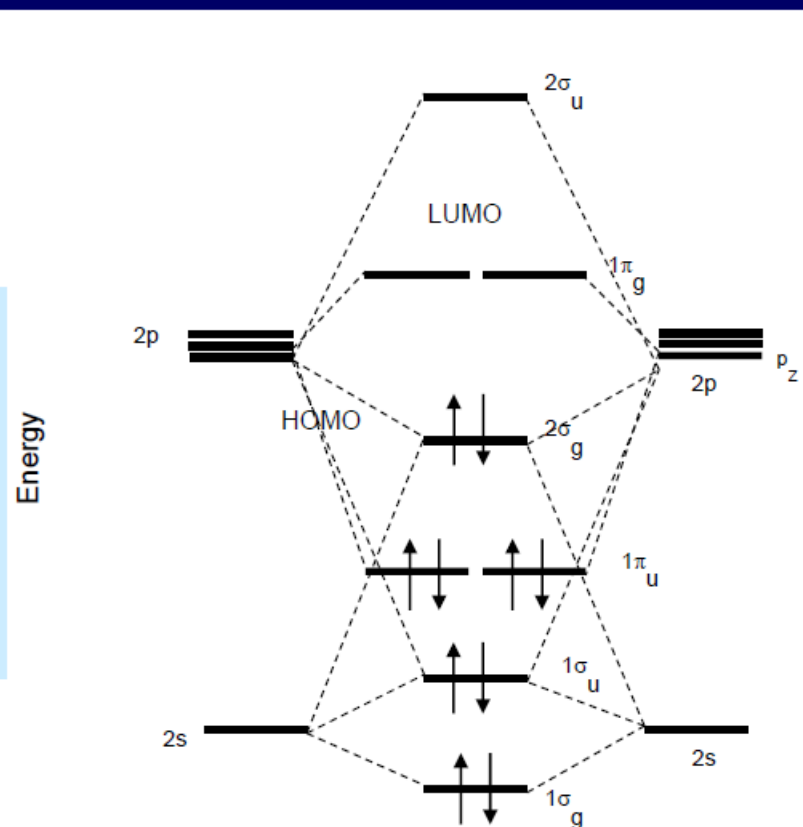
=

$$(c_1\phi_{2sA} \pm c_2\phi_{2p_zA}) + (c_1\phi_{2sB} \mp c_2\phi_{2p_zB})$$

sp-hybridization

$$\sigma_u(2sp) =$$

$$(c_1\phi_{2sA} \pm c_2\phi_{2p_zA}) - (c_1\phi_{2sB} \mp c_2\phi_{2p_zB})$$

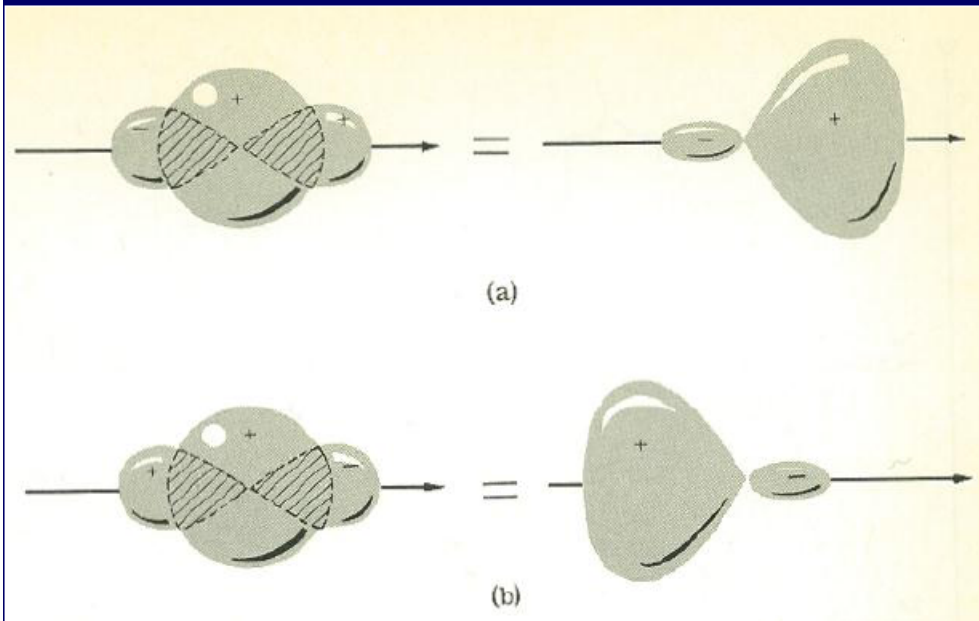


The narrow energy gap between 2s and 2p_z orbitals in a N atom also enables the interatomic interaction between 2s (N1) and 2p_z(N2)!

$$\sigma_g(2sp) =$$

$$c_1(\phi_{2sA} + \phi_{2sB}) \pm c_2(\phi_{2p_zA} + \phi_{2p_zB})$$

$$(c_1\phi_{2sA} \pm c_2\phi_{2p_zA}) + (c_1\phi_{2sB} \pm c_2\phi_{2p_zB})$$



Boundary surfaces of

(a) 2s+2p

$$(c_1\phi_{2sA} + c_2\phi_{2p_zA})$$

(b) 2s-2p

$$(c_1\phi_{2sA} - c_2\phi_{2p_zA})$$

Hybridization of 2s and 2p

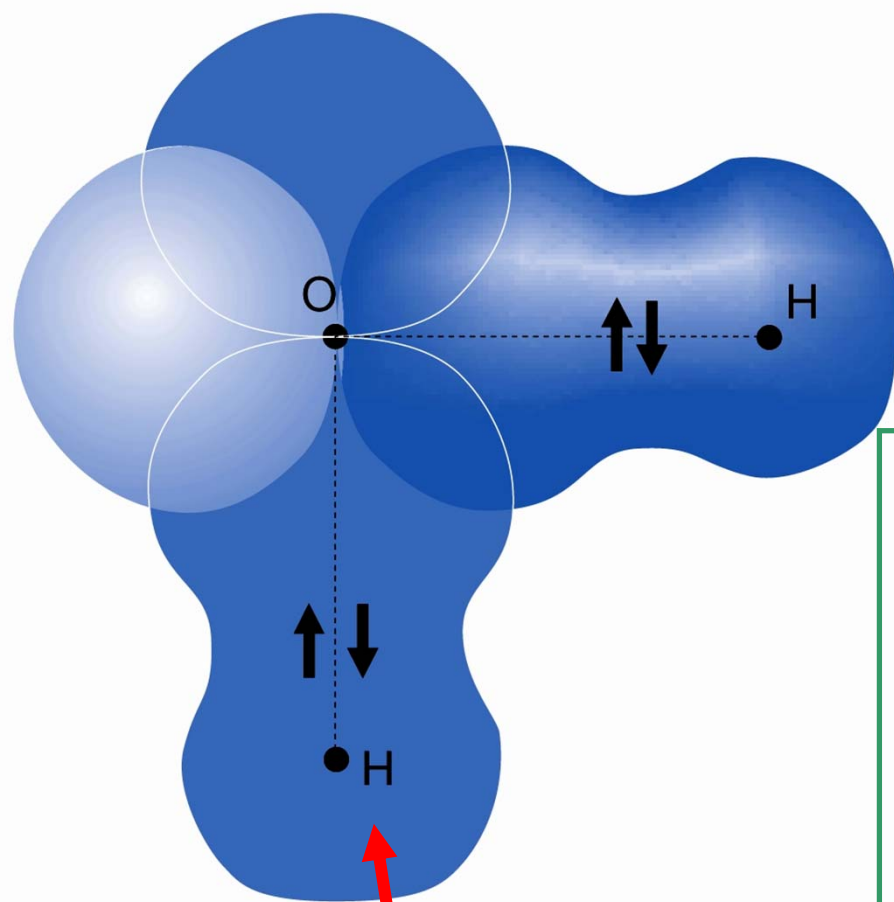
Central Themes of Valence Bond Theory

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.

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

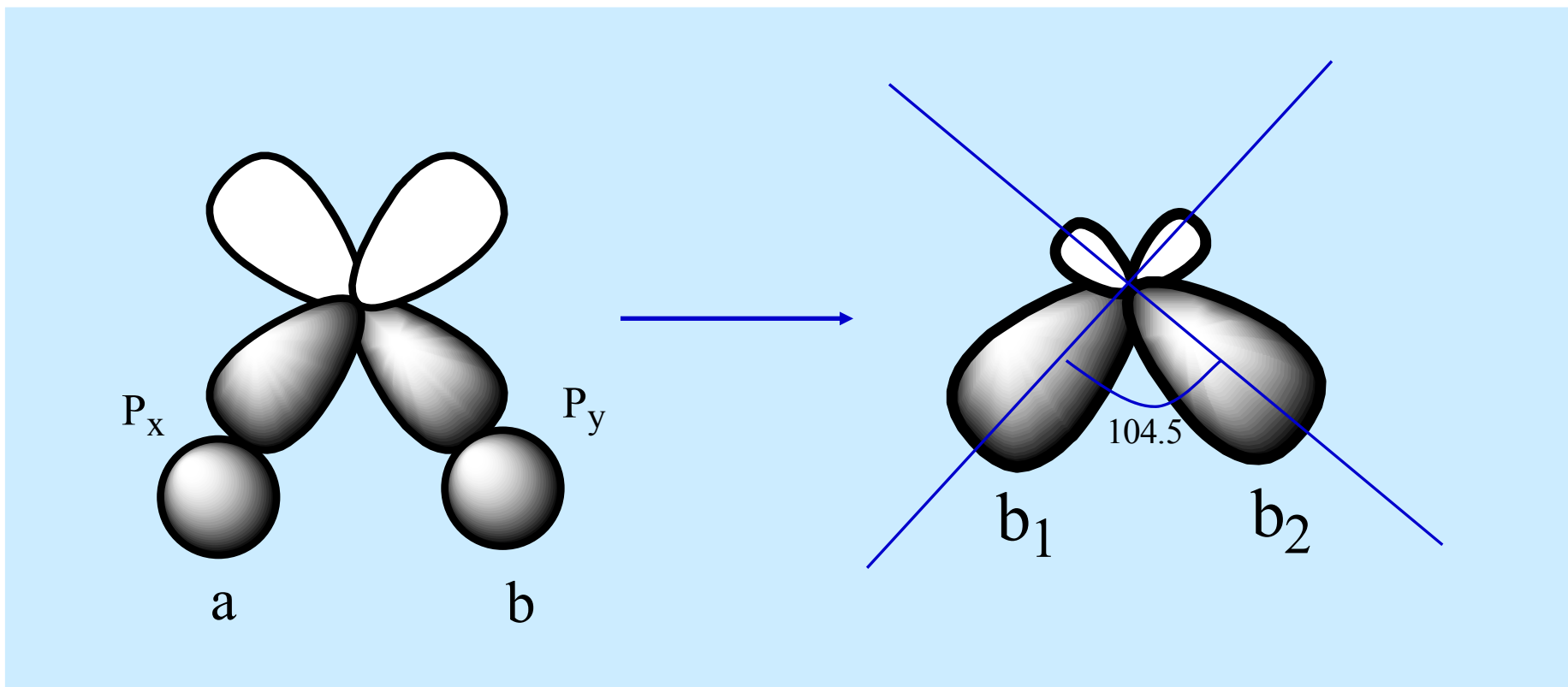
Why do atomic orbital need hybridization?



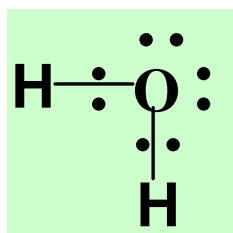
H₂O

Use of
p - orbitals

A first approximation to the valence-bond description of bonding in an H₂O molecule. Each σ bond arises from the overlap of an H1s orbital with one of the O2p orbitals. This model suggests that the bond angle should be 90°, which is significantly different from the experimental value.



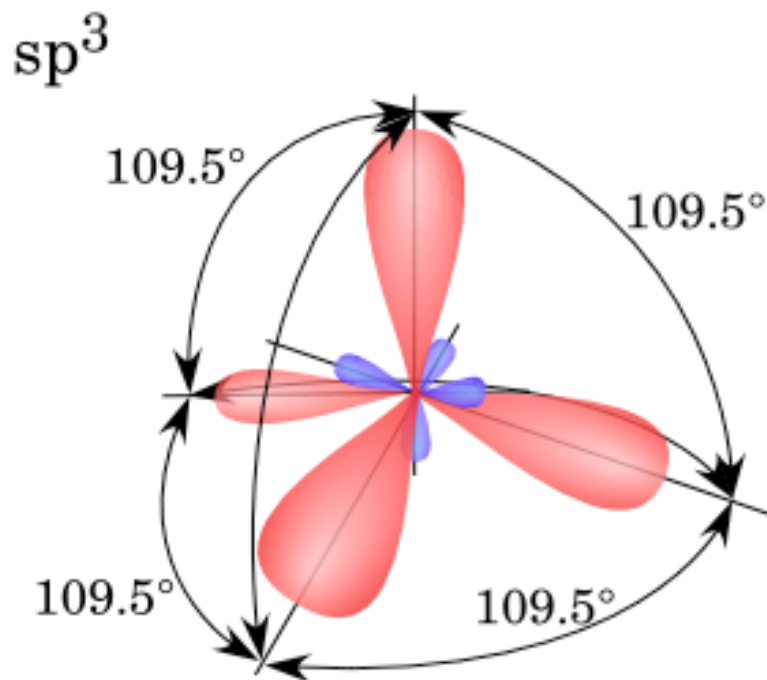
H_2O



The admixture of 2s & 2p orbitals is required.

Inequivalent sp^3 hybridization of O(2sp) AOs

a. Why do atomic orbitals need hybridization?



- Carbon has four valence electrons – four electrons that are typically involved in bond formation.
- For carbon atoms bonded to four other atoms, experimental evidence suggested that all of the bonds have similar molecular orbitals.

b. How do atomic orbitals hybridize?

$$\phi_h = c_1\phi_{2s} + c_2\phi_{2p_x} + c_3\phi_{2p_y} + c_4\phi_{2p_z}$$

$$\Phi_k = \sum_i c_{ik}\phi_i$$

$$\begin{aligned}\hat{H}\Phi_k &= \hat{H} \sum_i c_{ik}\phi_i = \sum_i \hat{H}c_{ik}\phi_i = \sum_i c_{ik}\hat{H}\phi_i \\ &= \sum_i c_{ik}E_i\phi_i = E_k \sum_i c_{ik}\phi_i\end{aligned}$$

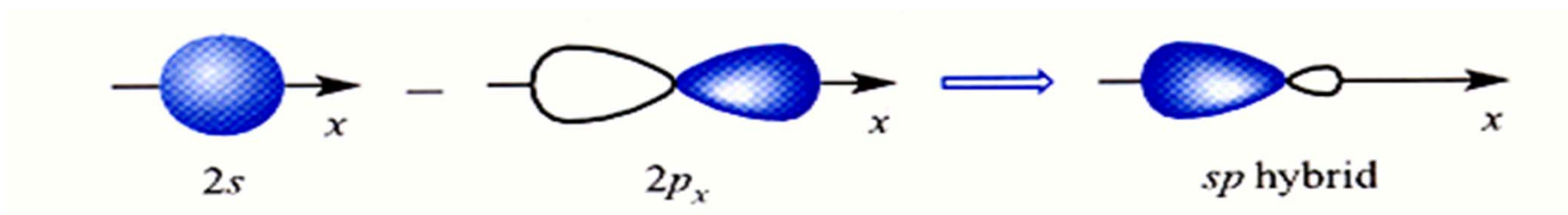
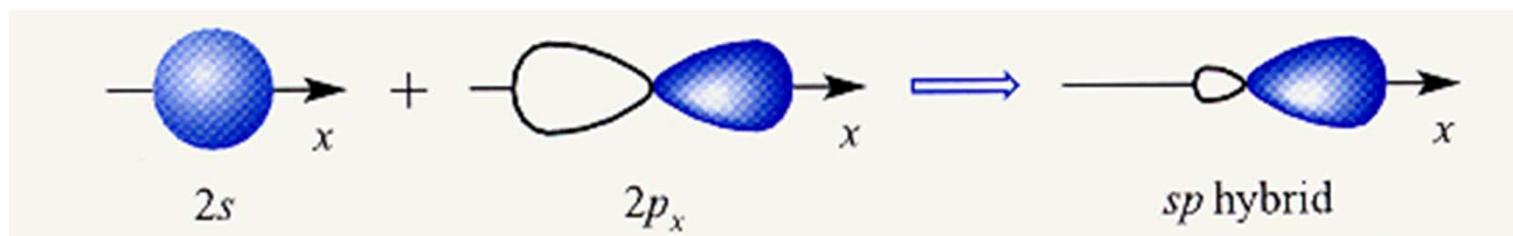
If we begin with n AO's, we must end up with n orbitals after hybridization.

All n hybrids are equivalent except for directionality \rightarrow same energy.

2. Construction of hybrid orbitals

a. sp hybridization (linear species)

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



$$\phi_{h1} = \sqrt{\frac{1}{2}} (\phi_s + \phi_{2p_x})$$

$$\phi_{h2} = \sqrt{\frac{1}{2}} (\phi_s - \phi_{2p_x})$$

sp, $\theta=180^\circ$, linear,

Normalization and orthogonality

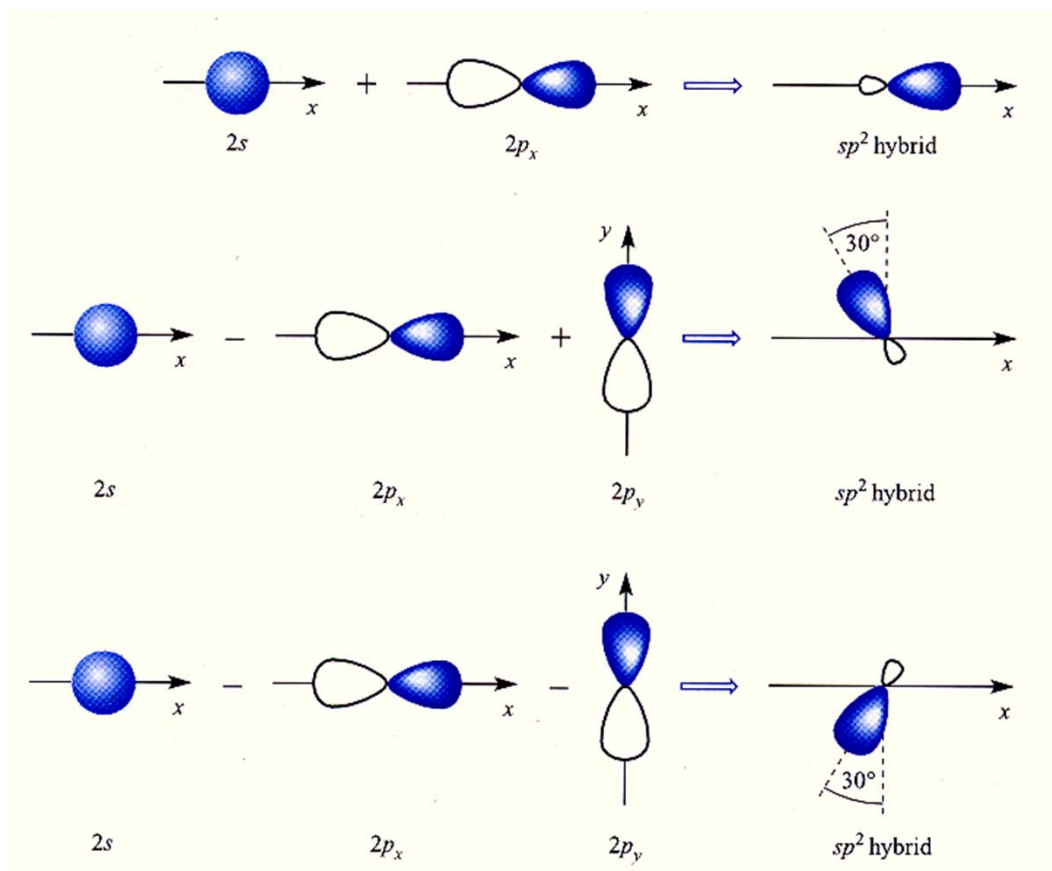
b. sp^2 hybridization (trigonal planar)

- One s and two p (p_x and p_y) AO's mix to form a set of three hybrid orbitals.

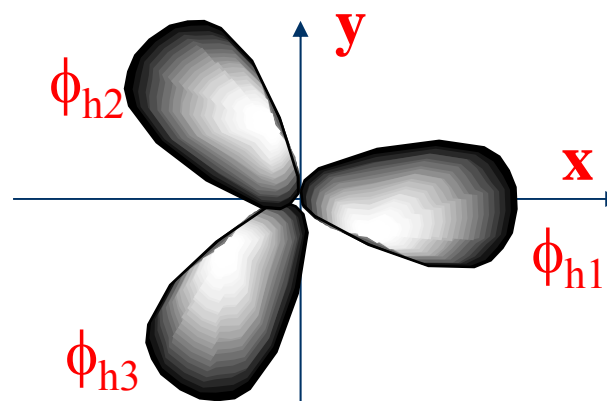
$$\phi_{h1} = \sqrt{\frac{1}{3}}\phi_s + \sqrt{\frac{2}{3}}\phi_{2px}$$

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

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



sp^2 , D_{3h} , $\theta=120^\circ$, triangular,
 $f=1.991$, $\alpha=1/3$



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

For equivalent hybridization: the weighting of s orbital in each hybrid orbital is 1/3, and therefore

$$a_i = \sqrt{1/3}$$

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

Supposing ϕ_{h1} is parallel to the x-axis and is perpendicular to the y-axis.

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

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

Normalization

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

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

Normalization and orthogonality

$$a_2^2 + b_2^2 + c_2^2 = 1$$

$$a_1a_2 + b_1b_2 + c_1c_2 = 0$$



$$1/3 + b_2^2 + c_2^2 = 1$$

$$1/3 + \sqrt{2/3}b_2 + 0 \cdot c_2 = 0$$

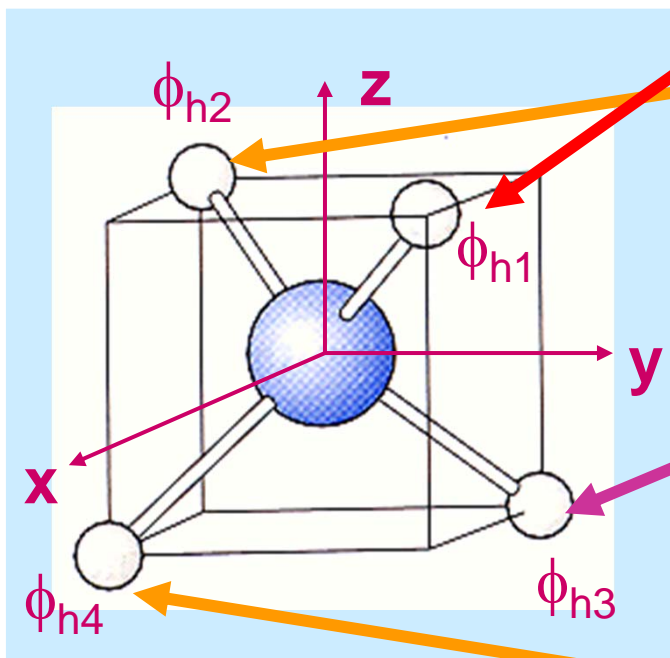
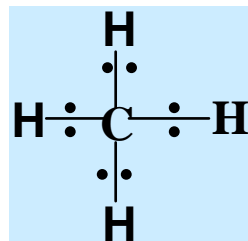
$$b_2 = -\sqrt{1/6} \quad c_2 = \pm\sqrt{1/2}$$

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

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

c. sp^3 hybrides (tetrahedral)

equivalent hybridization
 $\alpha=1/4$



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

along (x,y,z)

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

along (-x,-y,z)

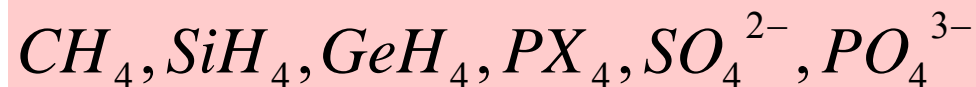
$$\phi_{h3} = \frac{1}{2} [s - p_x + p_y - p_z]$$

along (-x,y,-z)

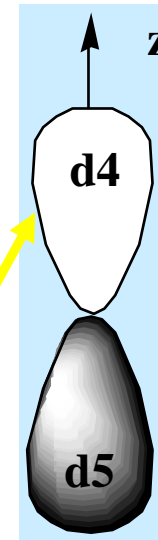
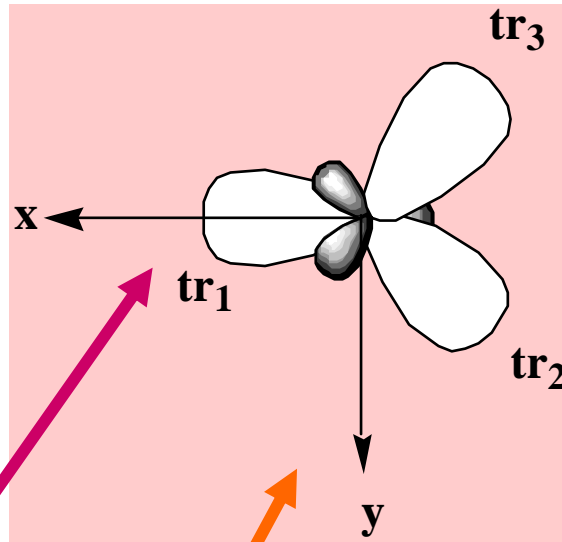
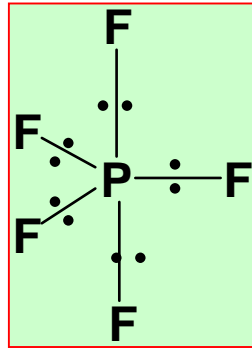
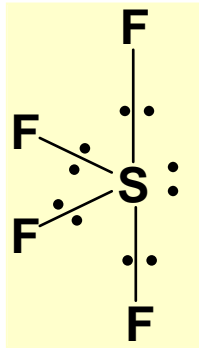
$$\phi_{h4} = \frac{1}{2} [s + p_x - p_y - p_z]$$

along (x,-y,-z)

- One s and 3 p AO's mix to form a set of four hybrid sp^3 orbitals.



d. dsp^3 (sp^3d) hybridides (bipyramidal)



$$tr_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x$$

$$tr_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \sqrt{\frac{1}{2}}p_y$$

$$tr_3 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \sqrt{\frac{1}{2}}p_y$$

$$d_4 = \sqrt{\frac{1}{2}}[p_z + d_{z^2}]$$

$$d_5 = \sqrt{\frac{1}{2}}[p_z - d_{z^2}]$$

e. dsp^2 hybridizes (square planar)

Square planar: D_{4h}

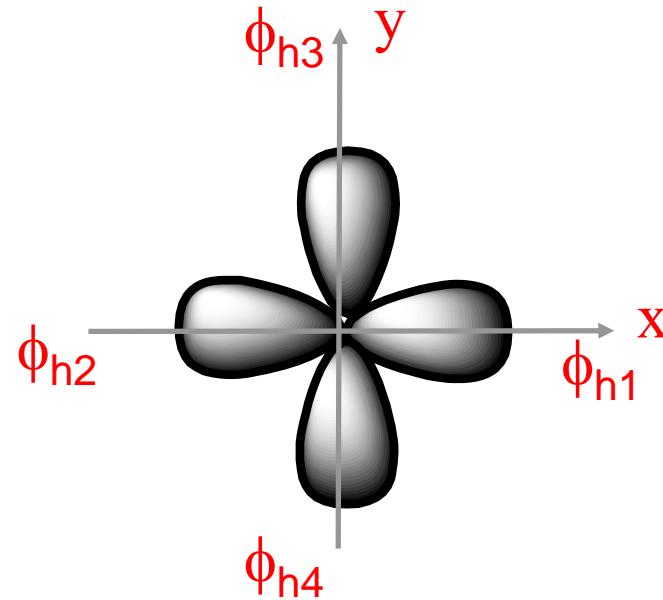
$$d_{x^2-y^2}, s, p_x, p_y$$

$$\phi_{h1} = \frac{1}{2}\phi_s + \sqrt{\frac{1}{2}}\phi_{px} + \frac{1}{2}d_{x^2-y^2}$$

$$\phi_{h2} = \frac{1}{2}\phi_s - \sqrt{\frac{1}{2}}\phi_{px} + \frac{1}{2}d_{x^2-y^2}$$

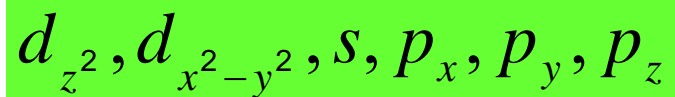
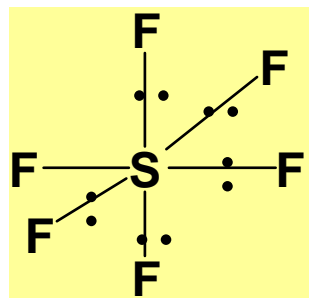
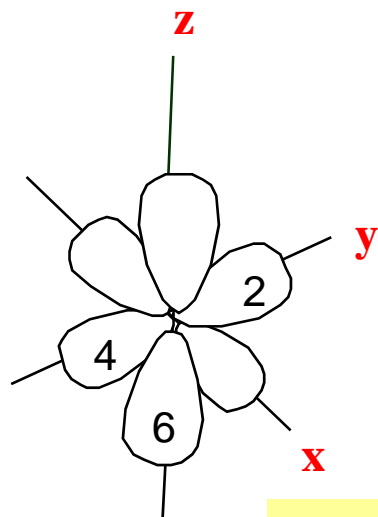
$$\phi_{h3} = \frac{1}{2}\phi_s + \sqrt{\frac{1}{2}}\phi_{py} - \frac{1}{2}d_{x^2-y^2}$$

$$\phi_{h4} = \frac{1}{2}\phi_s - \sqrt{\frac{1}{2}}\phi_{py} - \frac{1}{2}d_{x^2-y^2}$$



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

f. d^2sp^3 (sp^3d^2) hybridizes (Octahedral)



$$oc_1 = \frac{1}{\sqrt{6}}s + \sqrt{\frac{1}{2}}p_x + \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$$

$$oc_2 = \frac{1}{\sqrt{6}}s + \sqrt{\frac{1}{2}}p_y - \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$$

$$oc_3 = \frac{1}{\sqrt{6}}s - \sqrt{\frac{1}{2}}p_x + \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$$

$$oc_4 = \frac{1}{\sqrt{6}}s - \sqrt{\frac{1}{2}}p_y - \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$$

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

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

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-based pyramidal
sp^3d^2	octahedral
sp^2d	square planar

3. The angle between two hybrid orbitals

spⁿ hybridization

$$\phi_h = \sqrt{\alpha} \phi_{2s} + \sqrt{1-\alpha} \phi_{2p}$$

$$\phi_{hi} = \sqrt{\alpha_i} \phi_{2s} + \sqrt{1-\alpha_i} \phi_{2p_i}$$

$$\phi_{hj} = \sqrt{\alpha_j} \phi_{2s} + \sqrt{1-\alpha_j} \phi_{2p_j}$$

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

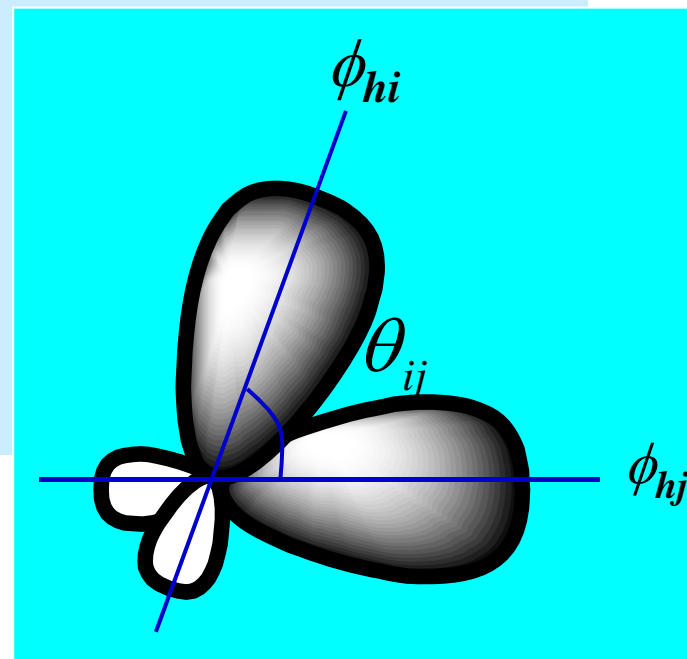
Normalization and orthogonality

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

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

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

($\cos \theta_{ij} < 0$, $\theta_{ij} > 90^\circ$)



$\alpha_i = \alpha_j$ Equivalent hybridization. Example: CH_4

$\alpha_i \neq \alpha_j$ Non-equivalent hybridization. Example: CHCl_3 , CH_3Cl

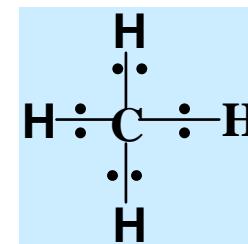
Equivalent hybridization

sp^3 – hybridizes

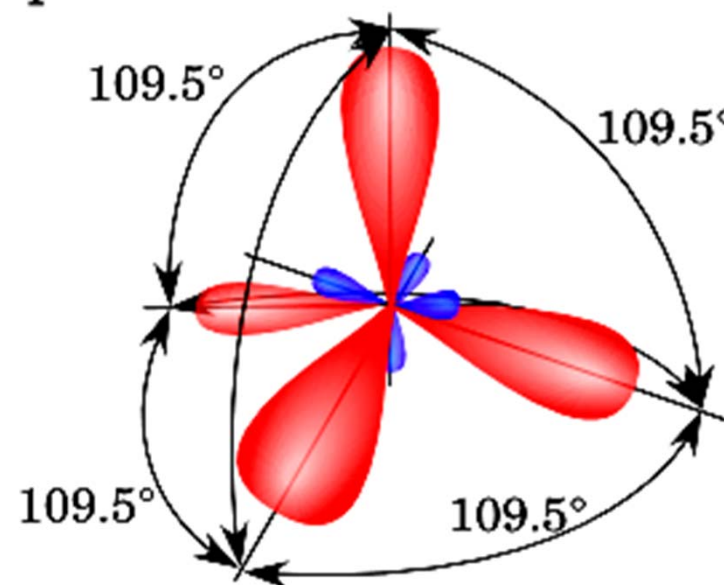
$$\alpha = \frac{1}{4}$$

$$\cos \theta_{ij} = -\frac{\sqrt{\alpha_i \alpha_j}}{\sqrt{(1-\alpha_i)(1-\alpha_j)}} = -\frac{\frac{1}{4}}{\frac{3}{4}} = -\frac{1}{3}$$

$$\theta = 109^{\circ}28''$$

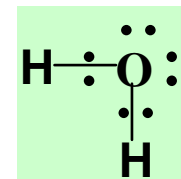
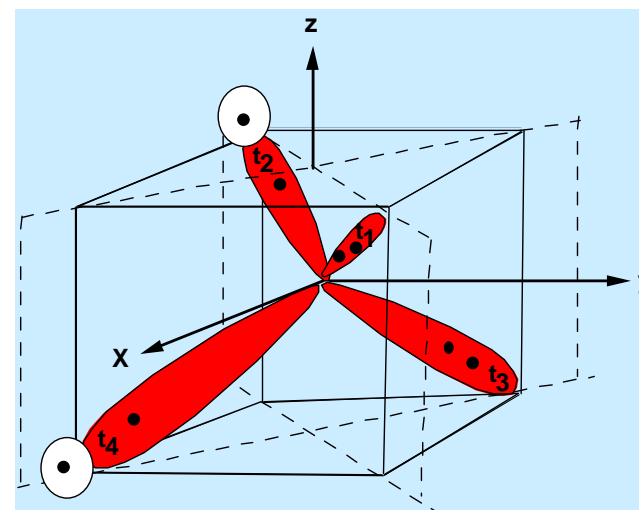
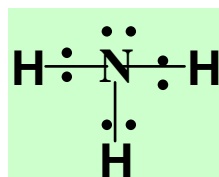
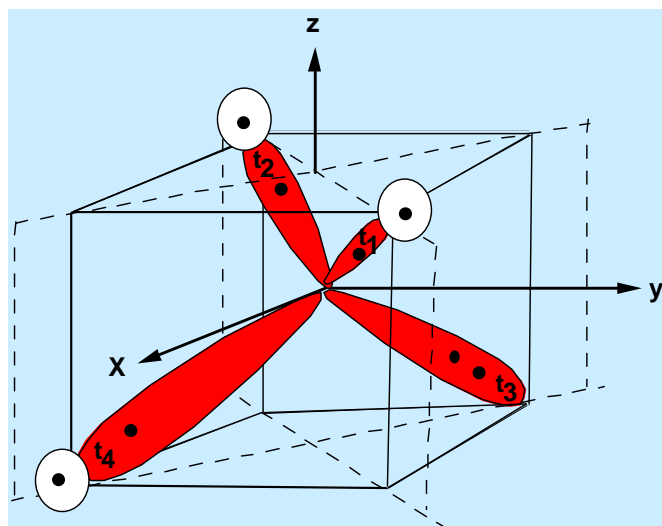


sp^3



Non-equivalent hybridization

sp^3 – hybrides



for NH_3

$$\theta = 107.3^\circ$$

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

$$\alpha = 0.23$$

$$L_s = 1 - 3 * 0.23 = 0.31$$

$$L_p = 3 - 3 * 0.77 = 0.69$$

$$\psi_{\text{bonding}} = \sqrt{0.23}s + \sqrt{0.77}p = 0.48s + 0.88p$$

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

Other example

PH_3 , PF_3 , NF_3 ,

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)

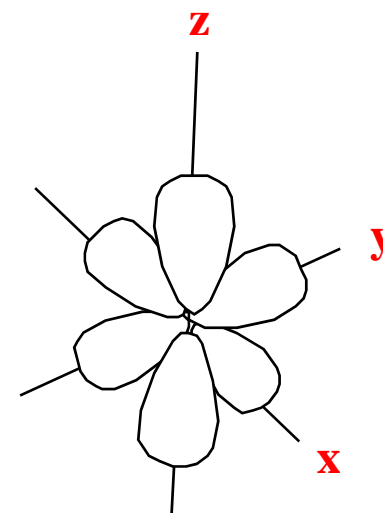
$$\alpha + \beta \cos \theta + \gamma \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) = 0$$

$$\text{for } d^2sp^3, \alpha = \frac{1}{6}, \beta = \frac{1}{2}, \gamma = \frac{1}{3},$$

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

$$\cos \theta_1 = 0, \quad \cos \theta_2 = -1$$

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



Octahedral

4. The bonding ability of the hybrid orbital

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

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

for the sp^n hybridizations,

$$\alpha = \frac{1}{2}, \beta = \frac{1}{2} \quad f_h = 1.932 \quad sp$$

$$\alpha = \frac{1}{3}, \beta = \frac{2}{3} \quad f_h = 1.992 \quad sp^2$$

$$\alpha = \frac{1}{4}, \beta = \frac{3}{4} \quad f_h = 2.00 \quad sp^3$$

$$\alpha = 0, \quad f_h = \sqrt{3}$$

$$\alpha = 1, \quad f_h = 1$$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

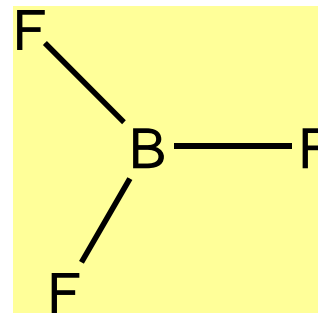
Linus Pauling

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

5. Discussions

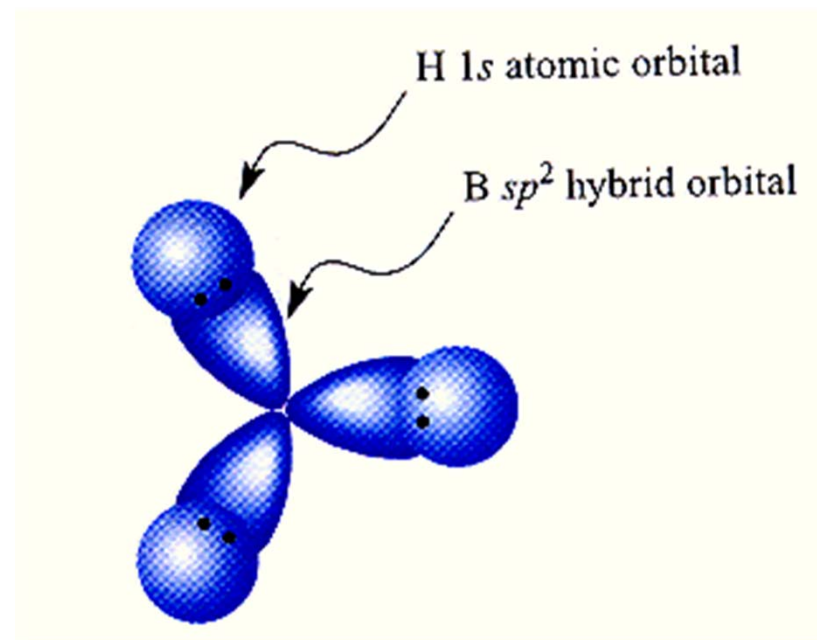
sp^2

ex. $\text{BF}_3(\text{D}_{3\text{h}})$, $\text{BH}_3(\text{D}_{3\text{h}})$, NO_3^- , CO_3^{2-} ,

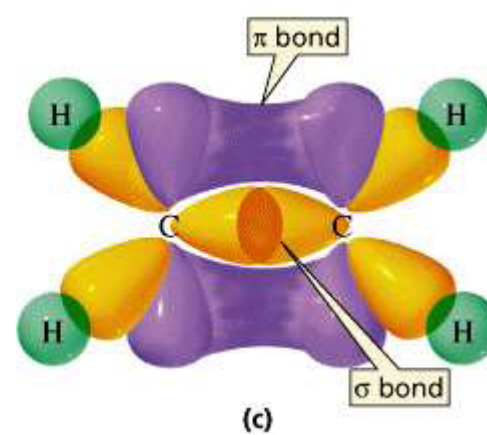
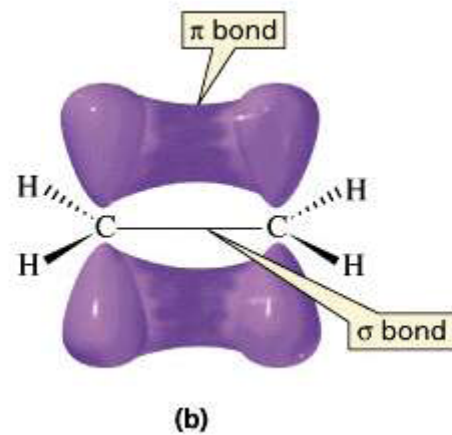
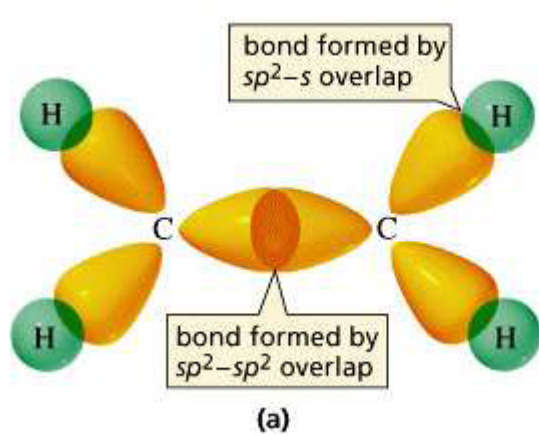
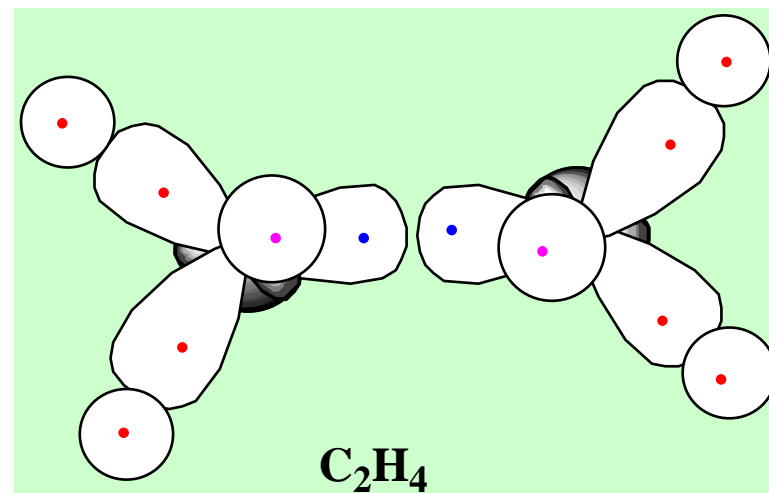
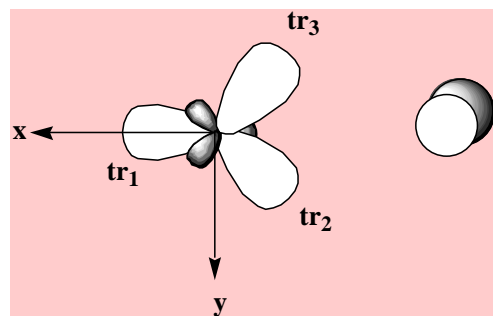
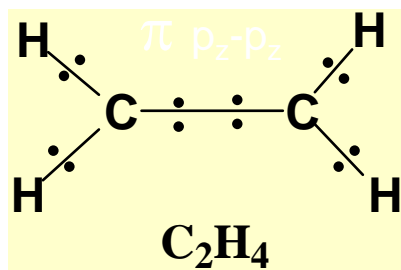


Example: BH_3

- 3 sp^2 hybrid orbitals each with one electron.
- This one electron pairs with the hydrogen electron.

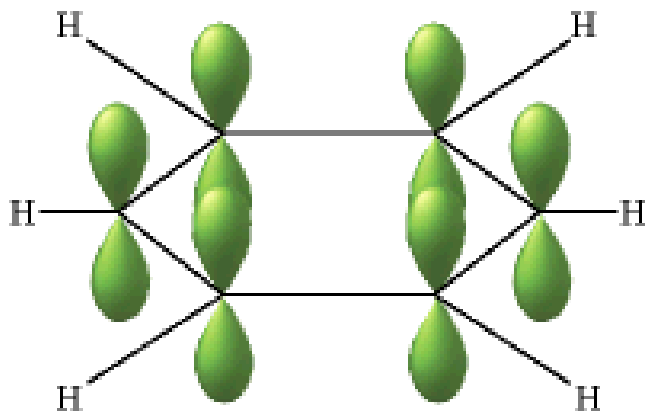


Example:

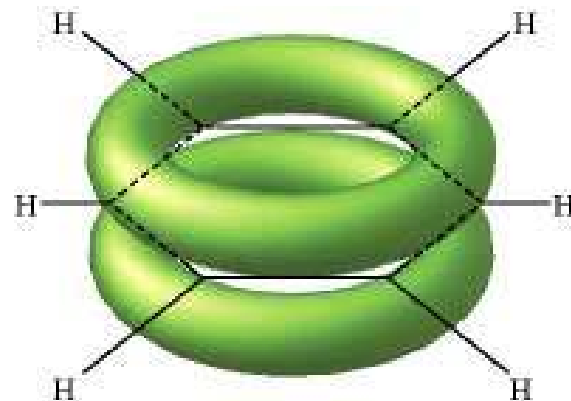


The sp^2 -hybridization and chemical bonding in C_2H_4 .

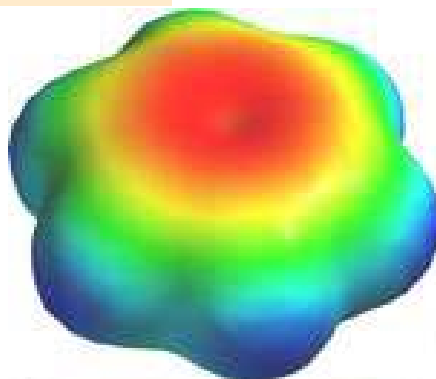
Example: Benzene --hybridization and delocalization



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

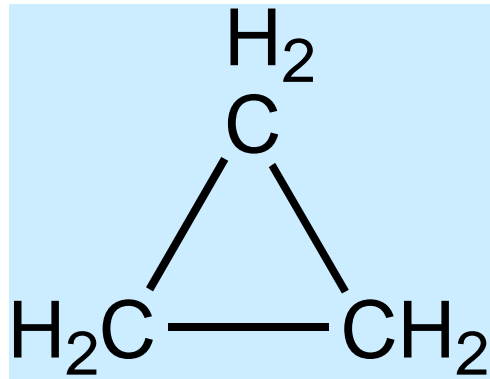


The unhybridized pz AO's of C atoms form a continuous cyclic bond of benzene. Π_6^6



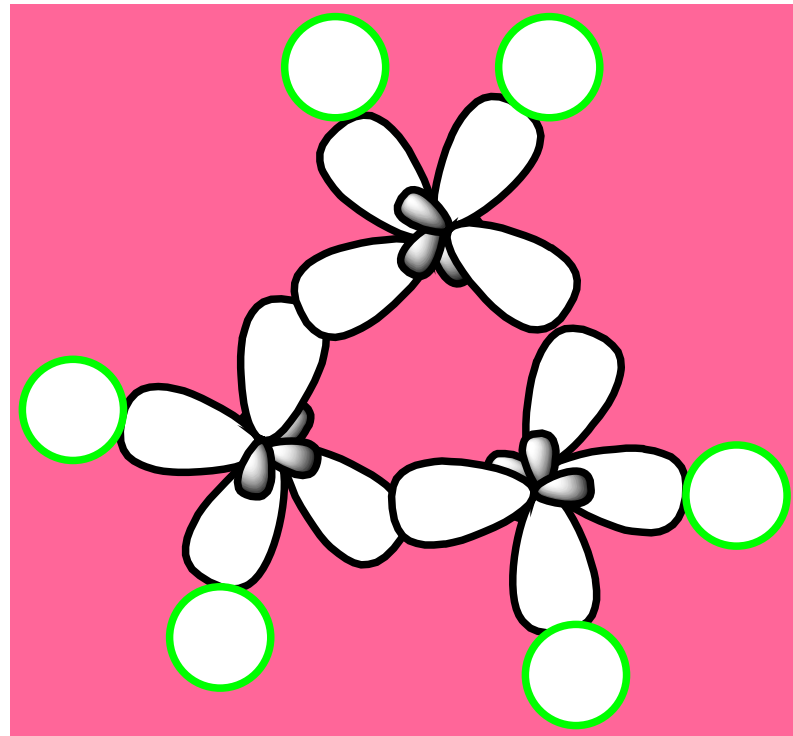
Bend bonding

cyclo-triethyle



sp^3

banana bonds



§ 5.2 Valence Shell Electron-Pair Repulsion (VSEPR) Model

- Quantum mechanical treatments have a number of advantages. However, the VSEPR model allows a simple qualitative prediction of molecular geometry.

VSEPR



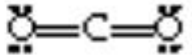

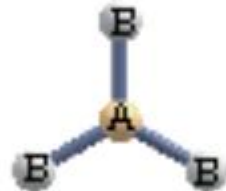
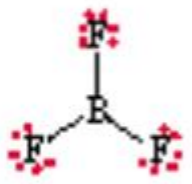
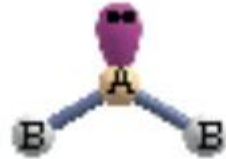
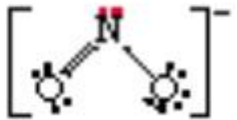
Atom B in AB_n lie on the surface of a sphere; electron pairs are “localized” on a sphere of smaller radius at maximum distances apart, so as to minimize overlap of different electron pairs.

- 1. Repulsion between two electron pairs is the greatest.**
- 2. Repulsion between between a lone electron pair and a bonding electron pair is less.**
- 3. Repulsion between two bonding pairs is the least.**
- 4. π electron pair do not influence stereochemistry.**

Arrangements of Maximum distance between valence shell electron pairs.

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

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	 Linear	
3 domains	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

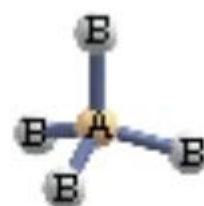
4 domains



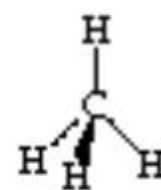
Tetrahedral

4

0

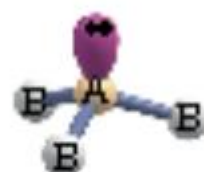


Tetrahedral



3

1

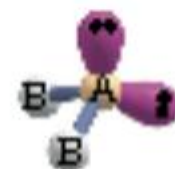


Trigonal
pyramidal




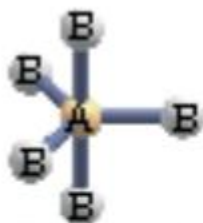
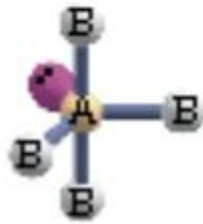
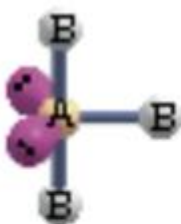

2

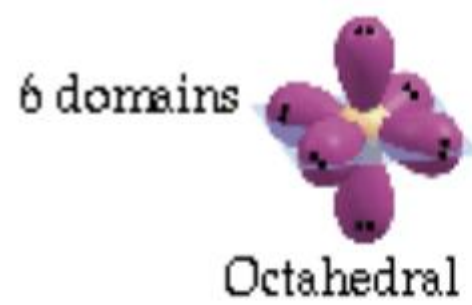
2



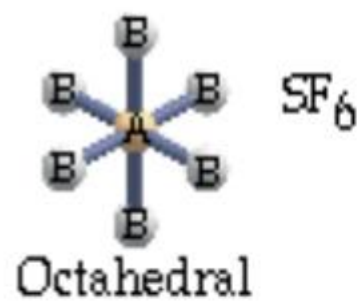
Bent



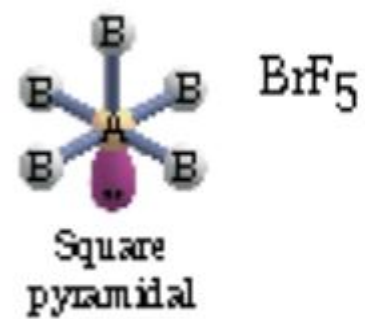
5 domains		5	0		PCl_5
	Trigonal bipyramidal			Trigonal bipyramidal	
		4	1		SF_4
				Sawtooth	
		3	2		ClF_3
				T-shaped	
		2	3		XeF_2
				Linear	



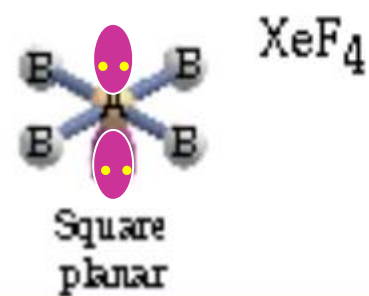
6 0



5 1



4 2



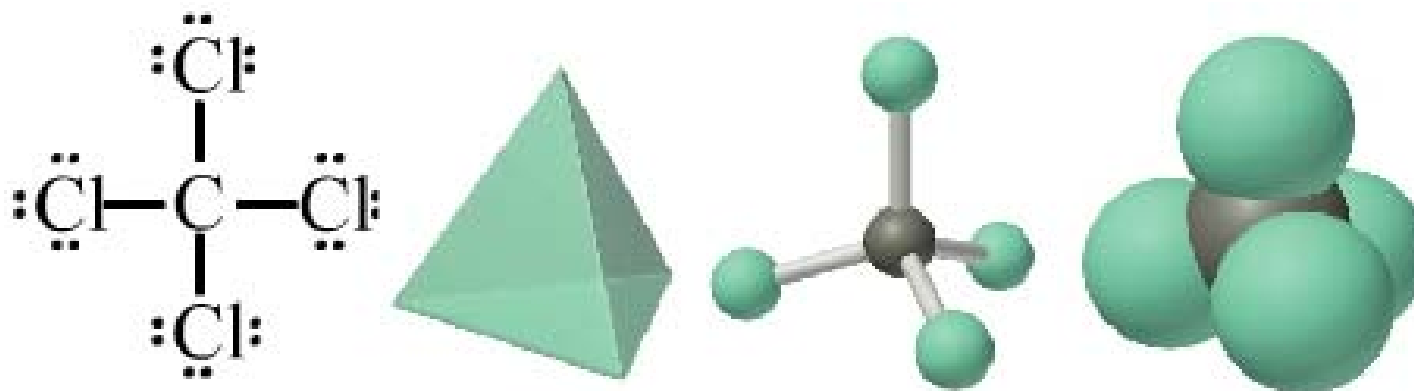
Molecular Stereochemistry

No. of pairs of e ⁻	formula	stereochemistry	point group
1	A ₂ , AB	none	D _{∞h} C _{∞v}
2	AB ₂	linear	D _{∞h}
3	AB ₂ e ¹	bend	C _{2v}
3	AB ₃	triangular	D _{3h}
4	AB ₂ e ²	bend	C _{2v}
4	AB ₃ e ¹	pyramidal	C _{3v}
4	AB ₄	tetrahedral	T _d

Molecular Stereochemistry

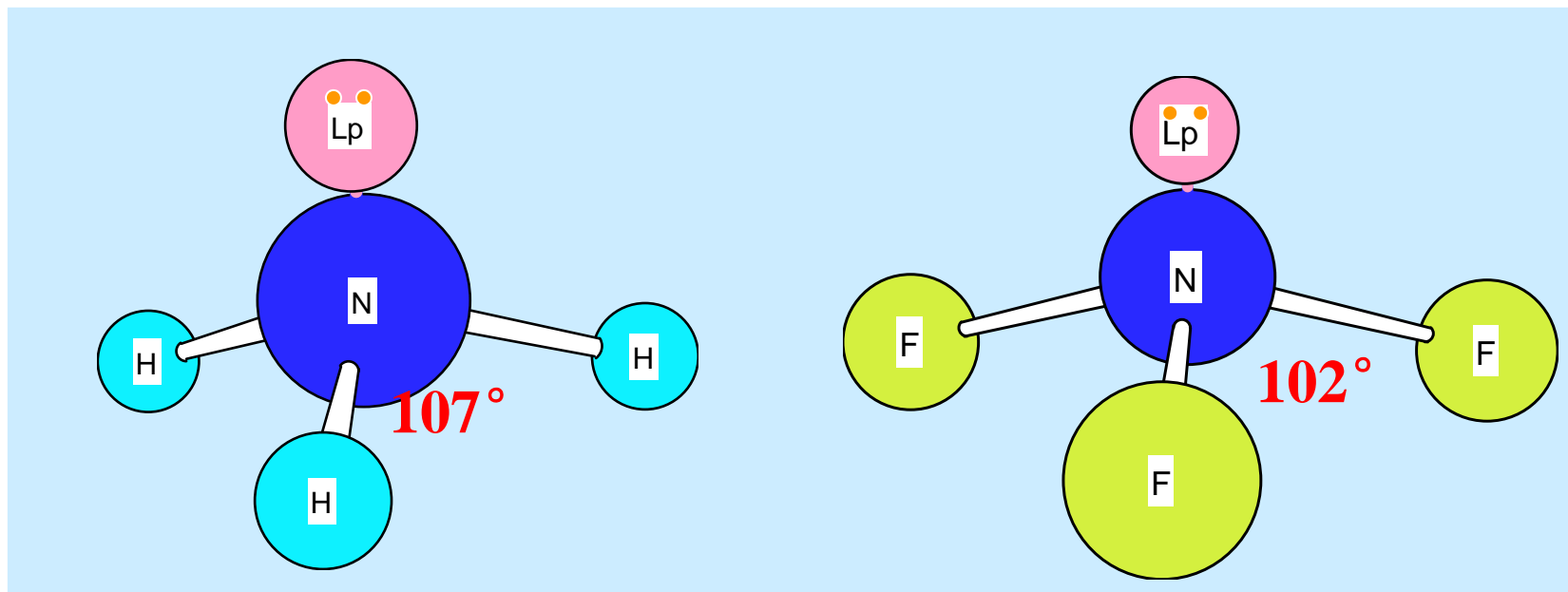
No. of pairs of e ⁻	formula	stereochemistry	point group
5	AB ₂ e ³	linear	D _{∞h}
5	AB ₃ e ²	T-shaped	C _{2v}
5	AB ₄ e ¹	non-planar	C _{2v}
5	AB ₅	trigonal bipyramid	D _{3h}
6	AB ₄ e ²	square planar	D _{4h}
6	AB ₅ e ¹	square pyramidal	C _{4v}
6	AB ₆	octahedral	O _h

VSEPR Example

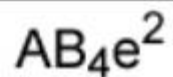


CCl_4 will adopt a tetrahedron geometry to minimize the repulsion between chlorines

VSEPR Example

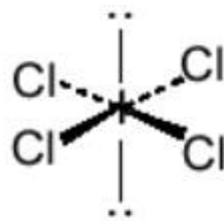
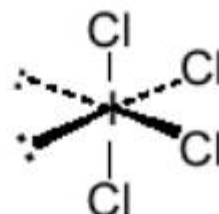


- Bond angles decrease with increasing electronegativity of the ligand or decreasing electronegativity of the central atom.
- Why? The BP is more distant from the central atom upon increasing electronegativity of the ligand.



6-pair case

possible structures:

 D_{4h}  C_{2v}

e/e

0

1

bp/e

8

6

bp/bp

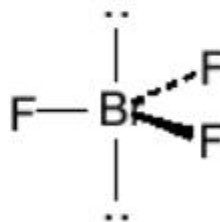
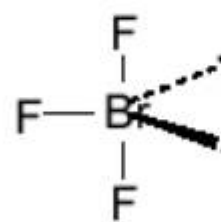
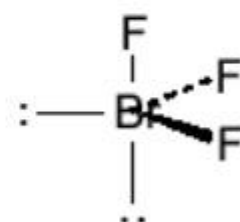
4

5



5-pair case

possible structures:

 D_{3h}  C_{2v}  C_s

e/e

0

0

1

bp/e

6

4

3

bp/bp

0

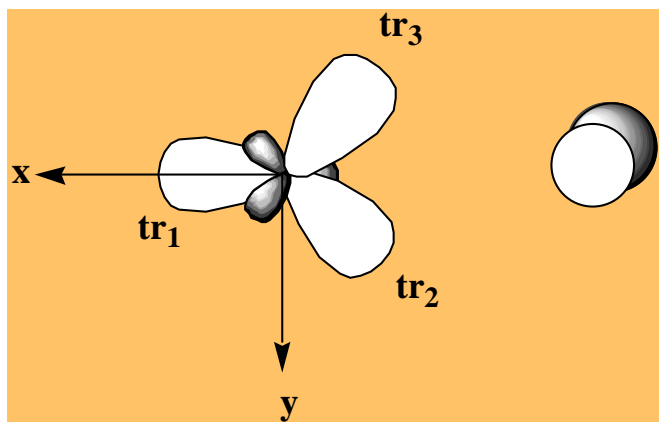
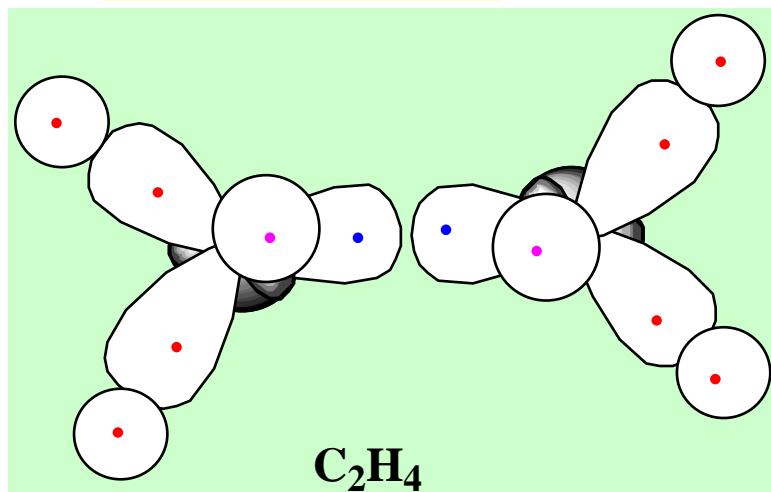
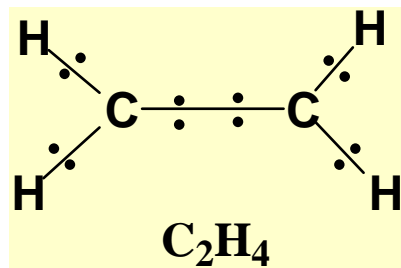
2

2

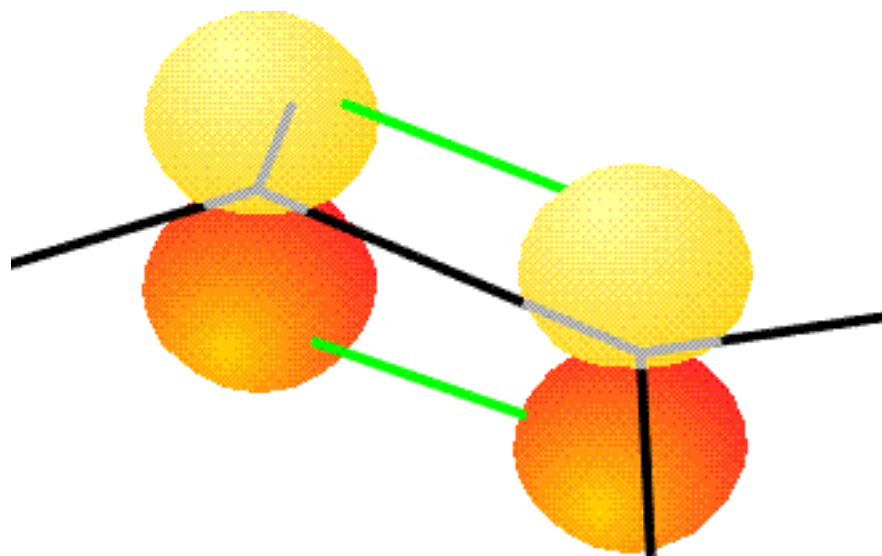
AB_2e^0	linear	$BeCl_{2(g)}$, $MX_{2(g)}$ (M = Zn, Cd, Hg), Hg_2Cl_2 , $M(CN)^{2-}$ (M = Ag, Au)
AB_2e^1	bent	NO_2^- , SO_2 , SnX_2 , PbX_2
AB_2e^2	bent	H_2O , SX_2 , SeX_2 , TeX_2 , ClO_2^-
AB_3e^0	trigonal planar	BX_3 , Gal_3 , $InMe_3$, CR_3^+
AB_3e^1	pyramidal	NH_3 , NR_3 , NX_3 , PX_3 , AsX_3 , SbX_3 , SO_3^{2-}
AB_3e^2	T-shaped	ClF_3 , BrF_3 , $PhlCl_2$
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 molecular orbital theory

1. Normal π bond



An s orbital and two p orbitals can be hybridized to form three equivalent orbitals that point towards the corners of an equilateral triangle. The remaining, unhybridized p orbital is perpendicular to the plane, forming the π bond.



2. Delocalized π bond

$$\prod_n^m$$

n-orbital numbers, m-electron numbers ($n > 2$)

Conditions for the formation of delocalized π bond

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

A. Some inorganic conjugated molecules

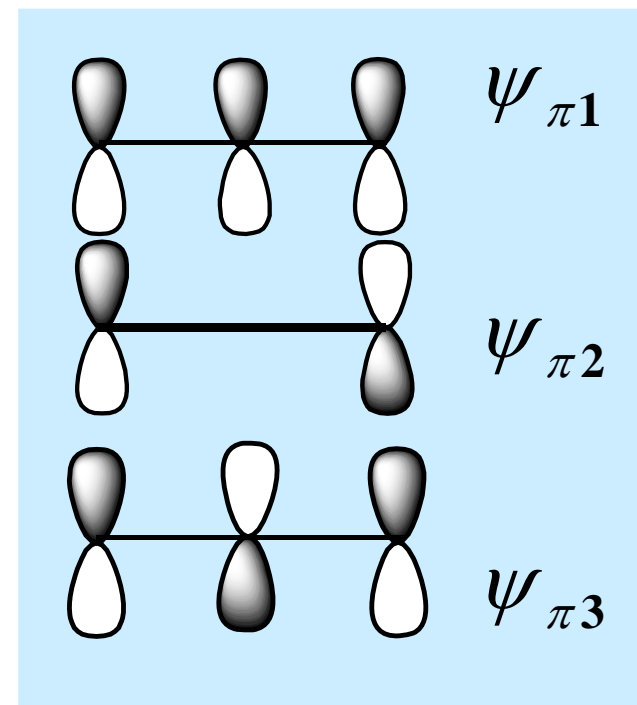
a. AB₂ type molecules

i. Linear type (16 valence electrons)

C: sp hybridization + p_x + p_y

$$\begin{aligned} \psi_{\pi 1} &= \frac{1}{2}[\phi_o(1) + \sqrt{2}\phi_c + \phi_o(2)] && \text{bonding} \\ \psi_{\pi 2} &= \frac{1}{\sqrt{2}}[\phi_o(1) - \phi_o(2)] && \text{non - bonding} \\ \psi_{\pi 3} &= \frac{1}{2}[\phi_o(1) - \sqrt{2}\phi_c + \phi_o(2)] && \text{anti - bonding} \end{aligned}$$

π electrons : 16 - 4 - 4 = 8



Isoelectronic analogy : CO₂, NO₂⁺, N₂O, N₃⁻, COS, BeCl₂, HgCl₂

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

ex. 18 O_3 (valence electron)

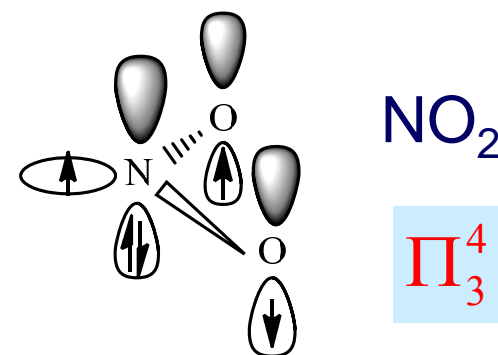
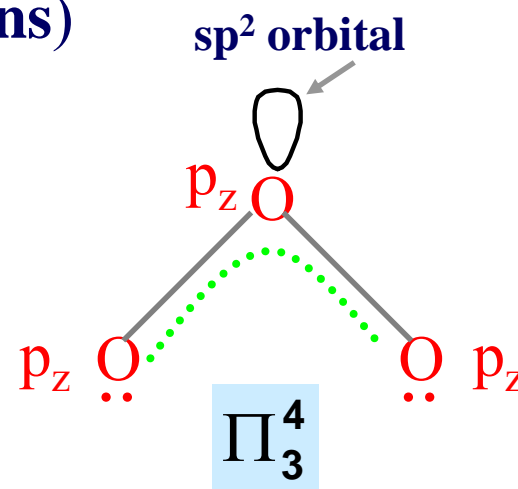
O: sp^2 hybridization + p_z

π electrons : $18 - 6 - 8 = 4$ Π_3^4

$\psi_{\pi_1} = \frac{1}{2}[\phi_1 + \sqrt{2}\phi_2 + \phi_3]$ bonding

$\psi_{\pi_2} = \frac{1}{\sqrt{2}}[\phi_1 - \phi_2]$ non-bonding

$\psi_{\pi_3} = \frac{1}{2}[\phi_1 - \sqrt{2}\phi_2 + \phi_3]$ anti-bonding



Isoelectron analogy: SO_2

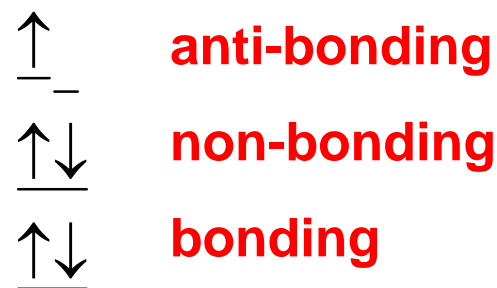
17 valence electron NO_2

19 valence electron ClO_2

Π_3^4

Π_3^3

Π_3^5



iii. Non-linear type

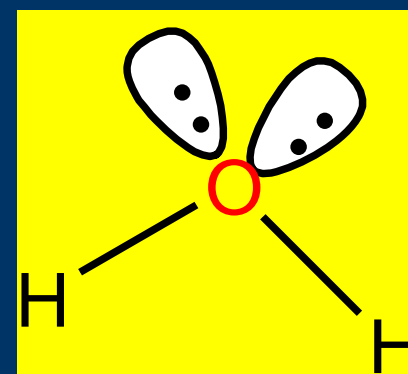
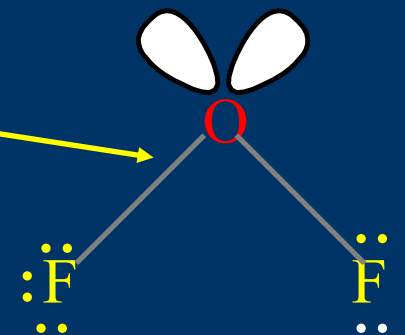
(20 valence electrons) OCl_2 , OF_2

sp^3 hybridization

$$\pi \text{ electrons : } 20 - 4 - 16 = 0$$

no delocalized π bond!

8 valence electron analogy: H_2Se , H_2S , H_2O



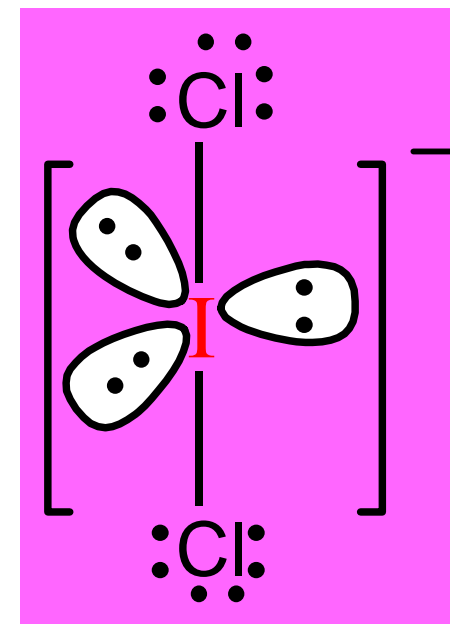
iv. Linear type (22 valence electrons) ICl_2^-

Centric atom I: sp^3d hybridization

$$\pi \text{ electrons : } 22 - 4 - 18 = 0$$

No delocalized π bond!

In fact, it is a little bent



Classification for AB₂ type molecular structure

triangular

II	III	IVB	VB	VIB	VIIB
BeX ₂		CO ₂	NO ₂	SO ₂	ClO ₂
-Zn-		COS	N ₂ O	SeO ₂	ICl ₂ ⁻
-Cd-		CS ₂	N ₃ ⁻	O ₃	IBr ₂ ⁻
-Hg-			[NO ₂] ⁺	H ₂ O	IBrCl ⁻
				OX ₂	I ₃ ⁻
				SX ₂	

linear

16 e

Non-linear

8 e; 17-20 e

Bent-linear

22 e

b. AB₃ type molecules

- i. PCl₃ : 26 valence electrons
centric atom: sp³ hybridization

Its valence electrons:

$$3 \cdot 6 + 3 \cdot 2 + 2 = 26$$

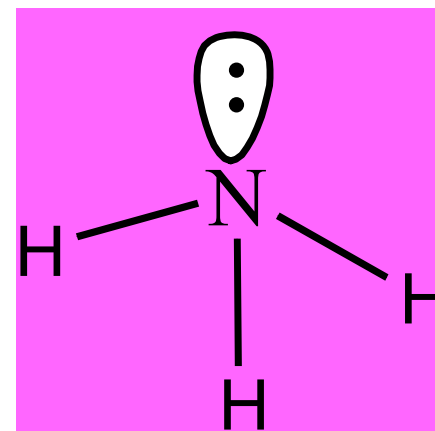
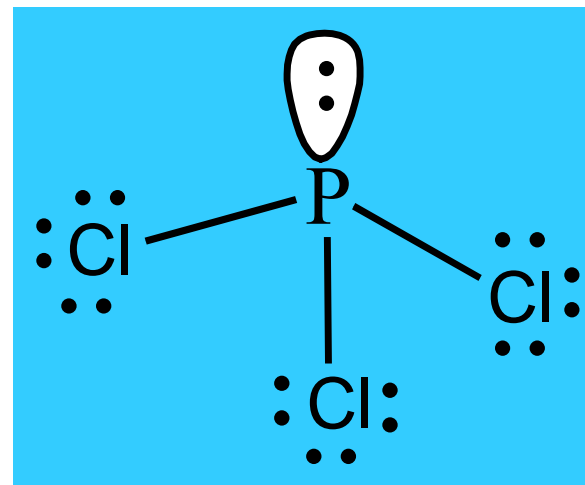
No delocalized π bond !

its analogy: PF₃, PBr₃, AsCl₃, SbCl₃

NH₃ : 8 valence electrons

Its valence electrons: $2 + 2 \cdot 3 = 8$

conjugated molecules

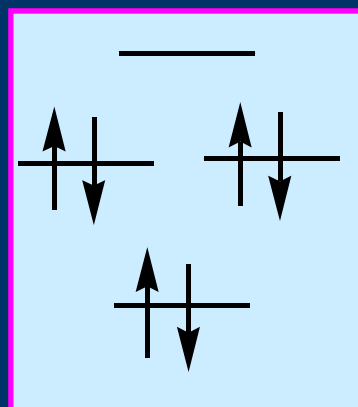


ii. Equilateral angular type BCl_3 D_{3h}

24 valence electrons

Centric atom B: sp^2 hybridization

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

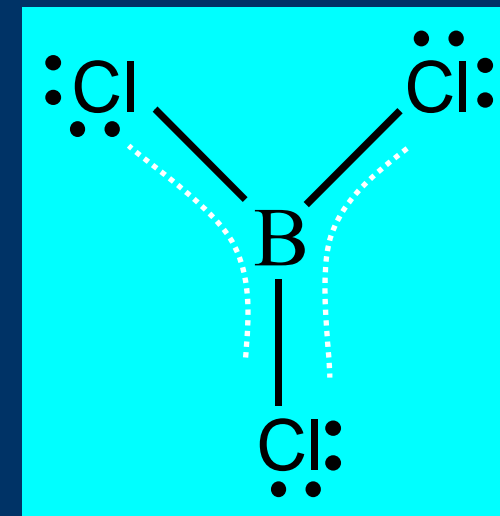


anti-bonding

non-bonding

bonding

24
-6
18
-12
6



π electrons :

Π_4^6

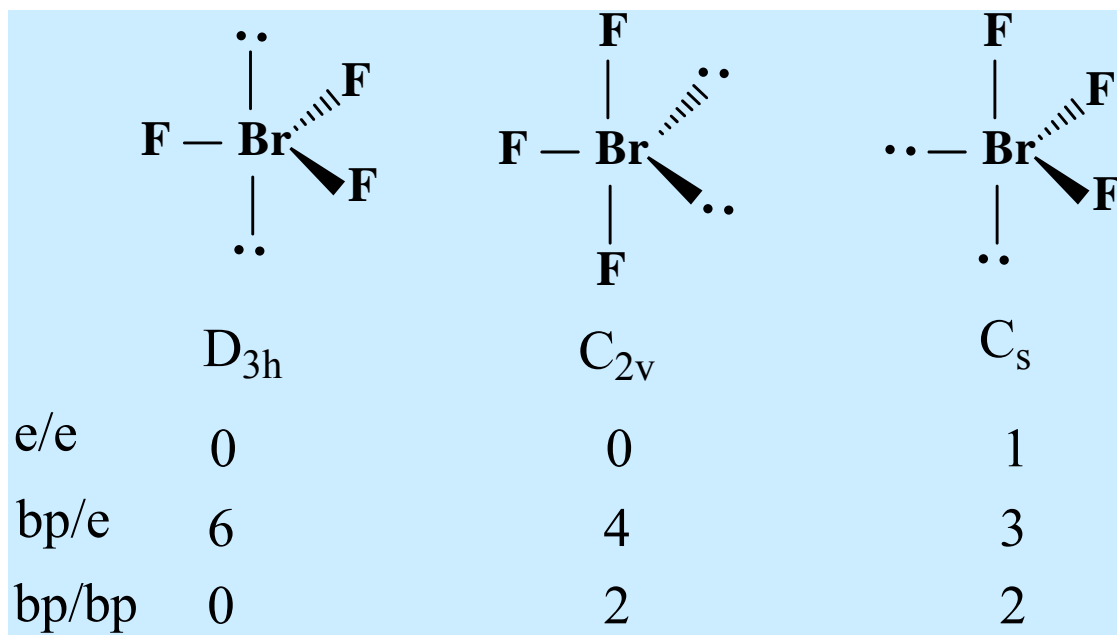
Isoelectron analogy: AlF_3 , NO_3^- , CO_3^{2-} , SO_3 , Cl_2CO ,
 $(\text{H}_2\text{N})_2\text{C}=\text{O}$, $\text{Cl}_2\text{C}=\text{S}$

For four atom angular type molecules, forming one bonding, two nonbonding and one antibonding orbitals, in general

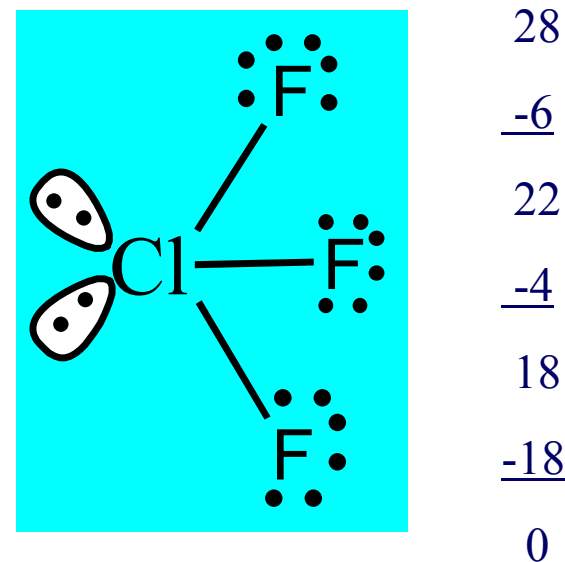
While, for four atom linear type molecules, forming two bonding and two antibonding orbitals,

iii. ClF_3 type 28 valence electrons
 centric atom Cl: sp^3d hybridization

T-shaped



π electrons :



no delocalized π bond !

Structure classification for AB₃ type

IIB	IIIB	VB	VIB	VIIB
BX ₃	CO ₃ ²⁻	NO ₃ ⁻	SO ₃	ClO ₃
AIX ₃	COX ₂	NF ₃	SO ₃ ²⁻	
	(HN ₂)CO	PF ₃		
		AsX ₃		ClF ₃
		SbX ₃		BrF ₃
		NH ₃		ICl ₃

24 e

**Equilateral
triangular**

pyramidal

8 e; 26 e

T-shaped

28 e

c. AB₄ type

i. CH₄ (8 valence electrons)

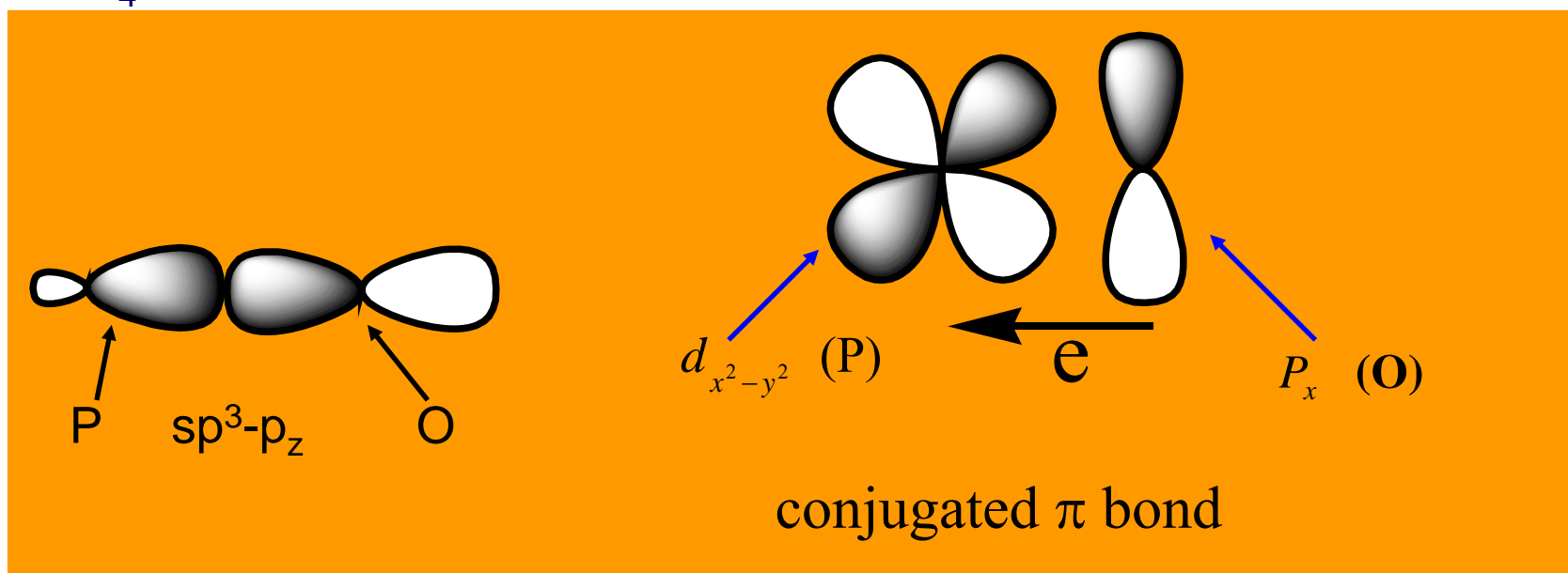
C atom takes sp³ hybridization, **no delocalized π bond**

analogy: CCl₄, CH₄⁺

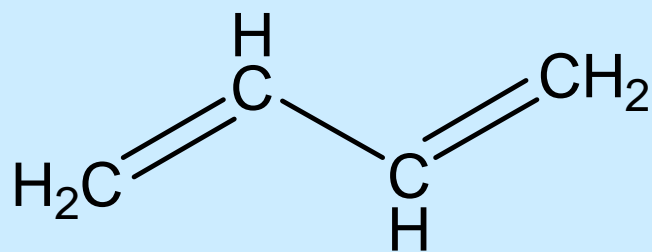
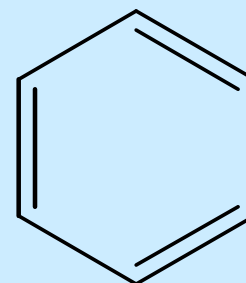
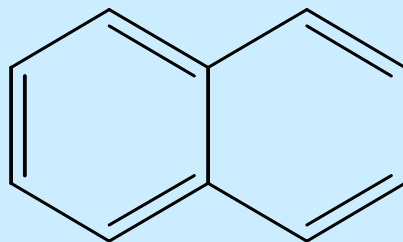
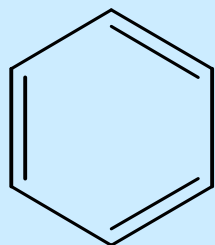
ii. PO₄³⁻ (32 valence electrons)

P atom takes sp³ hybridization, forming four σ P-O and d-p conjugated π bonds

SO₄²⁻



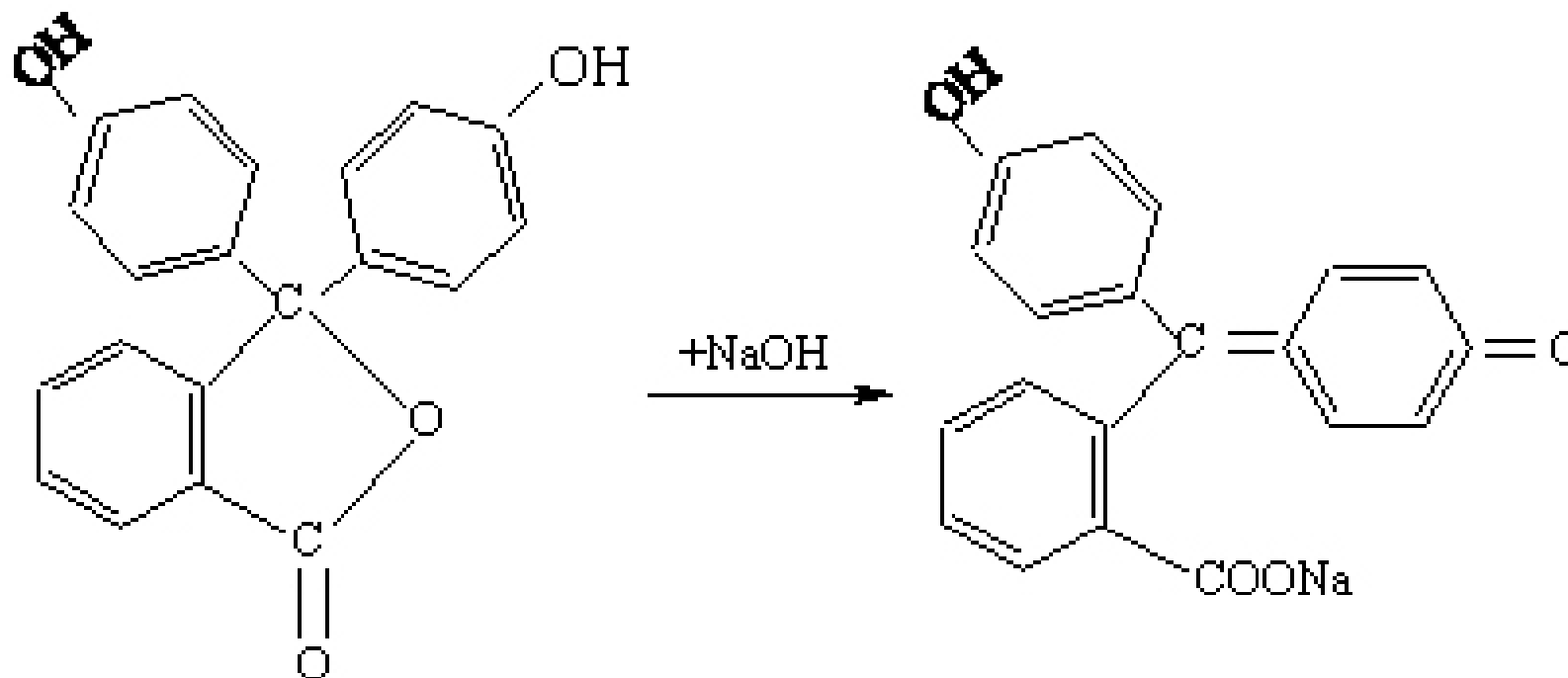
B. Some organic conjugated molecules



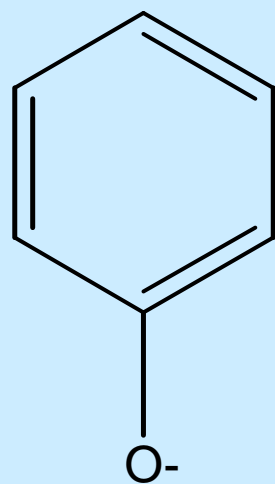
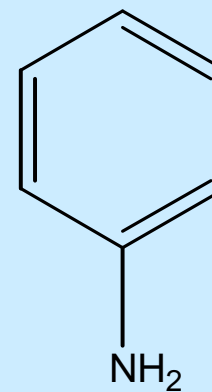
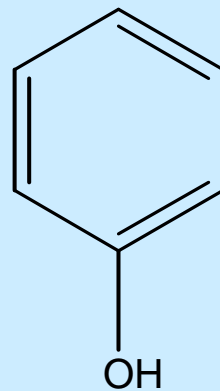
3. The conjugation effect.

i. The electrical conductivity is enhanced by the delocalization of π bond.

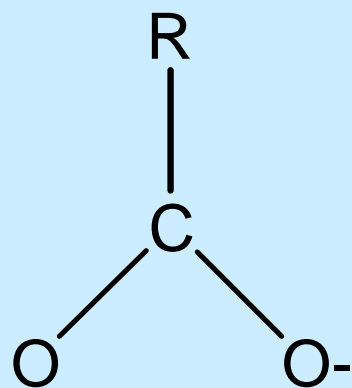
ii. Color. The formation of delocalized π bond increases the delocalized extent of the π electrons and causes the energy of the system to decrease.



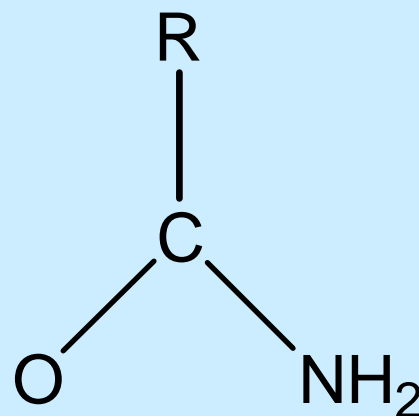
iii. Acidity and basicity.



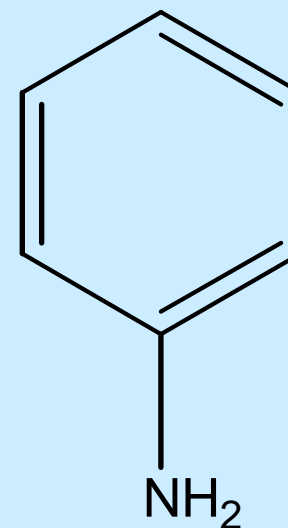
$$\Pi_7^8$$



$$\Pi_3^4$$



$$\Pi_3^4$$

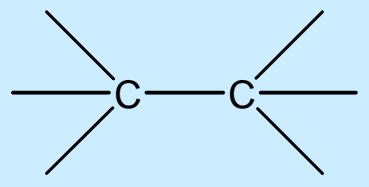
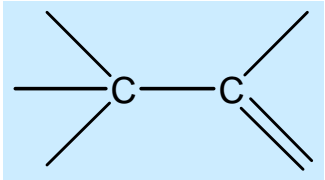
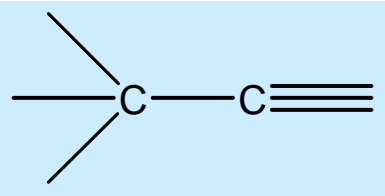


$$\Pi_7^8$$

iv. Chemical reactivity.

e.g. $\text{H}_2\text{C}=\text{CH}-\text{Cl}$ The formation of π_3^4 causes a contraction of the C-Cl bond, and reduces the lability of Cl.

4. The hyperconjugation.

Bond type	Hybridization	C-C bond length (\AA)	C-C bond energy($\text{kJ}\cdot\text{mol}^{-1}$)
	$\text{sp}^3\text{-sp}^3$	1.54	346.3
	$\text{sp}^3\text{-sp}^2$	1.51	357.6
	$\text{sp}^3\text{-sp}$	1.46	382.5

§ 5.4 Hückel molecular orbital theory and conjugated system

§ 4 Huckel molecular orbital theory and conjugated system

1. HMO method

$$(1) \psi = \sum_i c_i \phi_i$$

$$(2) E = \int \psi^* \hat{H} \psi d\tau$$

$$(3) \frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = \dots = \frac{\partial E}{\partial c_n} = 0$$

(4) secular equation

thus

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

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

HMO method

Modified Hückel molecular orbital theory

$$H_{ii} = \int \psi_i^* \hat{H} \psi_i d\tau = \alpha$$

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

$$S_{ij} = \int \psi_i^* \psi_j d\tau = 1 \quad (\text{if } i = j)$$
$$= 0 \quad (\text{if } i = j \pm 1)$$
$$= 0 \quad (\text{if } i \neq j \pm 1)$$

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

The Nobel Prize in Chemistry 1981

Frontier orbital theory & Conservation of orbital symmetry

"for their theories, developed independently, concerning the course of chemical reactions"



Kenichi Fukui



Roald Hoffmann

2. The HMO treatment for butadiene



$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

Secular equation

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

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

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

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

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

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

$$x_1^2 = 0.38 \quad x_1 = \pm 0.618$$

$$x_2^2 = 2.62 \quad x_2 = \pm 1.618$$

thus,

$$E_1 = \alpha + 1.618\beta$$

$$E_2 = \alpha + 0.618\beta$$

$$E_3 = \alpha - 0.618\beta$$

$$E_4 = \alpha - 1.618\beta$$

Bonding

Bonding

Anti-bonding

Anti-bonding

solve secular equation :

$$c_1 x + c_2 = 0$$

$$c_1 + c_2 x + c_3 = 0$$

$$c_2 + c_3 x + c_4 = 0$$

$$c_3 x + c_4 = 0$$

and,

$$c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$$

substituting $x = -1.618$

$$c_1 = c_4 = 0.372$$

$$c_2 = c_3 = 0.602$$

$$E_1 = \alpha + 1.618\beta$$

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

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

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

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

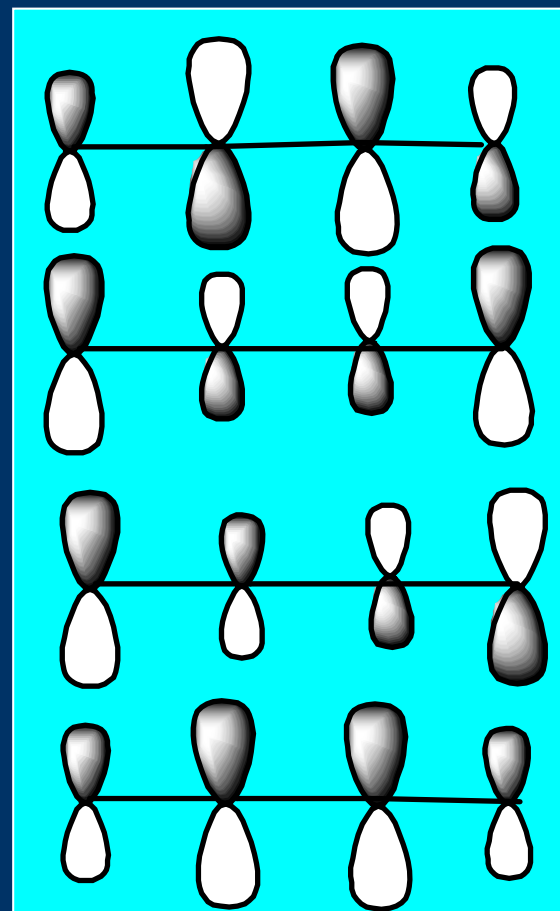
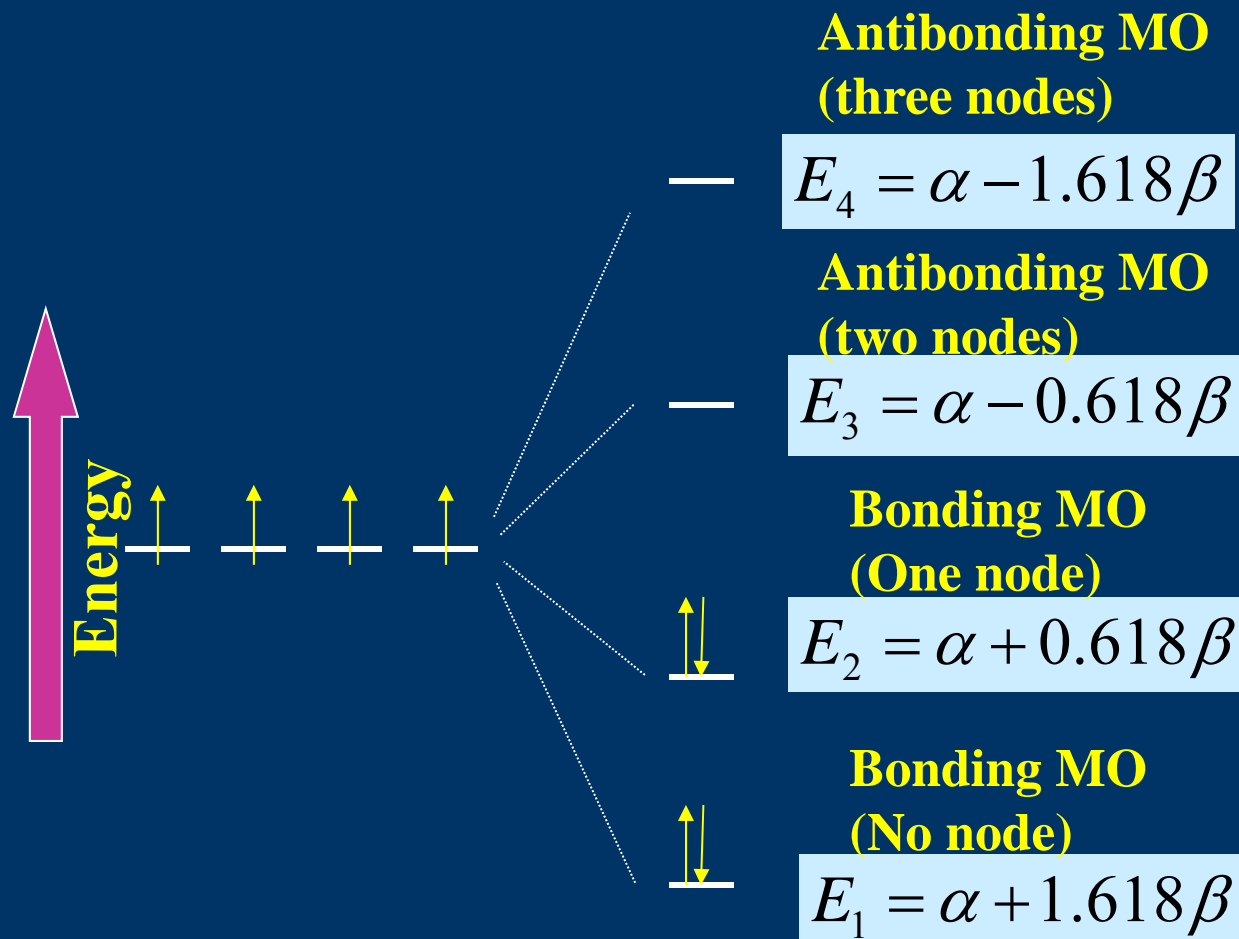
$$\psi_4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4$$

$$E_1 = \alpha + 1.618\beta$$

$$E_2 = \alpha + 0.618\beta$$

$$E_3 = \alpha - 0.618\beta$$

$$E_4 = \alpha - 1.618\beta$$



Delocalized energy

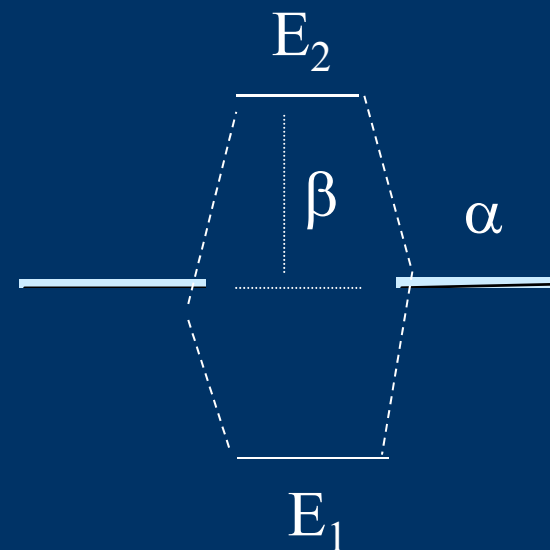
$$E_{\pi} = E_p - E_{total} = 4\alpha - [2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)] = -4.48\beta$$

if forms two localized π orbitals

$$E_{\pi} = -4\beta$$

thus, delocalized energy or resonance energy

$$E_{\pi d} = 0.48\beta$$



3. Population analysis and molecular diagrams of conjugated system

i. Charge density --- the probability of π electrons on the i^{th} atom

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

$$\rho_1 = 2 \times 0.372^2 + 2 \times 0.602^2 = 1.000$$

$$\rho_2 = 2 \times 0.602^2 + 2 \times 0.372^2 = 1.000$$

$$\rho_3 = \rho_4 = 1.000$$

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

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

$$\psi_{\pi}^3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$

$$\psi_{\pi}^4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4$$

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

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

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

$$p_{23} = 2 \times 0.602^2 + 2 \times 0.372^2 \times (-1) = 0.448$$

iii. Free valence index --- the relative magnitude of the residue bonding ability of the i^{th} atom

$$F_i = P_{\max} - \sum_{j=1} P_{ij}$$

$$P_{\max} = \sqrt{3}$$

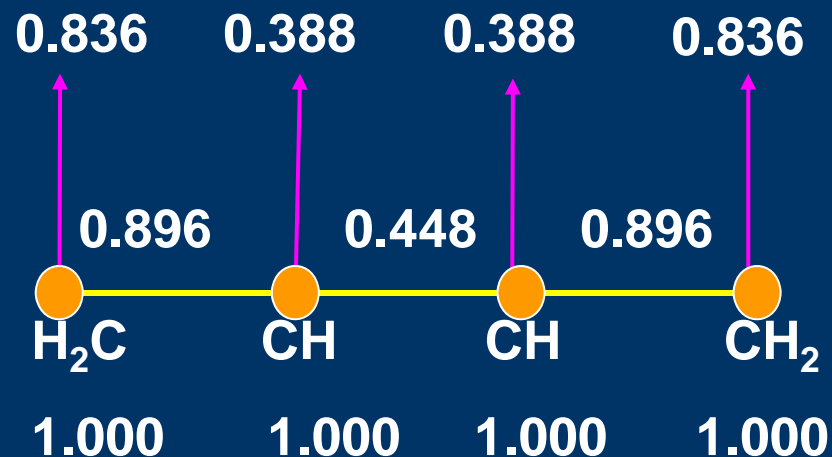
$$F_1 = \sqrt{3} - 0.896 = 0.836 = F_4$$

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

Example: 1,4 addition reaction of butadiene



iv. Molecular diagram.



4. The HMO treatment of cyclic conjugated polyene (C_nH_n)

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

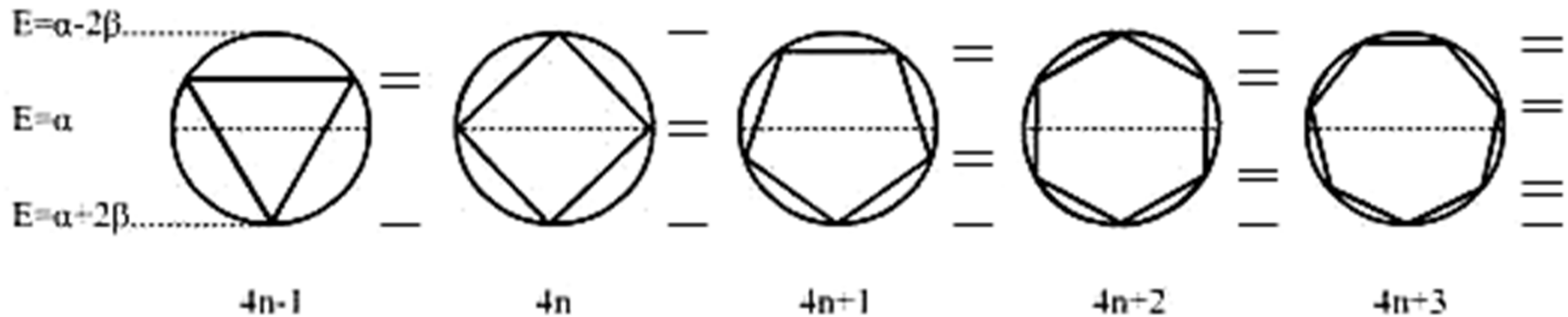
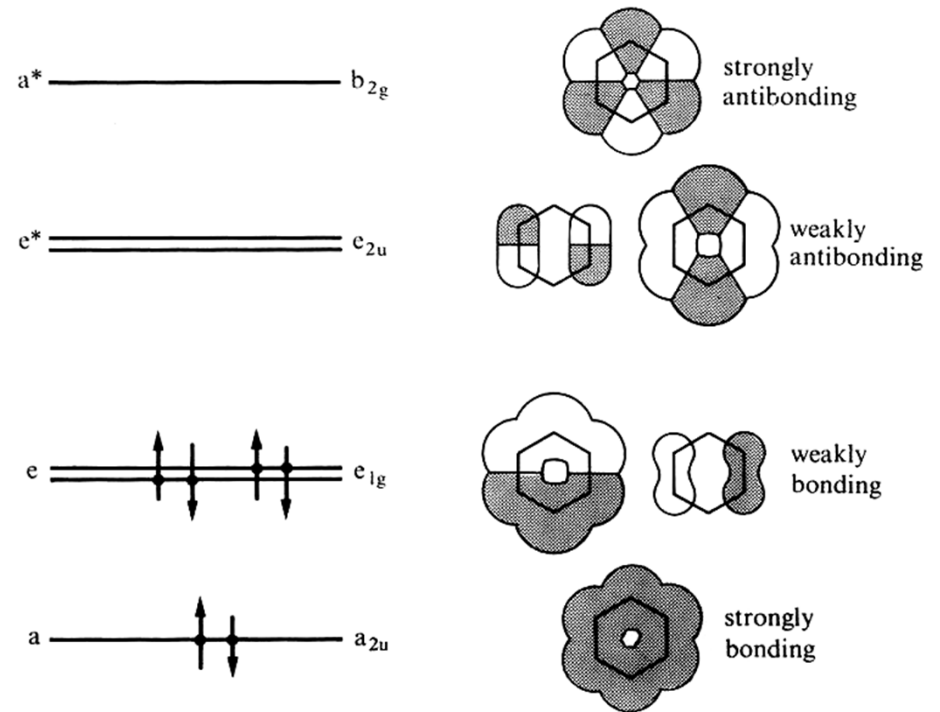
$$\psi_5(e_{2u}) = \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

$$\psi_4(e_{2u}) = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)$$

$$\psi_3(e_{1g}) = \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

$$\psi_2(e_{1g}) = \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

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



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

(AO = atomic orbital, MO = molecular orbital)

Molecular orbital method of pre-determined AO coefficients

Principle

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

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

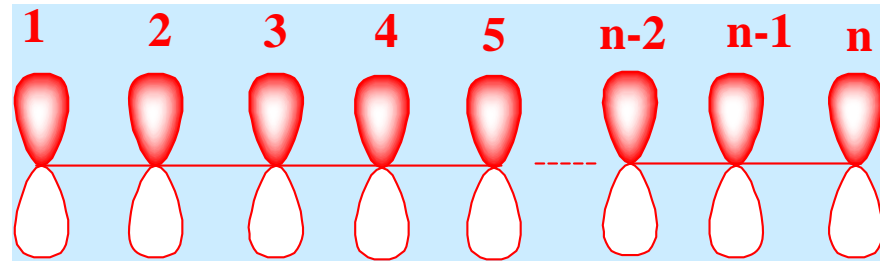
$$C_2\beta + C_3(\alpha - E) + C_4\beta = 0$$

.....

$$C_{k-1}\beta + C_k(\alpha - E) + C_{k+1}\beta = 0$$

.....

$$C_{n-1}\beta + C_n(\alpha - E) = 0$$



$$-xc_1 + c_2 = 0$$

$$c_1 - xc_2 + c_3 = 0$$

$$c_2 - xc_3 + c_4 = 0$$

...

$$c_{n-1} - xc_n = 0$$

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

$$xc_k = c_{k-1} + c_{k+1}$$

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

$$E = \alpha + x\beta$$

$$\text{let } x = 2\cos\theta$$

$$E = \alpha + 2\beta\cos\theta$$

$$-2\cos\theta C_1 + C_2 = 0$$

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

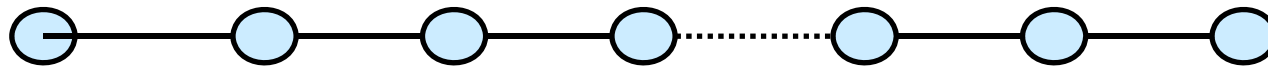
$$\text{let } C_1 = \sin\theta$$

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

$$C_3 = \sin 3\theta$$

thus :

$$C_1 = \sin\theta, \quad C_2 = \sin 2\theta, \quad C_3 = \sin 3\theta, \dots, C_n = \sin n\theta$$



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

$$\sin(n-1)\theta \quad \sin n\theta$$

$$c_1 - xc_2 + c_3 = 0 \Rightarrow c_3 = xc_2 - c_1$$

$$c_3 = 2\cos\theta \sin 2\theta - \sin\theta = \sin 2\theta \cos\theta + \sin 2\theta \cos\theta - \sin\theta$$

$$= \sin 2\theta \cos\theta + \sin\theta(2\cos^2\theta - 1) = \sin 2\theta \cos\theta + \sin\theta \cos 2\theta$$

$$= \sin 3\theta$$

From $C_{k-1}\beta + C_k(\alpha - E) + C_{k+1}\beta = 0$

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

$$\sin n\theta \neq 0, \quad \sin(n+1)\theta = 0$$

$$(n+1)\theta = m\pi \quad \Rightarrow \quad \theta = \frac{m\pi}{n+1} \quad (m = 1, 2, 3, \dots, n)$$

$$x = 2 \cos \theta = 2 \cos \frac{m\pi}{n+1}$$

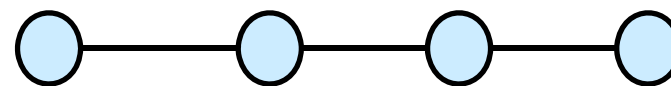
$$E = \alpha + x\beta = \alpha + 2\beta \cos \frac{m\pi}{n+1} \quad (m = 1, 2, 3, \dots, n)$$

$$\psi_m = \sum_{K=1}^n \sqrt{\frac{2}{n+1}} \sin \frac{km\pi}{n+1} \phi_k \quad (m = 1, 2, 3, \dots, n)$$

Normalization coefficients

Example

i) **butadiene** (n=4)



$$\sin 5\theta = 0$$

$$\theta = \frac{m\pi}{n+1} = \frac{m\pi}{5}$$

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

θ	36° (m = 1)	72° (m = 2)	108° (m = 3)	144° (m = 4)
$2 \cos \theta$	1.618	0.618	-0.618	-1.618
E	$\alpha + 1.618\beta$	$\alpha + 0.618\beta$	$\alpha - 0.618\beta$	$\alpha - 1.618\beta$

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

$$(m = 1, 2, 3, 4)$$

$$\psi_\pi^1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$

$$\psi_\pi^2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$

$$\psi_\pi^3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$

$$\psi_\pi^4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4$$

ii) hexatriene n=6



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

$$\sin 7\theta = 0$$

$$E_m = \alpha + 2\beta \cos \frac{m\pi}{7} \quad (m = 1, 2, 3, 4, 5, 6)$$

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

For even orbitals, there are $n/2$ bonding orbitals and $n/2$ antibonding orbitals.

For odd orbitals, there are $(n-1)/2$ bonding orbitals, $(n-1)/2$ antibonding orbitals and 1 non-bonding orbitals.

iii) Symmetry classification

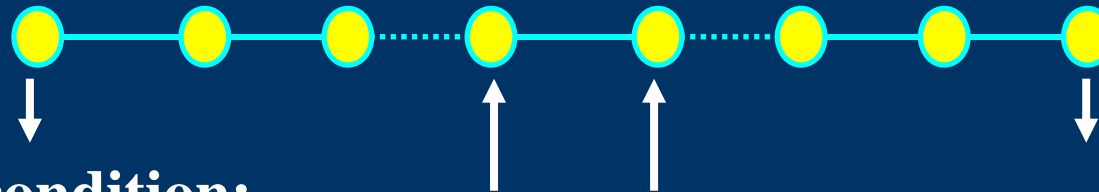
a. Molecules with even carbon atoms

Symmetric:

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

$$\cos \frac{1}{2} \theta, \cos \frac{1}{2} \theta$$

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

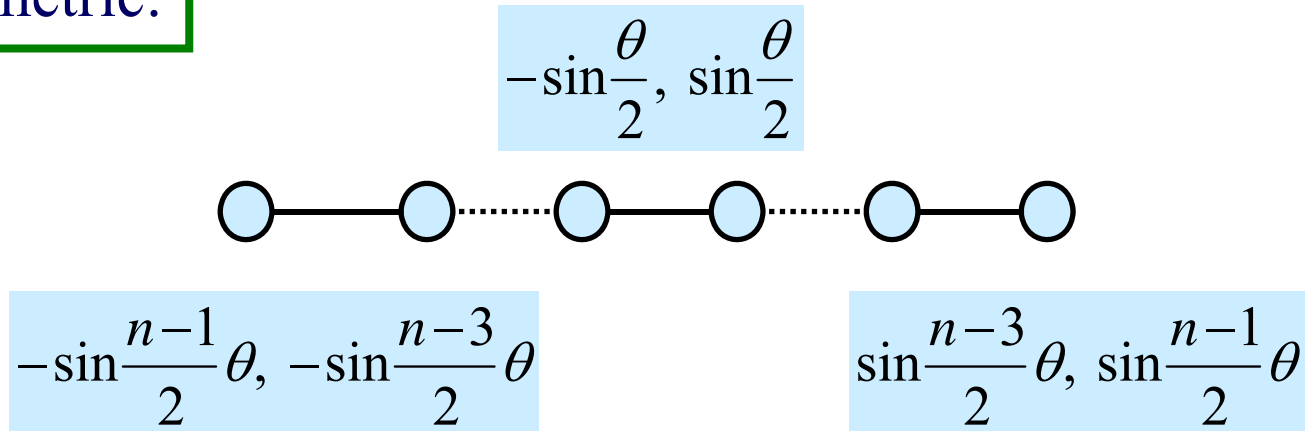


The boundary condition:

$$\cos \frac{n+1}{2} \theta = 0 \quad \Rightarrow \quad \theta = \frac{2m+1}{n+1} \pi$$

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

asymmetric:



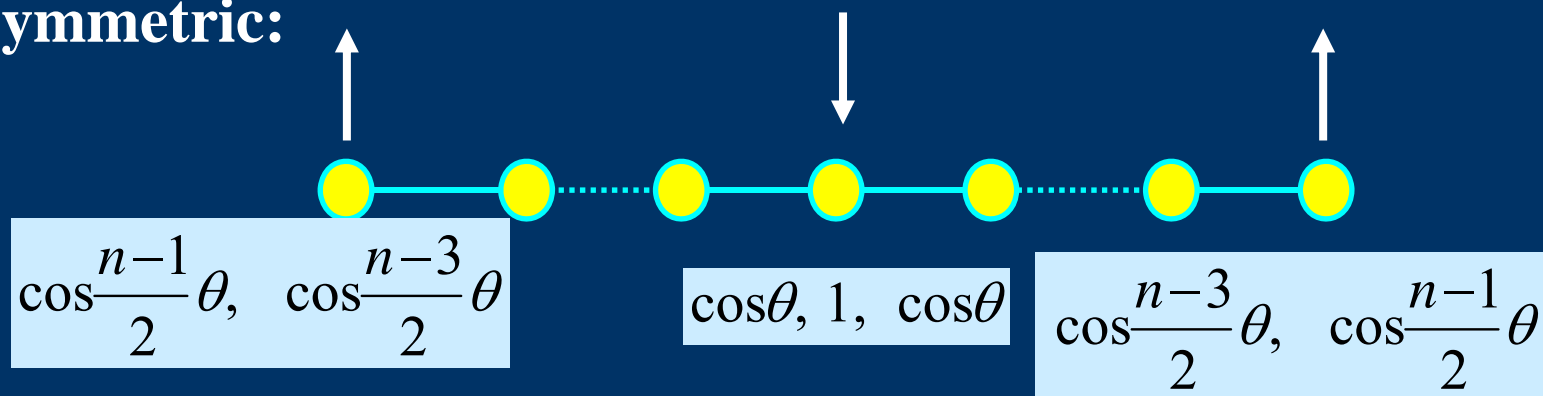
The boundary condition:

$$\sin\frac{n+1}{2}\theta = 0 \quad \Rightarrow \quad \theta = \frac{2m}{n+1}\pi \quad (m = 1, 2, \dots, \leq \frac{n}{2})$$

$$E = \alpha + 2\beta\cos\frac{2m}{n+1}\pi \quad (m = 1, 2, \dots, \leq \frac{n}{2})$$

b. Molecules with odd carbon atoms

Symmetric:

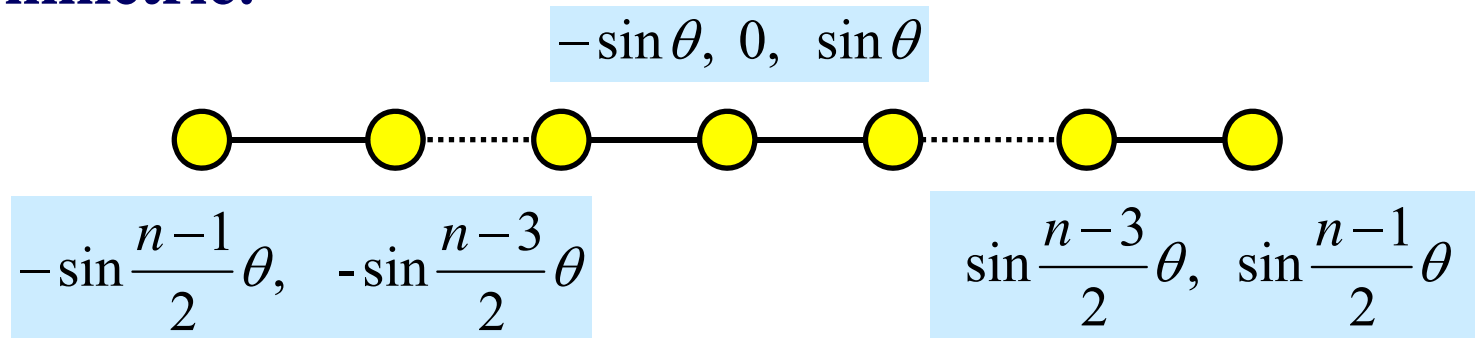


Boundary conditions:

$$\cos \frac{n+1}{2} \theta = 0 \quad \Rightarrow \quad \theta = \frac{2m+1}{n+1} \pi \quad (m = 0, 1, 2, \dots, < \frac{n}{2})$$

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

Asymmetric:



Boundary condition:

$$\sin \frac{n+1}{2} \theta = 0 \quad \Rightarrow \quad \theta = \frac{2m}{n+1} \pi \quad (m = 1, 2, \dots, < \frac{n}{2})$$

$$E = \alpha + 2\beta \cos \frac{2m}{n+1} \pi \quad (m = 1, 2, \dots, < \frac{n}{2})$$

Example:

$$\cos 2\theta, \quad \cos \theta, \quad 1, \quad \cos \theta, \quad \cos 2\theta$$



$$-\sin 2\theta, \quad -\sin \theta, \quad 0, \quad \sin \theta, \quad \sin 2\theta$$

symmetric

$$E = \alpha + 1.732\beta \quad (m = 0) \quad \text{bonding}$$

$$E = \alpha \quad (m = 1) \quad \text{non - bonding}$$

$$E = \alpha - 1.732\beta \quad (m = 2) \quad \text{anti - bonding}$$

$$\theta = \frac{2m+1}{5+1} \pi = \frac{2m+1}{6} \pi \quad (m = 0,1,2)$$

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

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

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

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

Example:

$$\cos 2\theta, \quad \cos \theta, \quad 1, \quad \cos \theta, \quad \cos 2\theta$$



$$-\sin 2\theta, \quad -\sin \theta, \quad 0, \quad \sin \theta, \quad \sin 2\theta$$

asymmetric

$$E = \alpha + \beta \quad (m = 1) \quad \text{bonding}$$

$$E = \alpha - \beta \quad (m = 2) \quad \text{anti-bonding}$$

$$\theta = \frac{2m}{5+1} \pi \quad (m = 1, 2)$$

$$E = \alpha + 2\beta \cos \frac{2m}{5+1} \pi \quad (m = 1, 2)$$

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

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

c. Cyclic conjugated molecules

Example 1: benzene ---solution I

i) Symmetric MOs

Boundary condition:

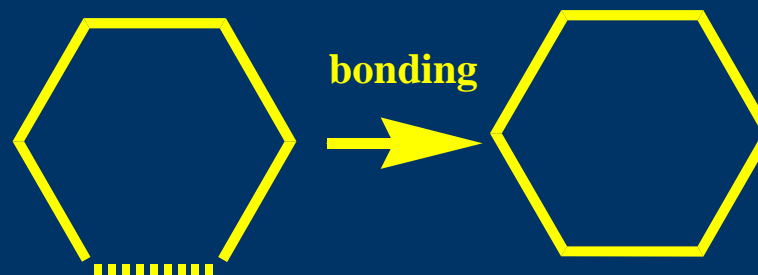
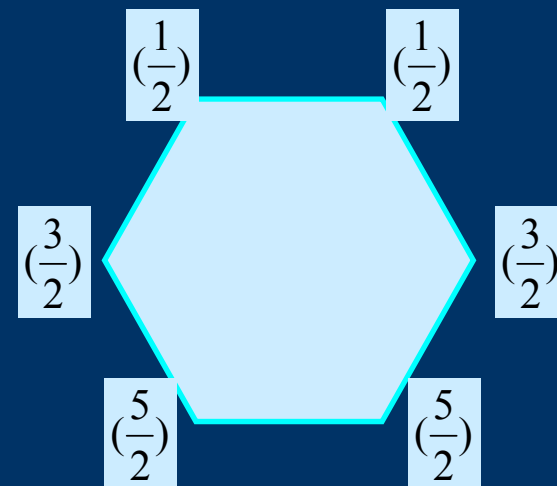
$$2 \cos \theta C_k = C_{k+1} + C_{k-1}$$

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

$$\cos \frac{7}{2} \theta - \cos \frac{5}{2} \theta = 0$$

$$-2 \sin 3\theta \sin \frac{\theta}{2} = 0$$

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



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

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

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

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

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

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

θ	$0^\circ,$	$60^\circ,$	120°
$\cos \theta$	1	1/2	-1/2
$2 \cos \theta$	2	1	-1
E	$\alpha + 2\beta$	$\alpha + \beta$	$\alpha - \beta$
	ψ_1	ψ_2	ψ_3

$$\psi_1 = N(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

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

$$\psi_2 = N\left(0 + \frac{\sqrt{3}}{2}\phi_2 + \frac{\sqrt{3}}{2}\phi_3 + 0 - \frac{\sqrt{3}}{2}\phi_5 - \frac{\sqrt{3}}{2}\phi_6\right)$$

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

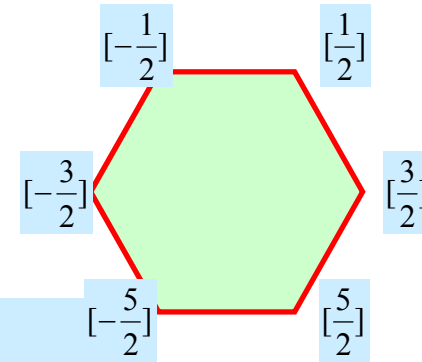
$$\psi_3 = N\left(-\phi_1 + \frac{1}{2}\phi_2 + \frac{1}{2}\phi_3 - \phi_4 + \frac{1}{2}\phi_5 + \frac{1}{2}\phi_6\right)$$

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

ii) Asymmetric MOs

Boundary condition:

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



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

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

$$\sin \frac{7}{2} \theta + \sin \frac{5}{2} \theta = 0$$

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

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

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

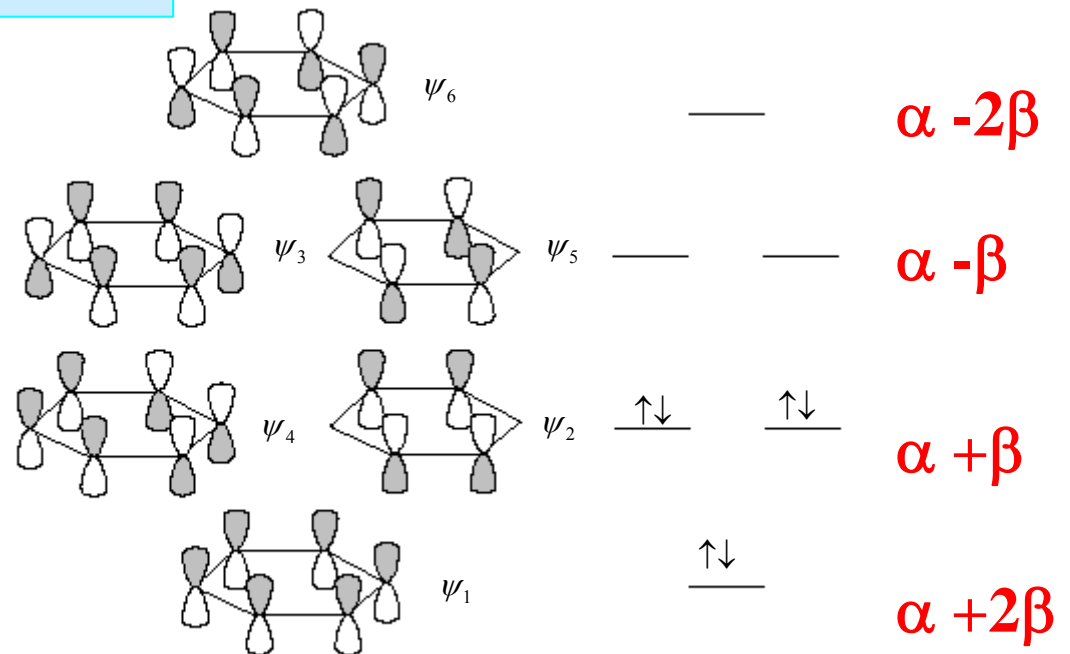
$$= \frac{1}{\sqrt{6}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

$$\psi_5 = N(0 + \frac{\sqrt{3}}{2}\phi_2 - \frac{\sqrt{3}}{2}\phi_3 + 0 + \frac{\sqrt{3}}{2}\phi_5 - \frac{\sqrt{3}}{2}\phi_6)$$

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

$$\psi_6 = N(-\phi_1 + \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6)$$

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



Example 2: benzene ---solution II

i) Symmetric

Boundary condition:

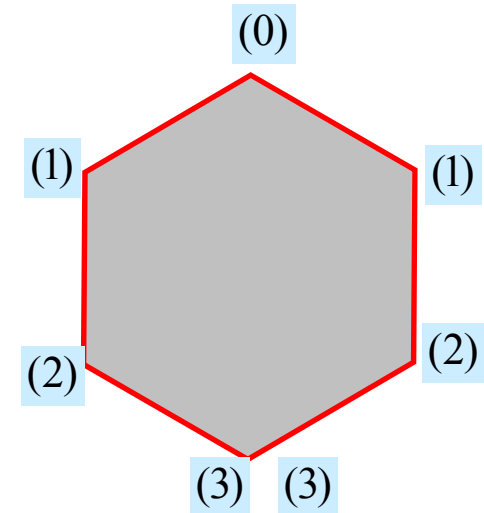
$$2 \cos \theta C_k = C_{k+1} + C_{k-1}$$

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

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

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

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	

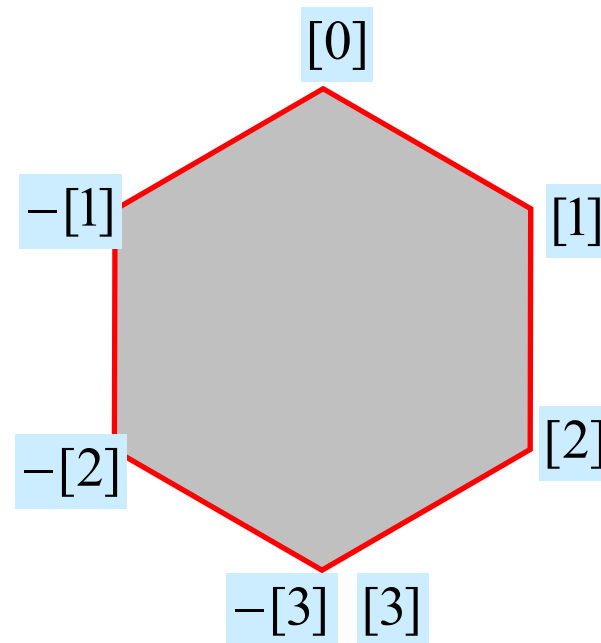


ii) asymmetric

$$\sin 3\theta = -\sin 3\theta$$

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

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



Complicated p-conjugation: e.g., benzyl

How to get the coefficient of atom 7?

1) Symmetric MOs:

The secular equation centred at atom 6:

$$C_6(\alpha - E) + C_4\beta + C_5\beta + C_7\beta = 0$$

$$\text{let } -2\cos\theta = (\alpha - E) / \beta$$

$$\therefore C_7 = 2\cos\theta C_6 - C_4 - C_5$$

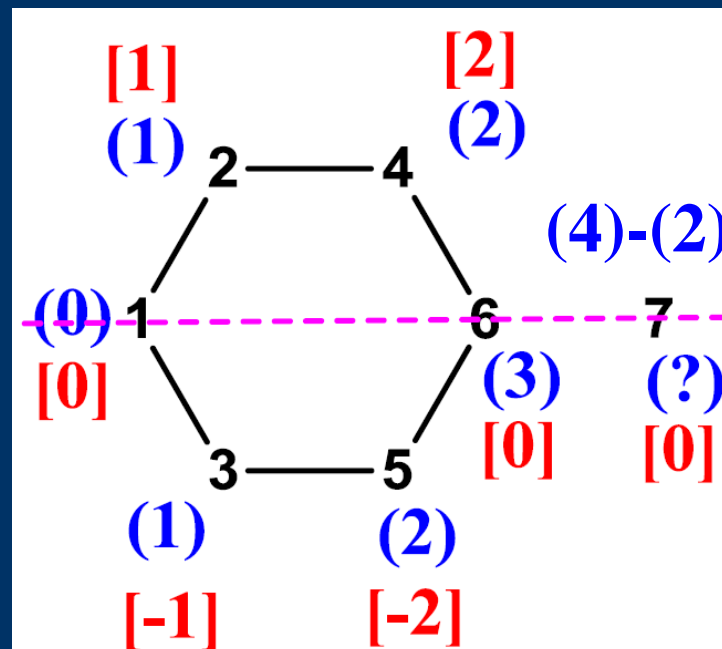
$$= 2\cos\theta \cos 3\theta - 2\cos 2\theta$$

$$= \cos 4\theta - \cos 2\theta$$

Boundary condition:

$$2\cos\theta C_7 = C_6 \Rightarrow$$

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



2) Asymmetric MOs:

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

$$\therefore 2\cos\theta = \pm 1$$

§ 5 The symmetry of molecular orbital and symmetry rules for molecular reactions

Brief introduction:

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



§ 5 The symmetry of molecular orbital and symmetry rules for molecular reactions

1. Frontier molecular orbitals (1951)

We need to consider only two molecular orbitals, the HOMO and LUMO, to predict the structure of the product; called frontier MO's

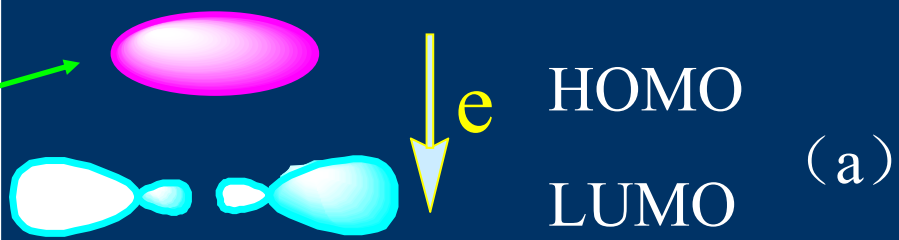
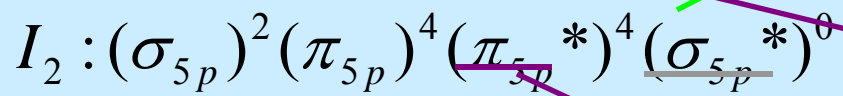
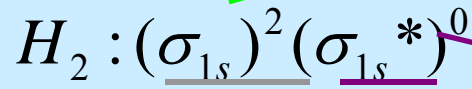
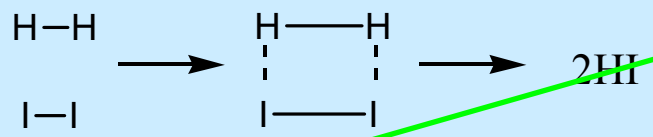
Highest occupied molecular orbital (HOMO)

Lowest unoccupied molecular orbital (LUMO)

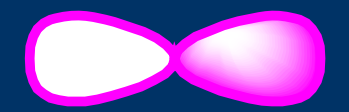
- A deeper understanding of chemical reactivity can be gained by focusing on the *frontier orbitals* of the reactants.

Reaction condition

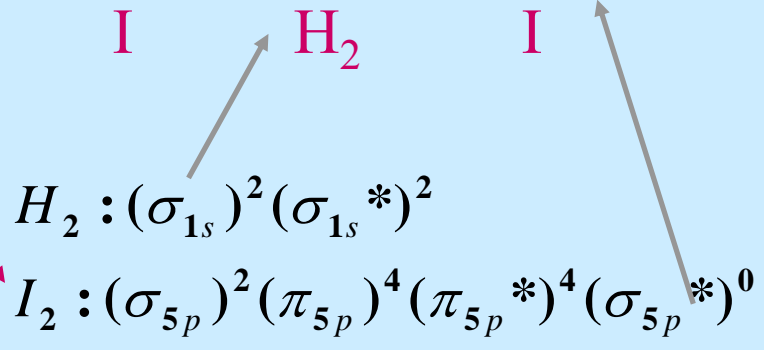
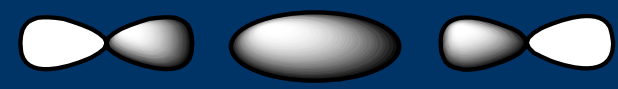
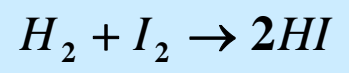
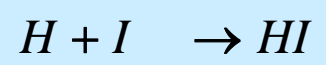
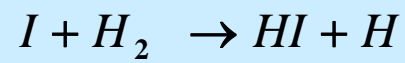
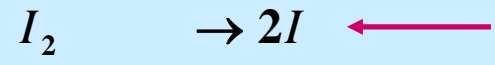
1. *During the course of a chemical reaction, the orbitals that are most readily accessible for interaction are the frontier orbitals. When two molecules approach each other, the symmetry of the HOMO of one molecule must be compatible with that of the LUMO of the other molecule, i.e. orbitals with the same sign will overlap. This forms a transition state which is relatively stable and is a symmetry allowed state.*
2. *The energy levels of the interacting HOMO and LUMO must be comparable (within 6 eV).*
3. *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.*



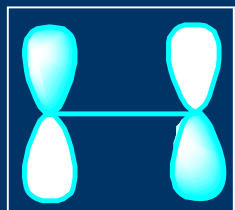
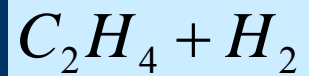
overlap=0



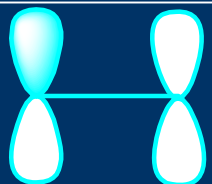
Its mechanics



Example B:



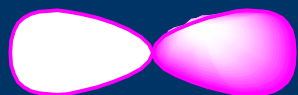
LUMO



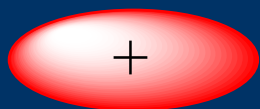
HOMO



The π MOs of Ethylene

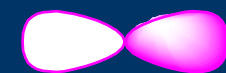
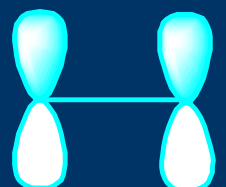
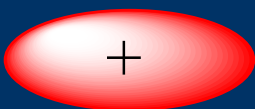
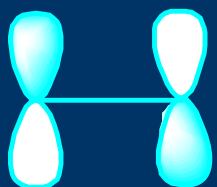
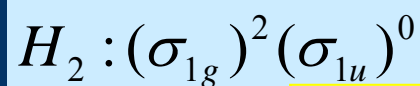


LUMO



HOMO

The MOs of Hydrogen

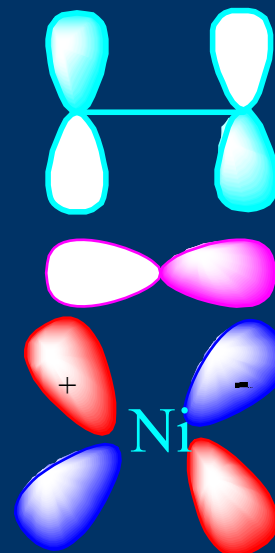


C_2H_4

H_2

Overlap=0, Not compatible in symmetry

The reaction
requires
catalyst



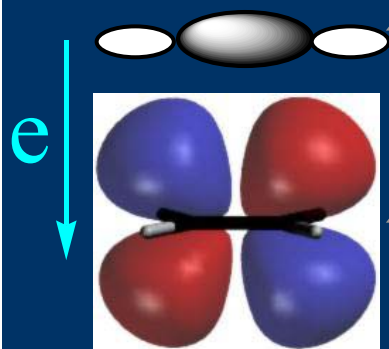
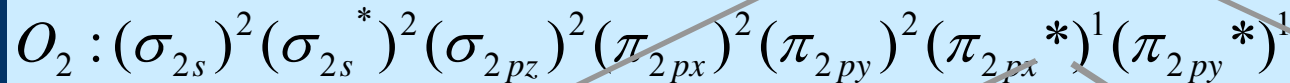
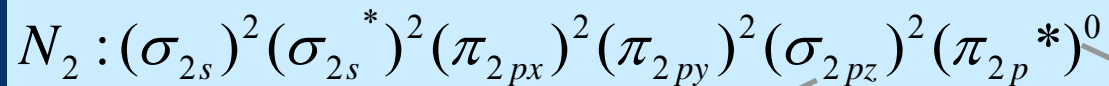
C_2H_4

H_2

Ni

e

Example C, $N_2 + O_2 \rightarrow 2NO$



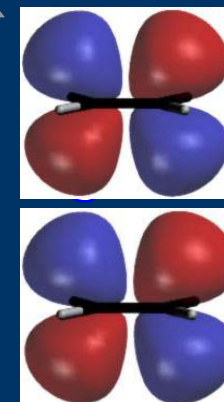
HOMO

LUMO

overlap=0

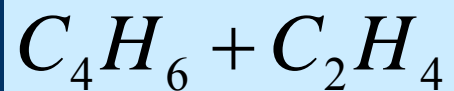
LUMO

HOMO

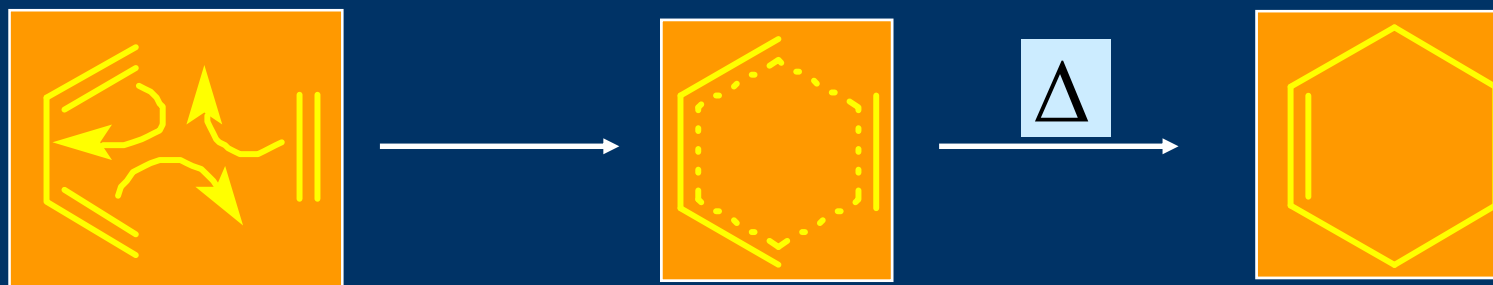


**Electron transferring
is not reasonable**

Example D:

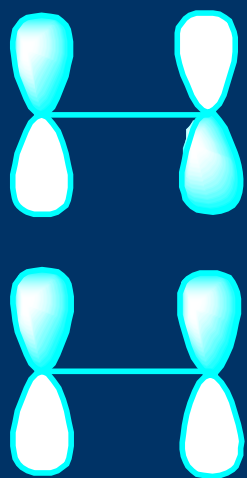


Diels-Alder Reaction [4+2]- π -electrons



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

The π MOs of Ethylene

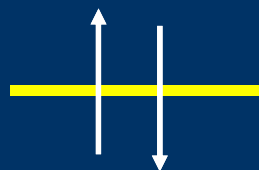


LUMO

Antibonding π orbital of ethylene;
no electrons in this orbital

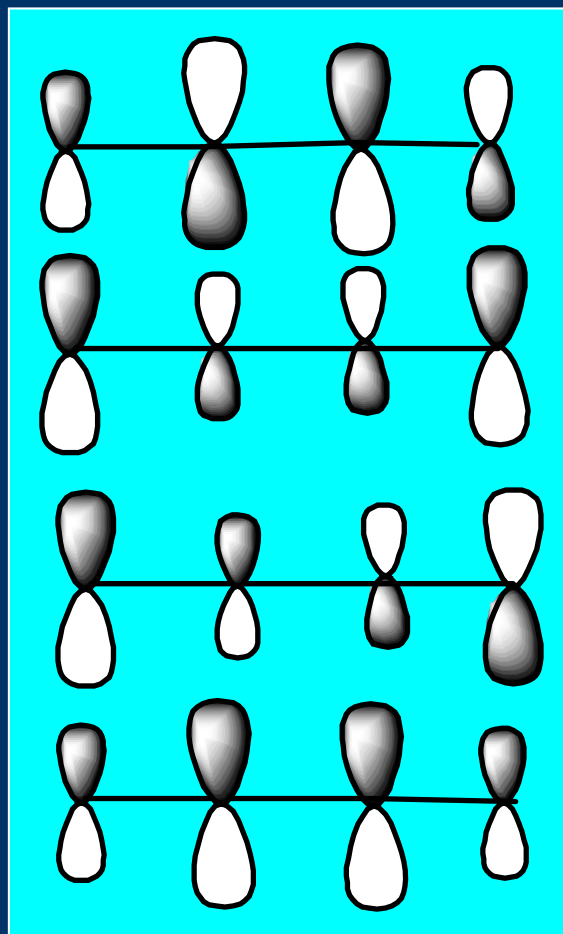


HOMO



Bonding π orbital of ethylene;
two electrons in this orbital

π MOs of 1,3-Butadiene



Highest energy orbital

LUMO

Both antibonding



orbitals are vacant

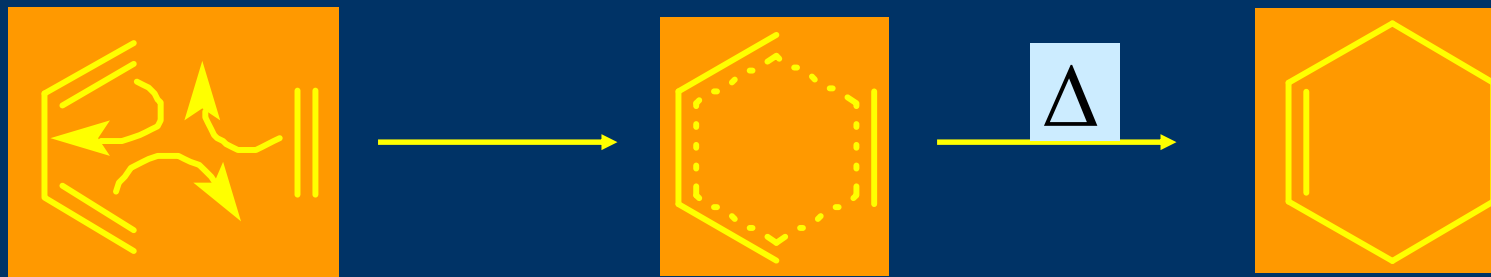
HOMO



4 π electrons; 2 in
each orbital

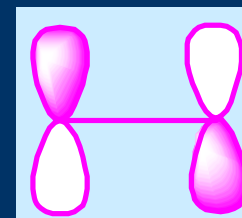
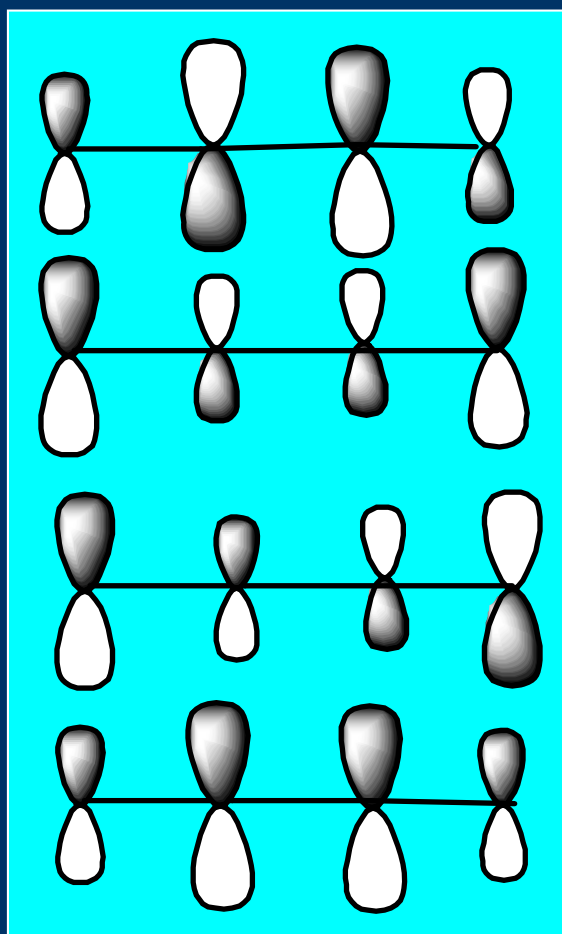


Lowest energy orbital

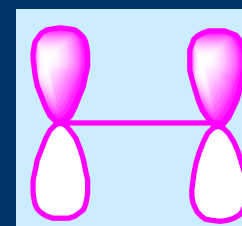


LUMO

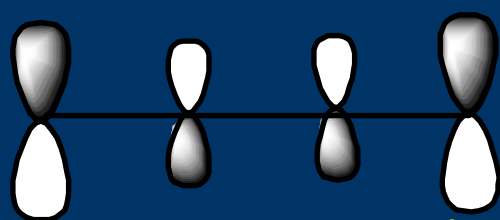
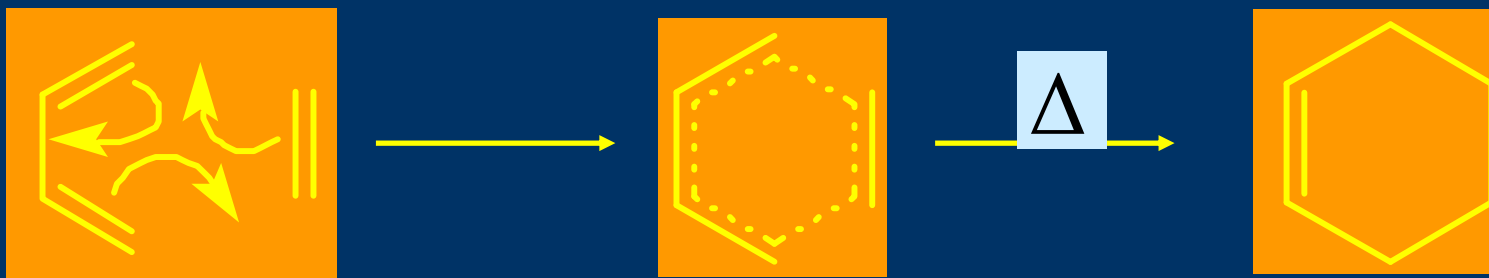
HOMO



LUMO

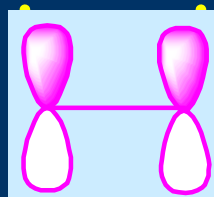
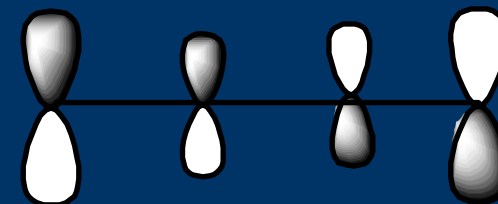


HOMO



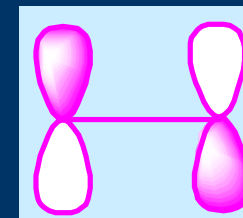
LUMO

HOMO



HOMO

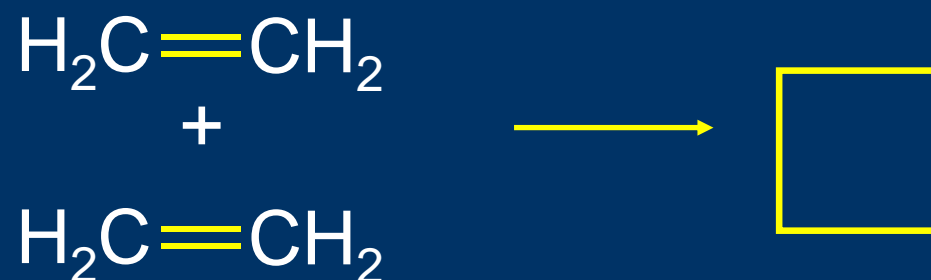
LUMO



This cycloaddition reaction can proceed by heating because the symmetry of the frontier orbitals are compatible.

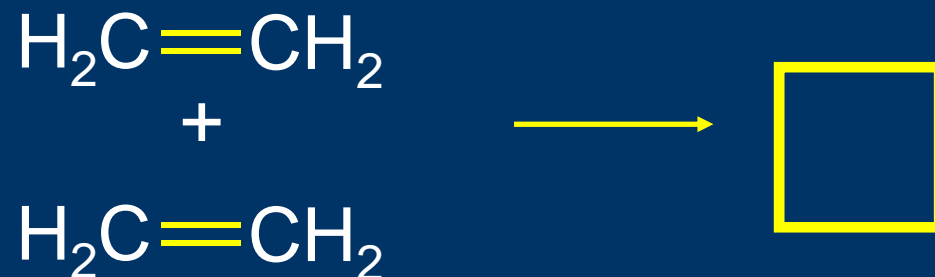
Example E:

A "forbidden" reaction

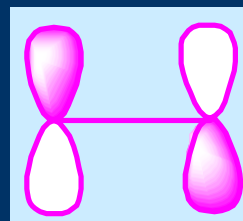


- The dimerization of ethylene to give cyclobutane does not occur under conditions of typical Diels-Alder reactions. Why not?

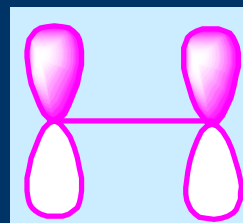
A "forbidden" reaction



HOMO-LUMO mismatch of two ethylene molecules precludes single-step formation of two new σ bonds



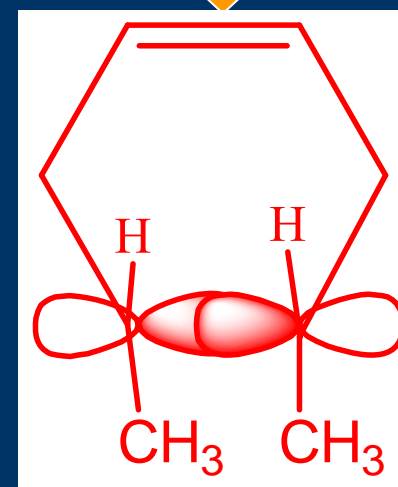
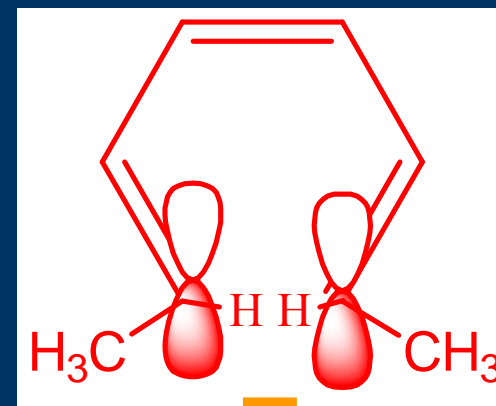
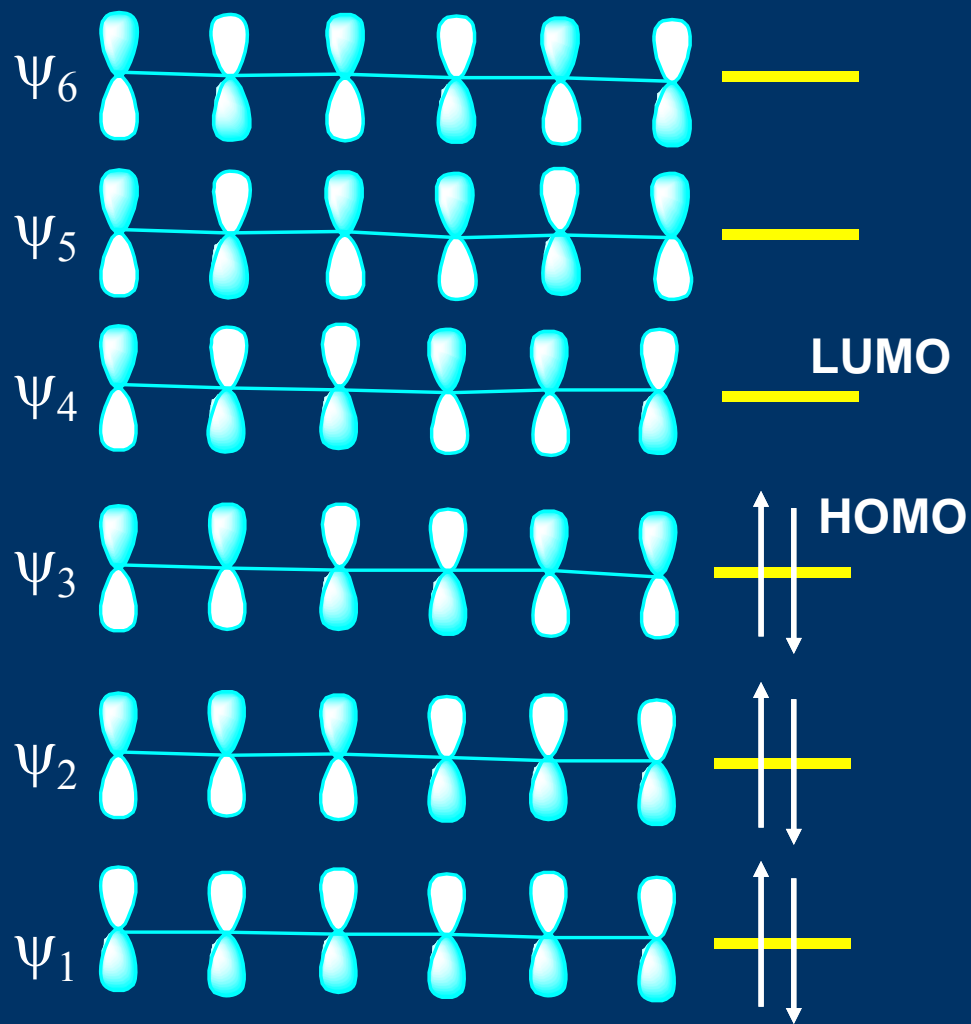
HOMO of one ethylene molecule



LUMO of other ethylene molecule

Example E: Octatriene

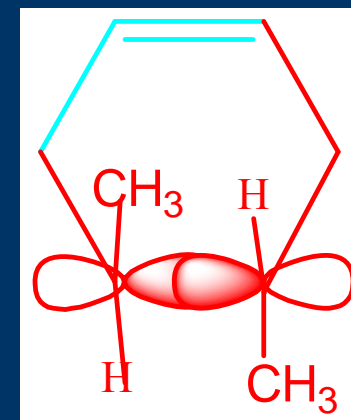
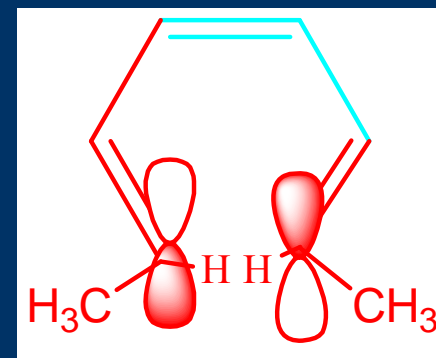
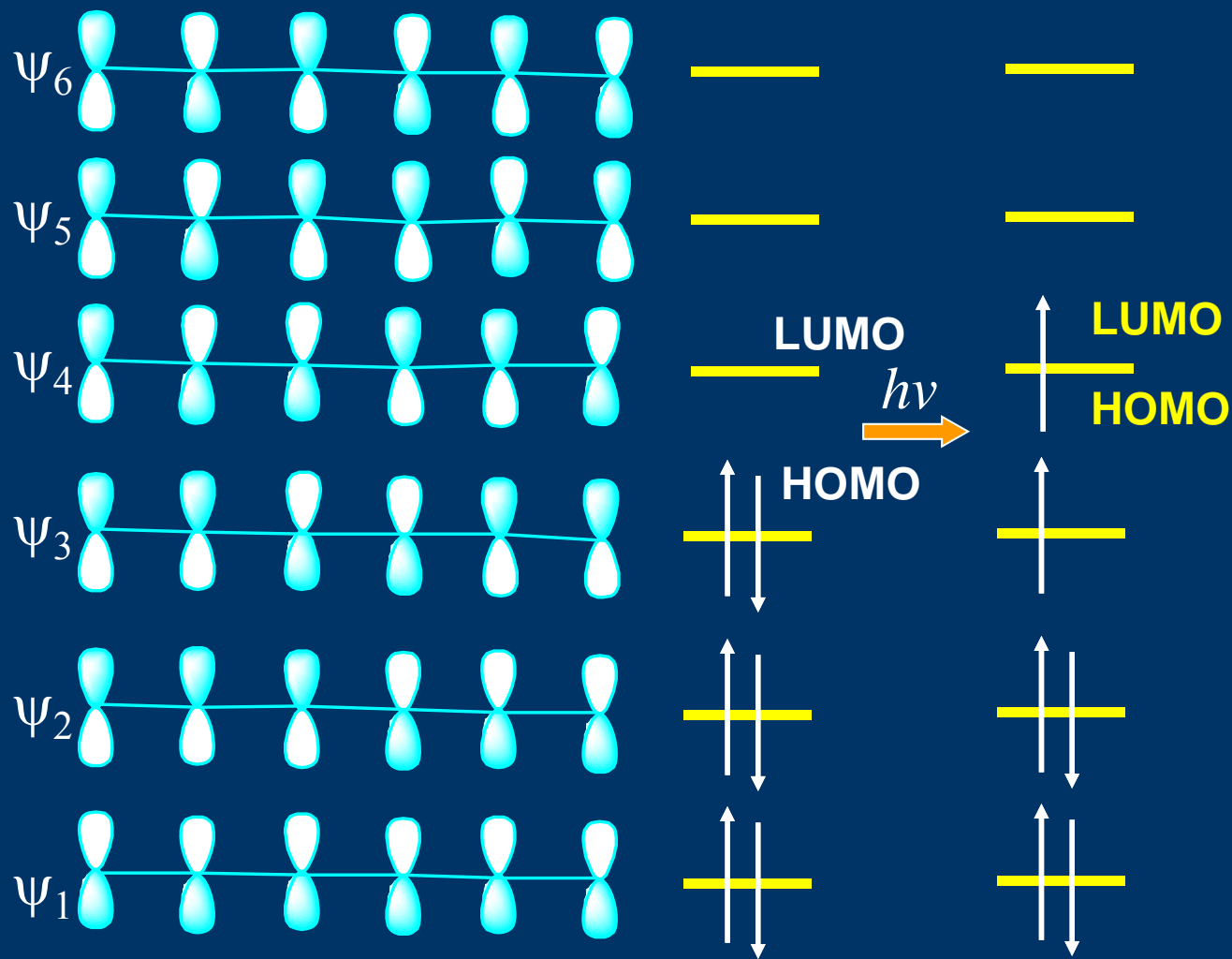
Thermal Electrocyclic Reactions



disrotary

Example E: Octatriene

Photochemical Electrocyclic Reactions



conrotatory

Stereochemical Rules for the Electrocyclic Reactions

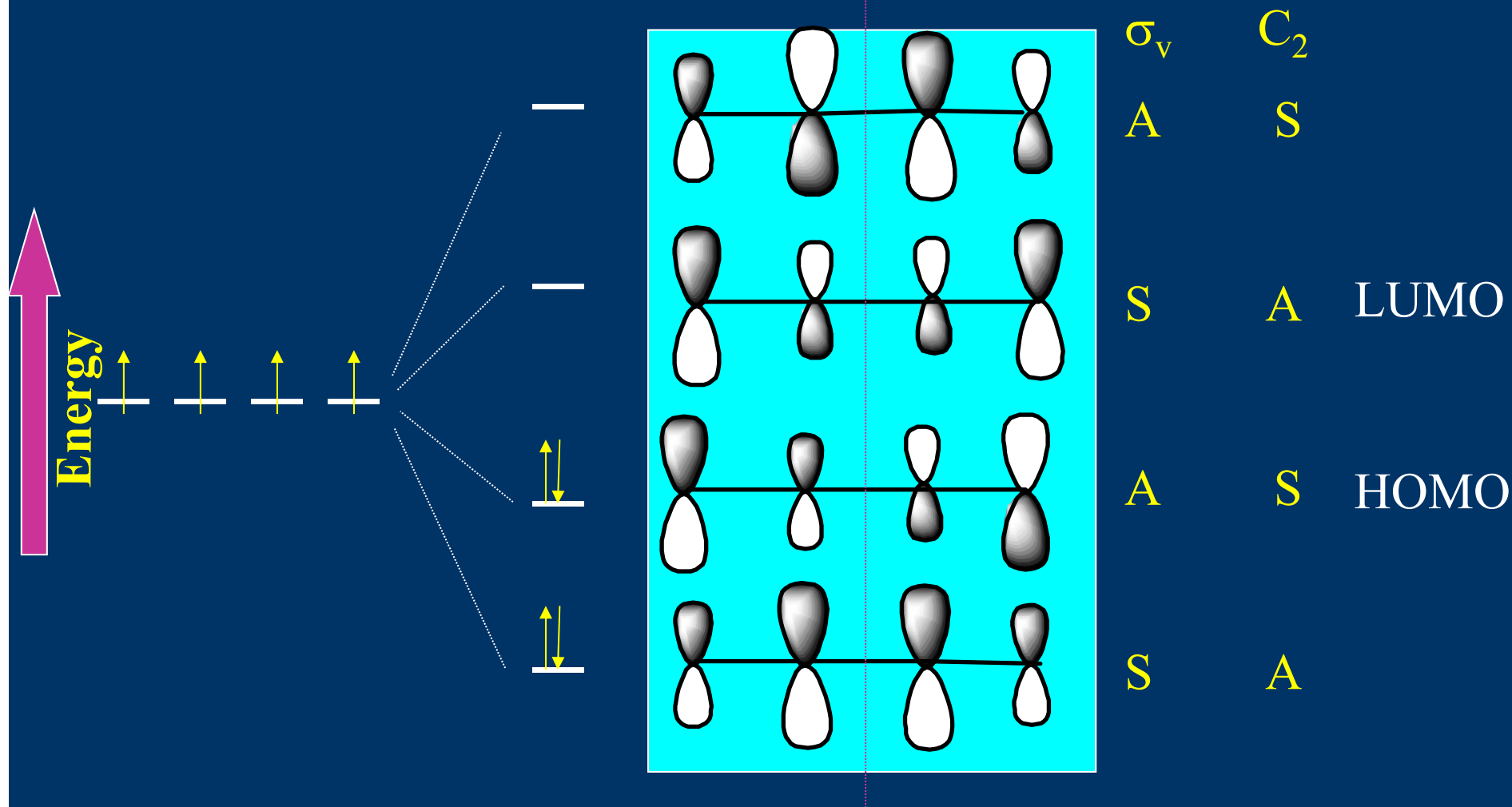
Electron pairs (double bonds)	Thermal Reaction	Photochemical Reaction
even number	conrotary	disrotary
odd number	disrotary	conrotary

2. Woodward-Hoffmann rules --- Symmetry principle of molecular orbital

- i. There is a one to one correspondence between the m.o.'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 compatible symmetry do not intersect.**

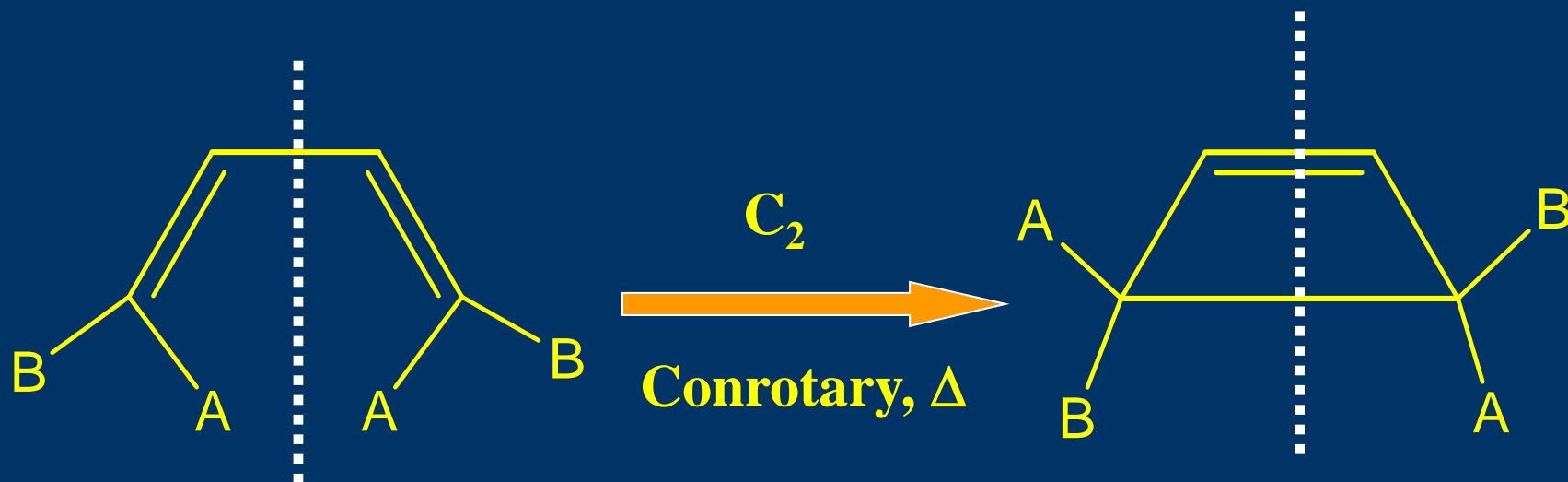
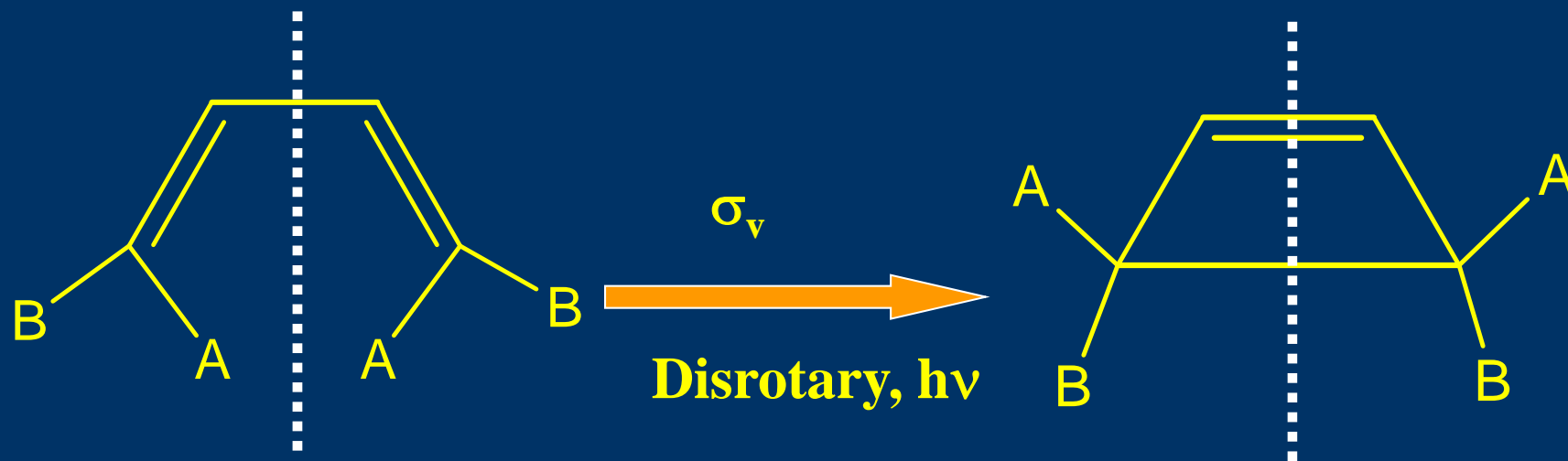
Example A: *Electrocyclic Reactions of butadiene*

π MOs of butadiene

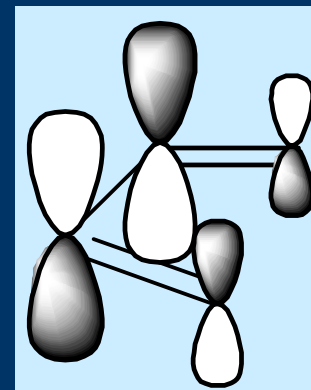
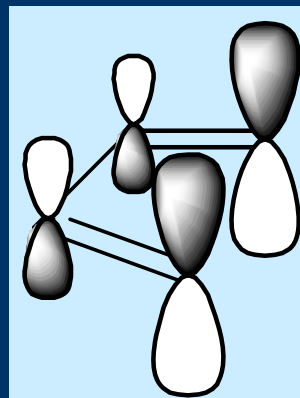
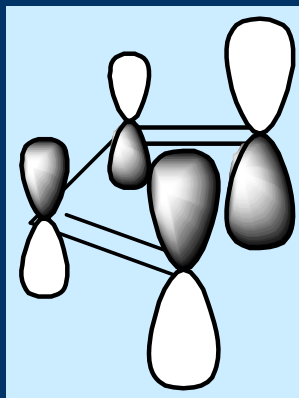
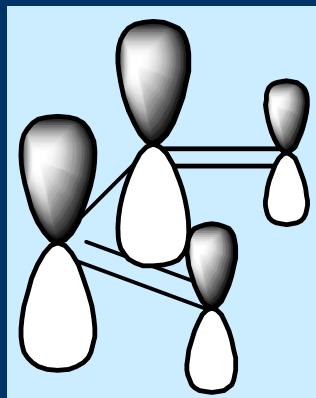


Orbital Symmetry Conservation

Orbital Symmetry Conservation



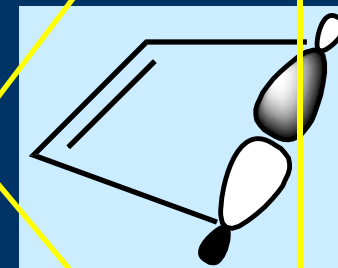
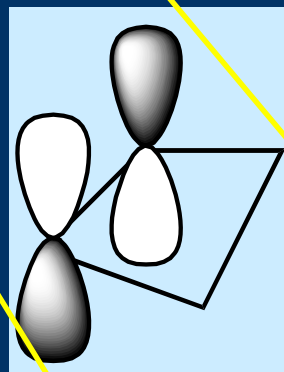
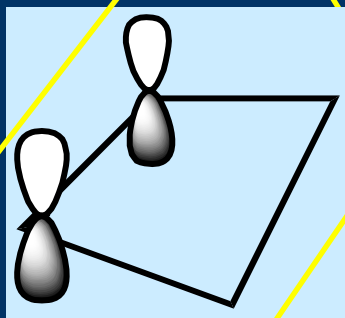
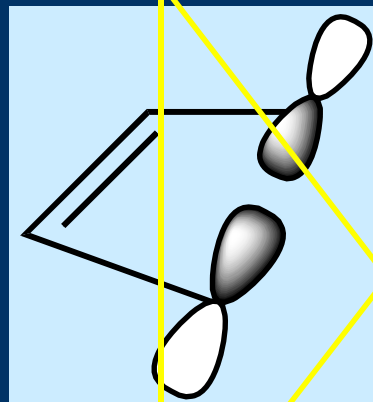
R



σ_v

C_2

P



σ_v

C_2

S

A

S

S

A

S

S

A

S

A

A

S

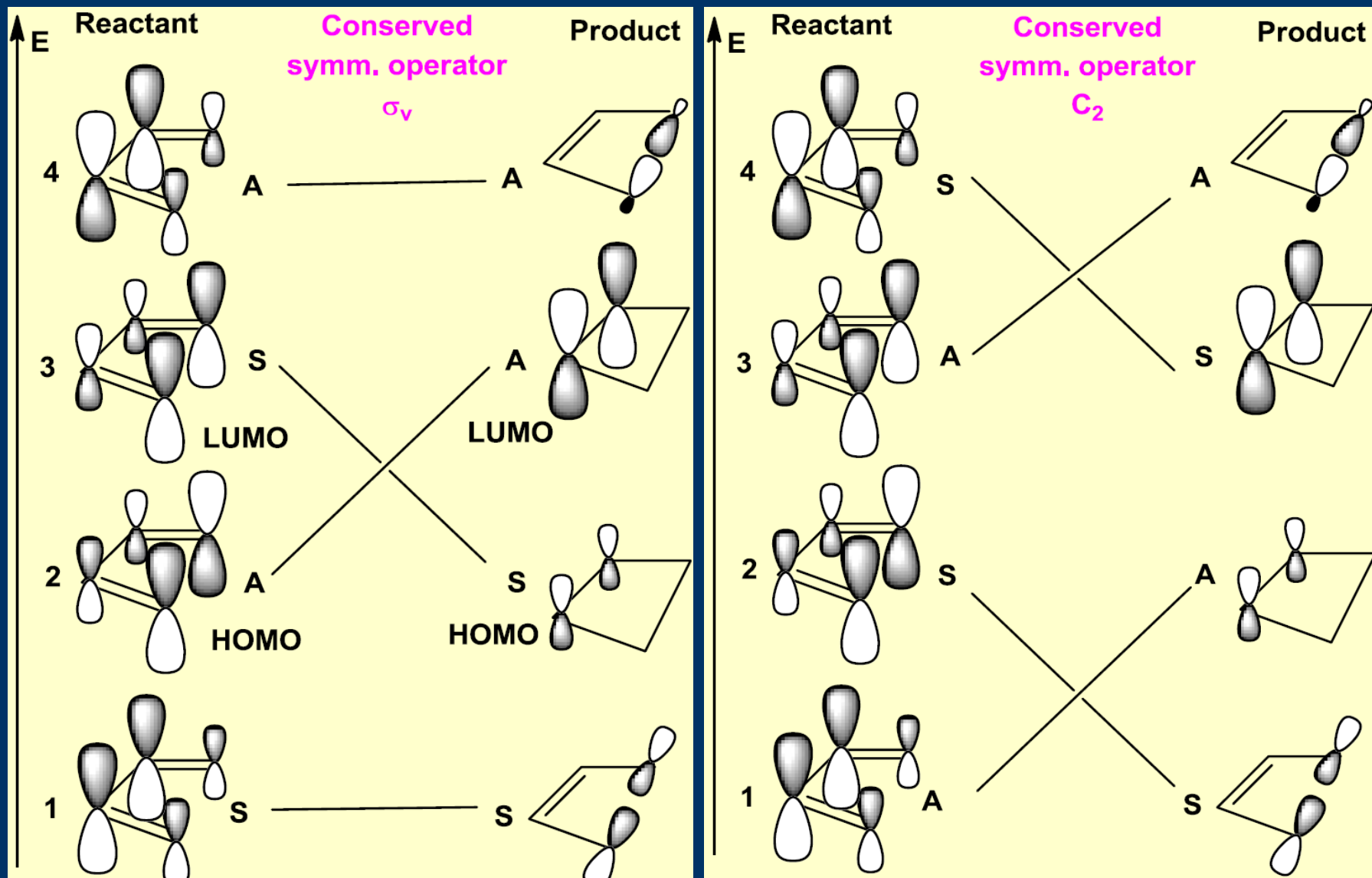
A

S

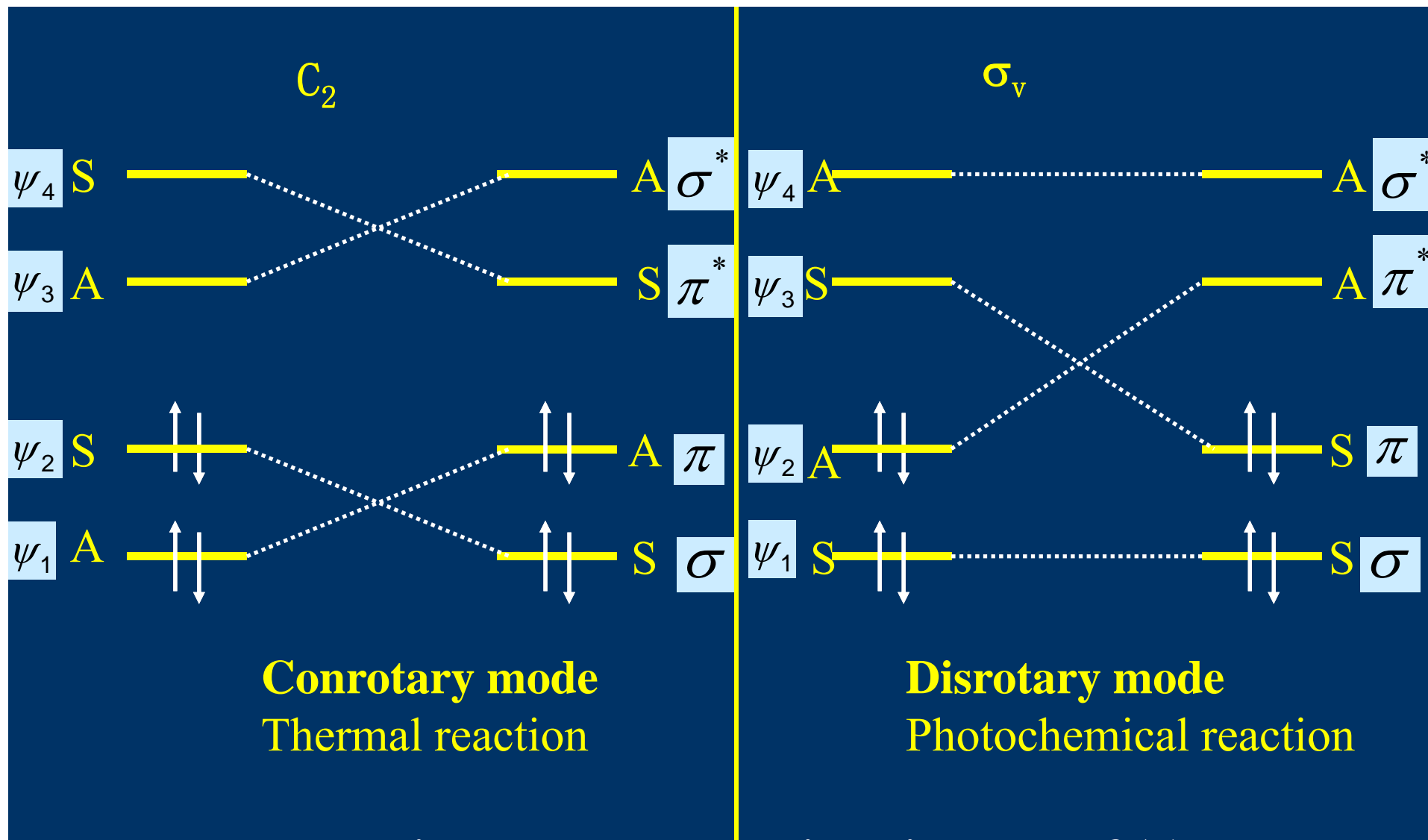
A

A

Energy correlation diagram



Energy correlation diagram



The molecular orbital energy correlation diagrams of (a) conrotary and (b) disrotary reactions of butadiene with cyclobutene

Example B:

Cycloaddition of ethylene



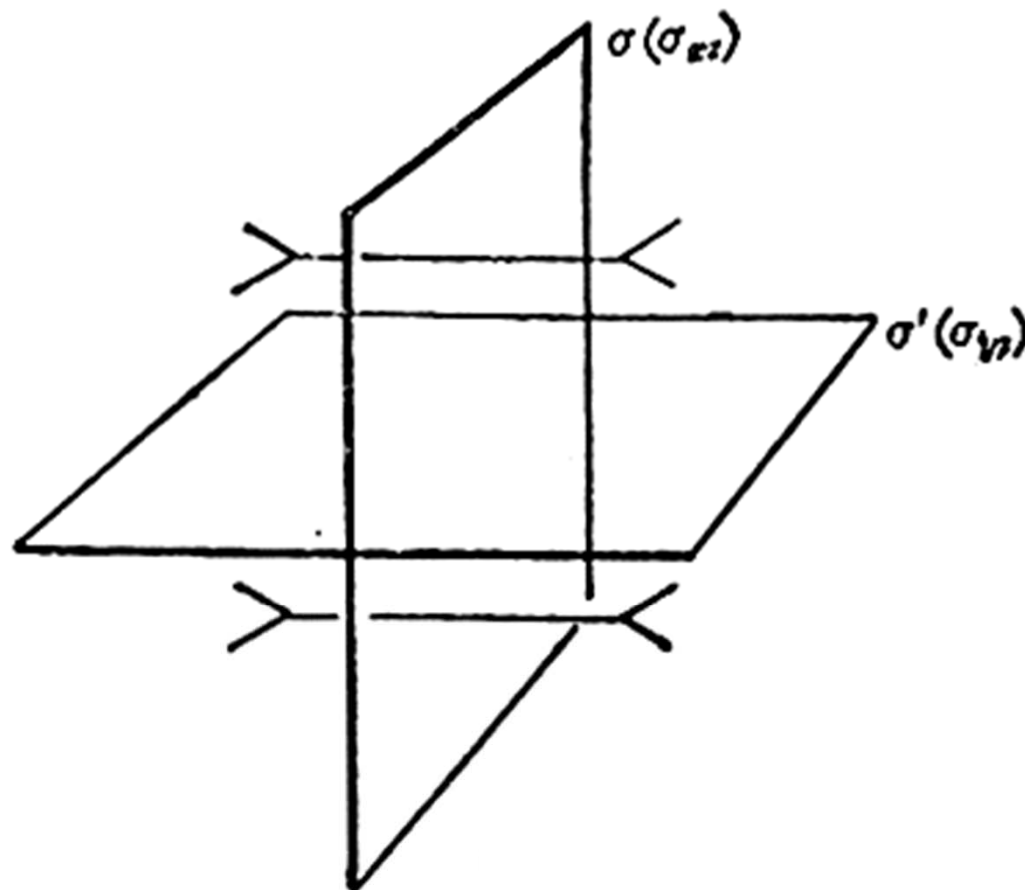
+



reactants



MO

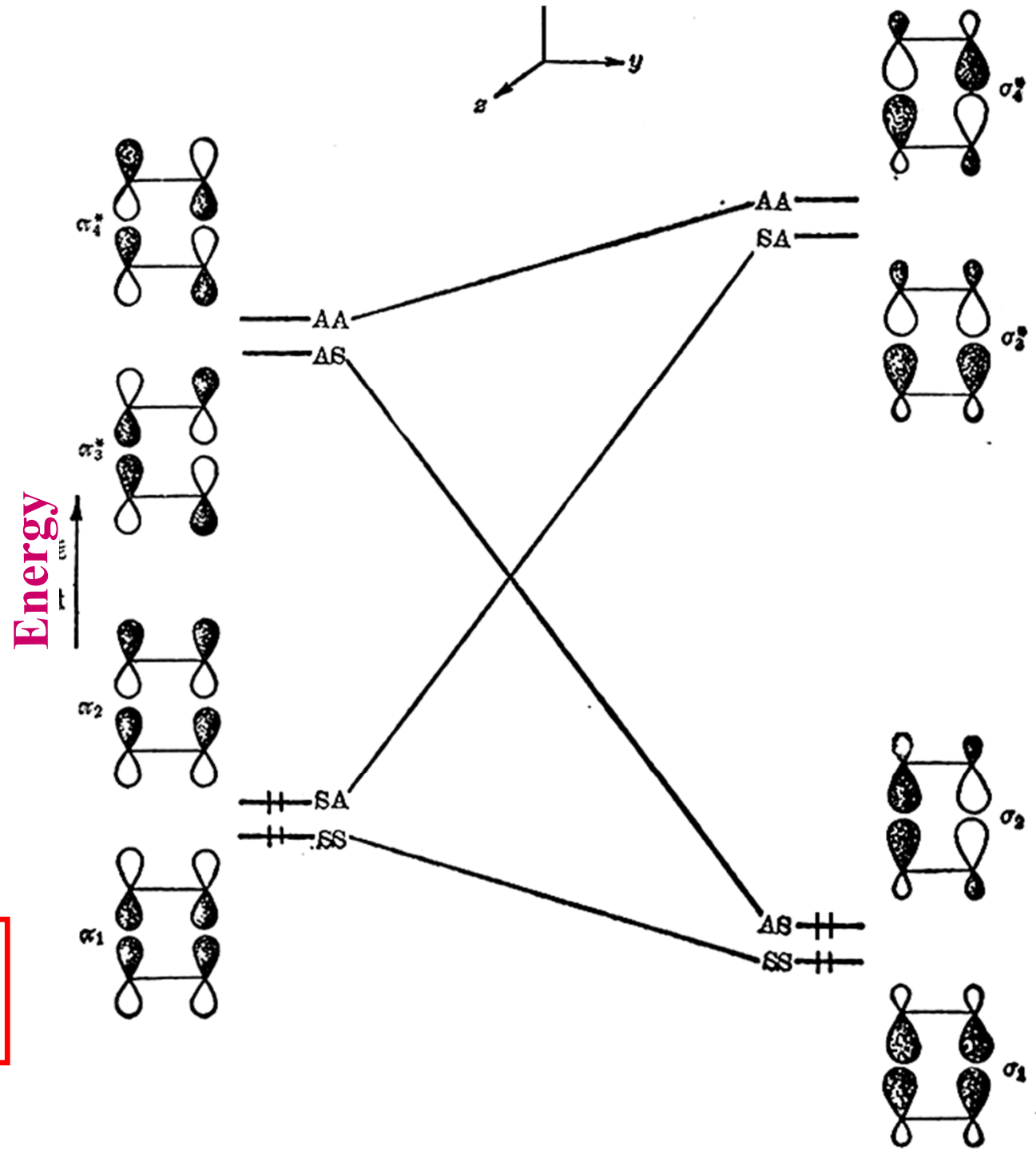


product



MO

In photochemical reaction mode



The shortest π^* - π^* CC bond¹ (2.827 Å)



SOMO: π^*

