Chapter 5 Stucture of polyatomic molecules (A)

---

§ 5.1 Theory of hybrid orbital and atomic orbital hybridization

1. Theory of hybrid orbital

Two Theories of Bonding

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.

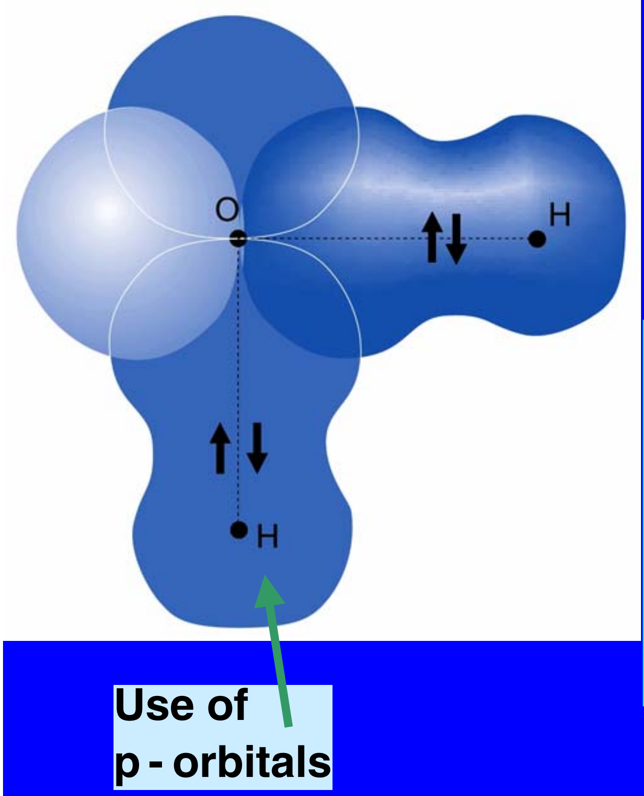
Central Themes of Valence Bond Theory

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!**

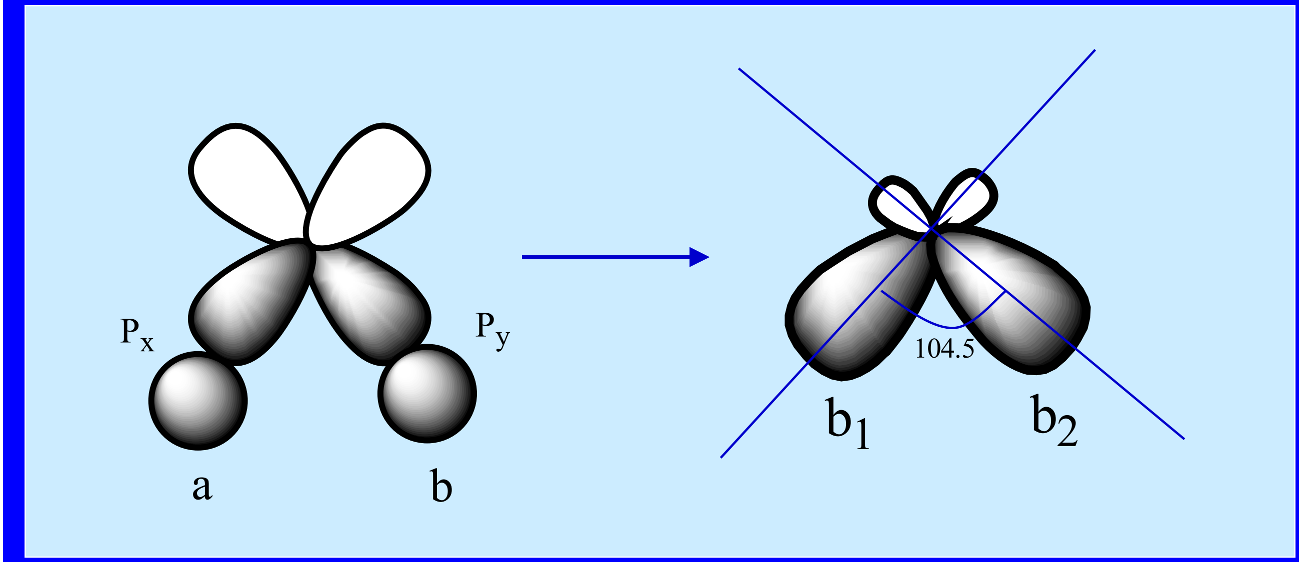
Why do atomic orbital need hybridization?



Use of p - orbitals

H_2O

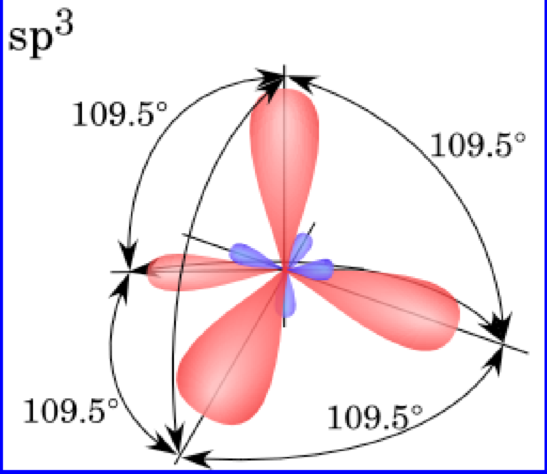
Each σ bond arises from the overlap of an H1*s* orbital with one of the O2*p* orbitals. This model suggests that the bond angle should be 90°, which is significantly different from the experimental value.



H_2O

Why do atomic orbital need hybridization?

CH_4



- 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 orbital hybridize?

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

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

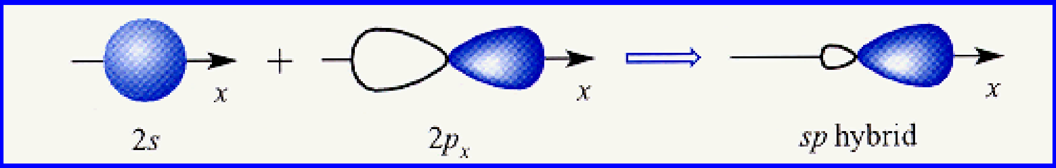
All *n* hybrids are equivalent except for directionality → same energy.

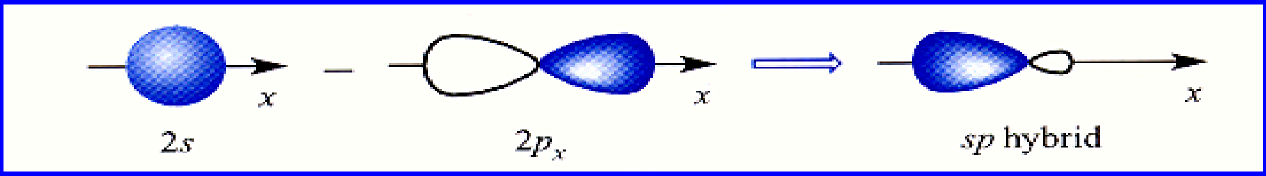
---

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.





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

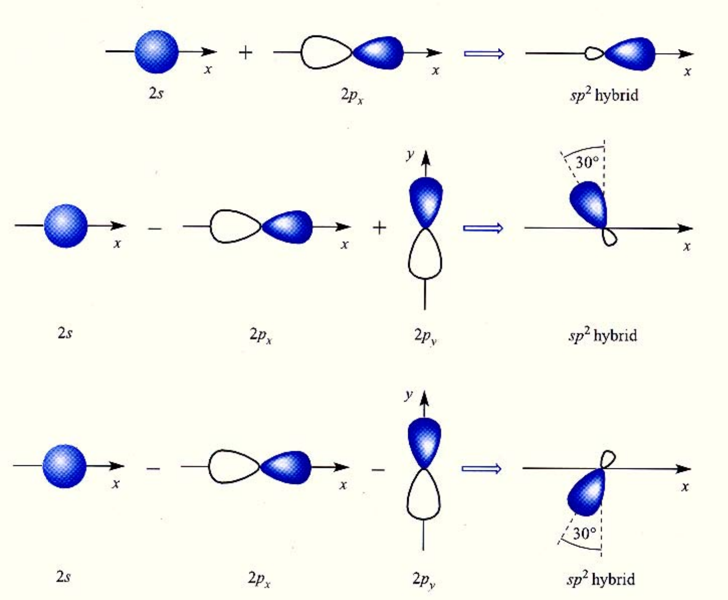
$$\phi_{h2} = \sqrt{\frac{1}{2}}(\phi_s - \phi_{2px})$$

sp, θ=180° , 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.

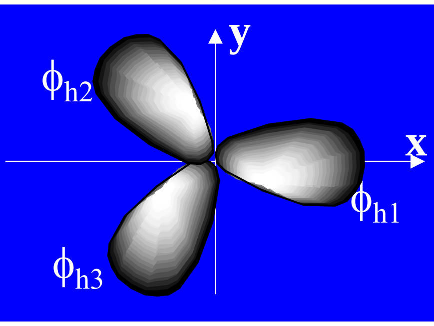


$$\phi_{h1} = \sqrt{\frac{1}{3}}\phi_s + \sqrt{\frac{2}{3}}\phi_{2px}$$

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

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

sp^2, D_{3h}, θ=120°, triangular,
f=1.991， α=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

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

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

Supposed 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

$$\begin{aligned} a_2{}^2 + b_2{}^2 + c_2{}^2 &= 1 \\ a_1a_2 + b_1b_2 + c_1c_2 &= 0 \end{aligned} \quad \longrightarrow \quad \begin{aligned} 1/3 + b_2{}^2 + c_2{}^2 &= 1 \\ 1/3 + \sqrt{2/3}b_2 + 0\cdot c_2 &= 0 \end{aligned}$$

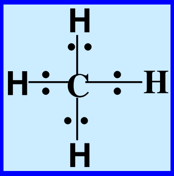
$$b_2 = -\sqrt{1/6} \qquad c_2 = \pm\sqrt{1/2}$$

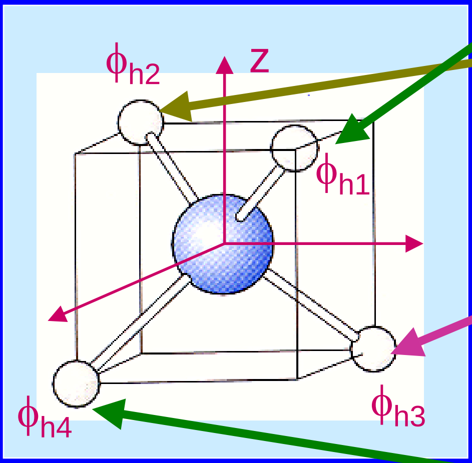
$$\phi_{h2} = \sqrt{1/3}\phi_s - \sqrt{1/6}\phi_{2px} + \sqrt{1/2}\phi_{2py}$$

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

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)

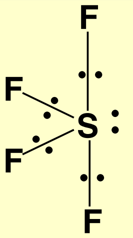
$$\phi_{h3}=\frac{1}{2}[\,s-p_x+p_y-p_z\,]$$
along (-x,y,-z)

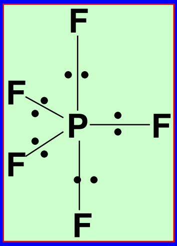
$$\phi_{h4}=\frac{1}{2}[s+p_x-p_y-p_z]$$
along (x,-y,-z)

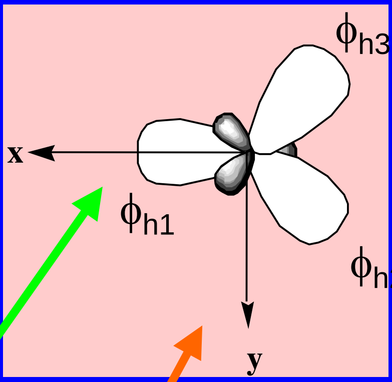
- One s and 3 p AO's mix to form a set of four hybrid sp^3 orbitals.

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

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







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

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

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

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

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

e. dsp^2 hybrides (square planar)

Square planar: D_{4h}

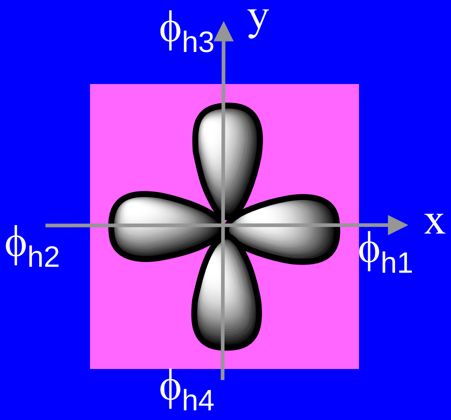
$$d_{x^2-y^2}, s, p_x, p_y$$

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

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

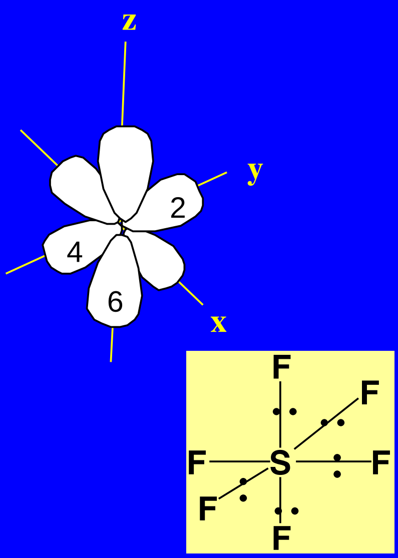
$$\phi_{h3} = \frac{1}{2}\phi_s + \sqrt{\frac{1}{2}}\phi_{py} - \frac{1}{2}d_{x^2-y^2}$$

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



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

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



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

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

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

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

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

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

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

Hybridization schemes

sp^nd^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 orbital

sp^n hybridation

$$\phi_{\mathbf{h}} = \sqrt{\alpha}\,\phi_{2\mathbf{s}} + \sqrt{1-\alpha}\,\phi_{2\mathbf{p}}$$

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

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

where ϕ_{pi} is

$$\phi_{p_i} = x_i\phi_{px} + y_i\phi_{2py} + z_i\phi_{2pz}$$

Normalization and orthogonality

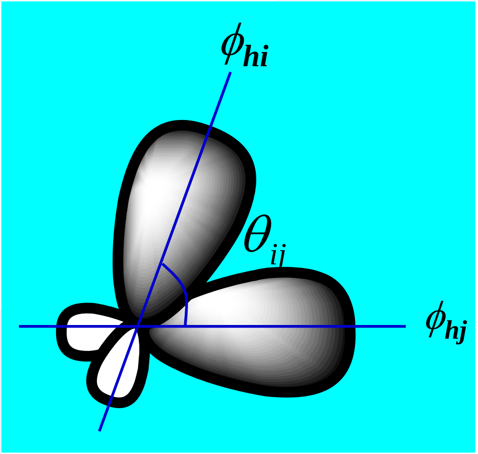
$$0=\int \phi_{hi}\phi_{hj}d\tau=\int (\sqrt{\alpha_i}\phi_{2s}+\sqrt{1-\alpha_i}\phi_{pi})(\sqrt{\alpha_j}\phi_{2s}+\sqrt{1-\alpha_j}\phi_{pj})d\tau$$

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

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

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

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



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

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

---

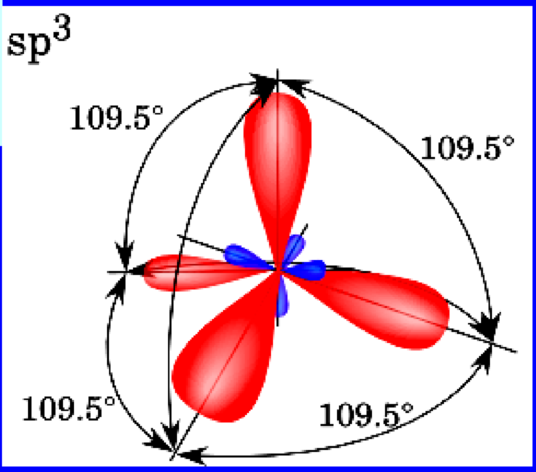
Equivalent hybridization

sp^3 – hybrides

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

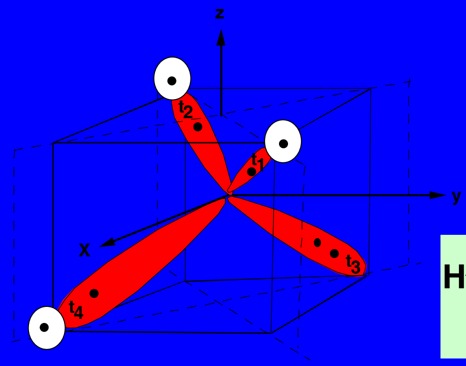
$$\cos\theta_{ij}=-\frac{\sqrt{\alpha_i\alpha_j}}{\sqrt{(1-\alpha_i)(1-\alpha_j)}}=-\frac{\frac{1}{4}}{\frac{3}{4}}=-\frac{1}{3}$$

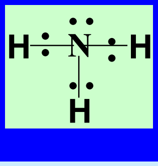
$$\theta=109^0 28''$$



Non-equivalent hybridization

sp^3 – hybrides





$$for \quad NH_3$$

$$\theta = 107.3^\circ$$

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

$$\alpha = 0.23$$

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

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

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

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

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)

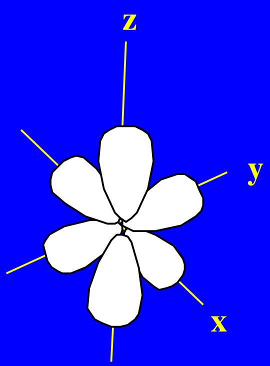
$$\alpha + \beta\cos\theta + \gamma(\frac{3}{2}\cos^2\theta - \frac{1}{2}) = 0$$

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

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

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

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



Octahedral

4. The ability of the hybrid orbital

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

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

for the sp^n hybridizations,

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

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

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

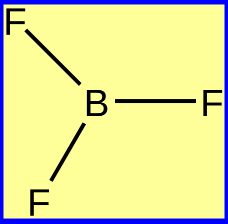
$\alpha = \frac{1}{6}, \beta = \frac{1}{2}, \gamma = \frac{1}{3}$ $f_h = 2.925$ d^2sp^3

---

5. Discussions

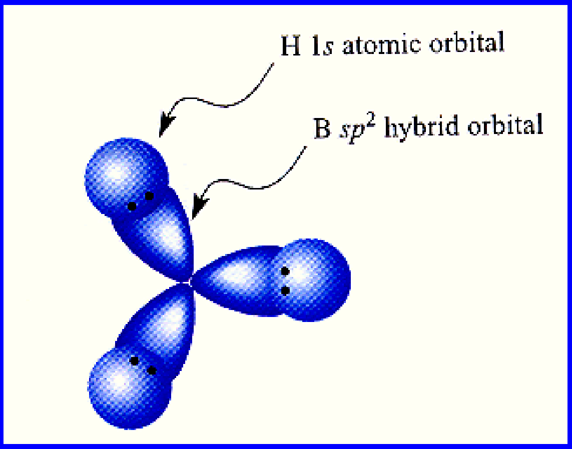
sp^2

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

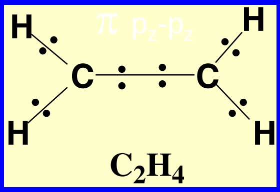


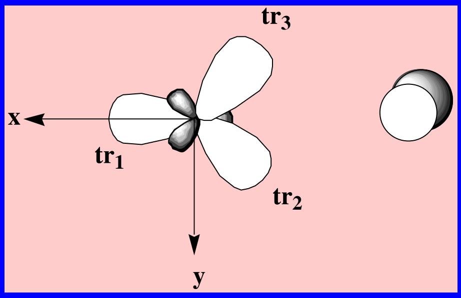
Example: BH_3

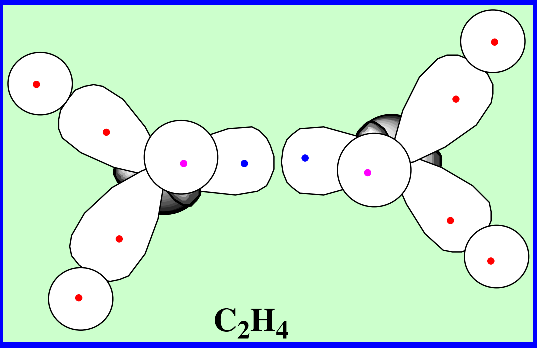
- 3 sp2 hybrid orbitals each with one electron.
- This one electron pairs with the hydrogen electron.



Example:

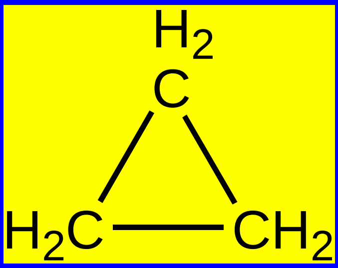




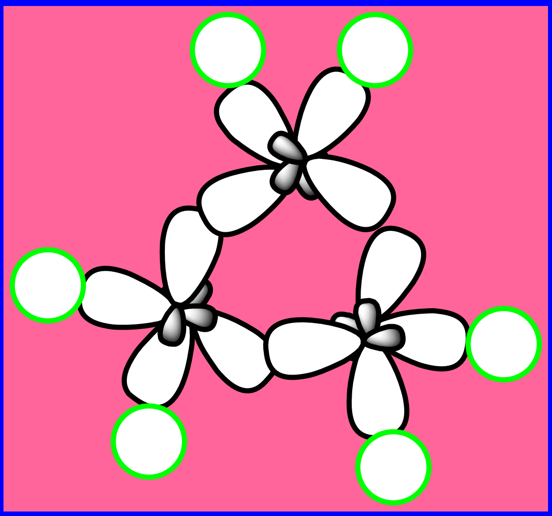


Bend bonding

cyclo-triethyle



sp^3



§ 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

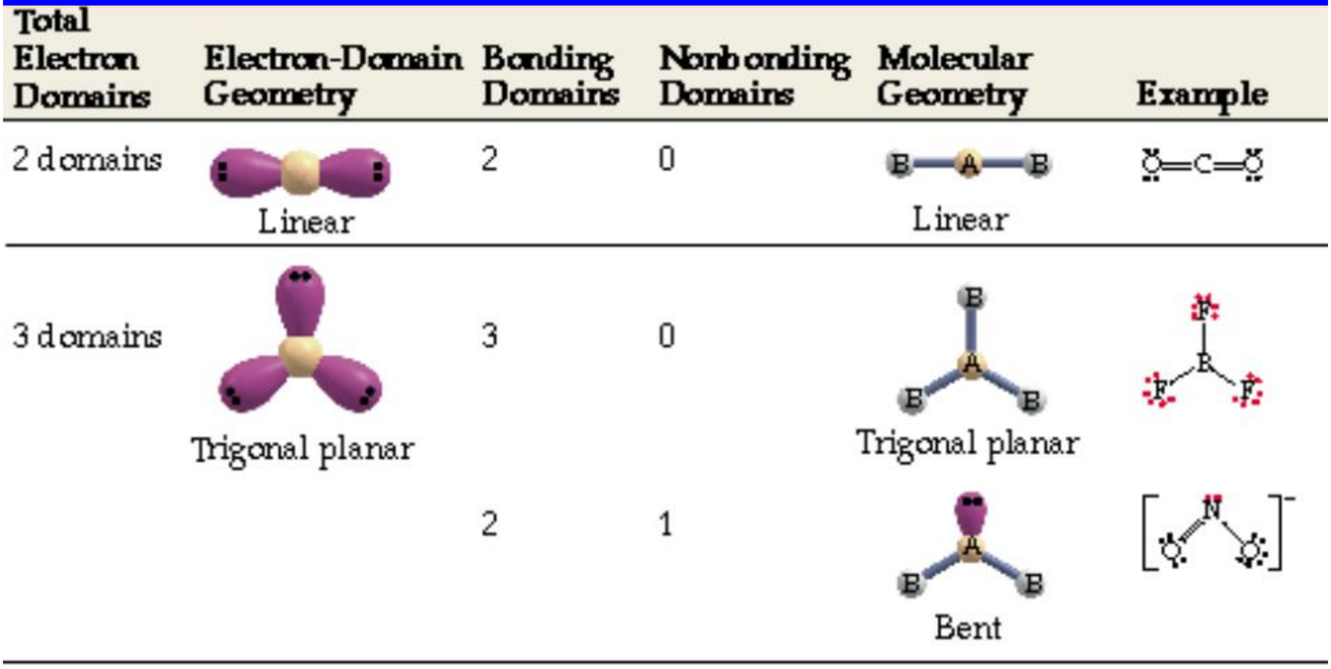
Atom B in Ab$_n$ lie on the surface of a sphere; electron pairs are "localized" on a sphere of smaller radius at maximum distances apart, so as to minimize overlap of different electron pairs.

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.

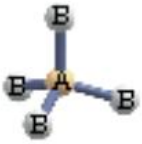
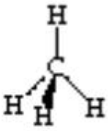
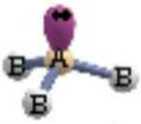
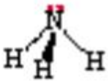
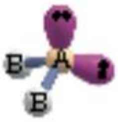
Arrangements of Maximum distance between valence shell electron pairs.

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

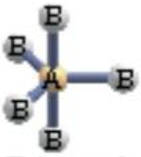
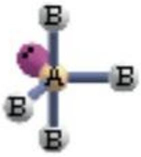
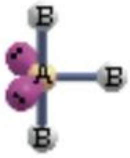
Spatial Arrangements of Electron Pairs in Terminal Atoms in AB_n

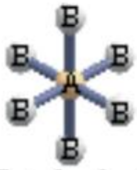
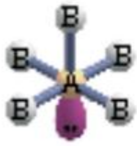
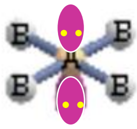


Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2 domains	Linear	2	0	Linear	O=C=O
3 domains	Trigonal planar	3	0	Trigonal planar	
		2	1	Bent	

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

Molecular Stereochemistry

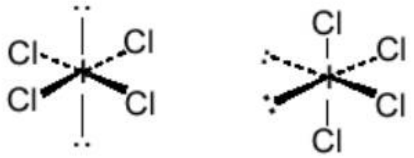
No. of pairs of e^-	formula	stereochemistry	point group
1	A_2, AB	none	$D_{\infty h}$ $C_{\infty v}$
2	AB_2	linear	$D_{\infty h}$
3	AB_2e^1	bend	C_{2v}
3	AB_3	triangular	D_{3h}
4	AB_2e^2	bend	C_{2v}
4	AB_3e^1	pyramidal	C_{3v}
4	AB_4	tetrahedral	T_d

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	non-planar	C_{2v}
5	AB_5	trigonal bypyramid	D_{3h}
6	AB_4e^2	square planar	D_{4h}
6	AB_5e^1	square pyramidal	C_{4v}
6	AB_6	octahedral	O_h

ICl_4^- AB_4e^2 6-pair case

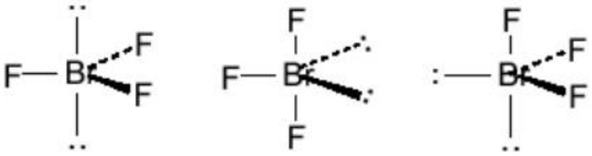
possible structures:



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

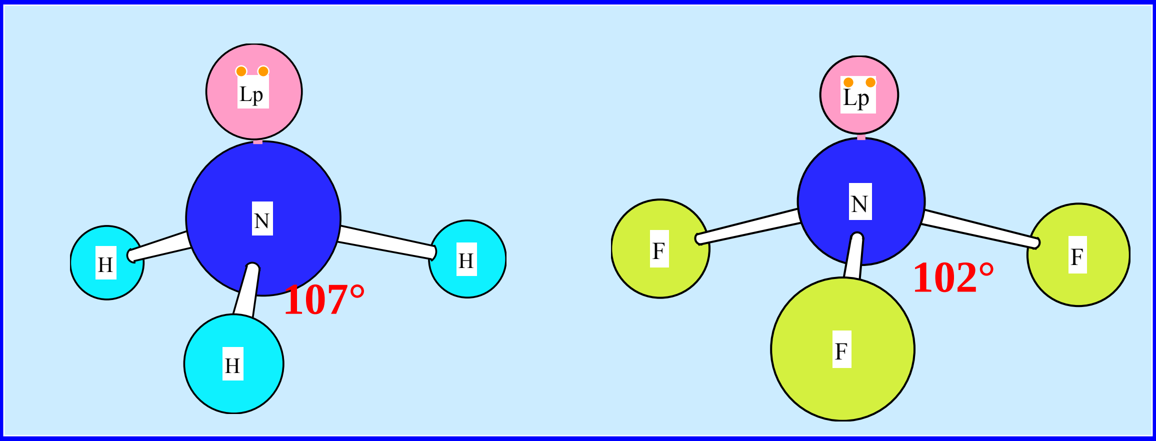
BrF_3 AB_3e^2 5-pair case

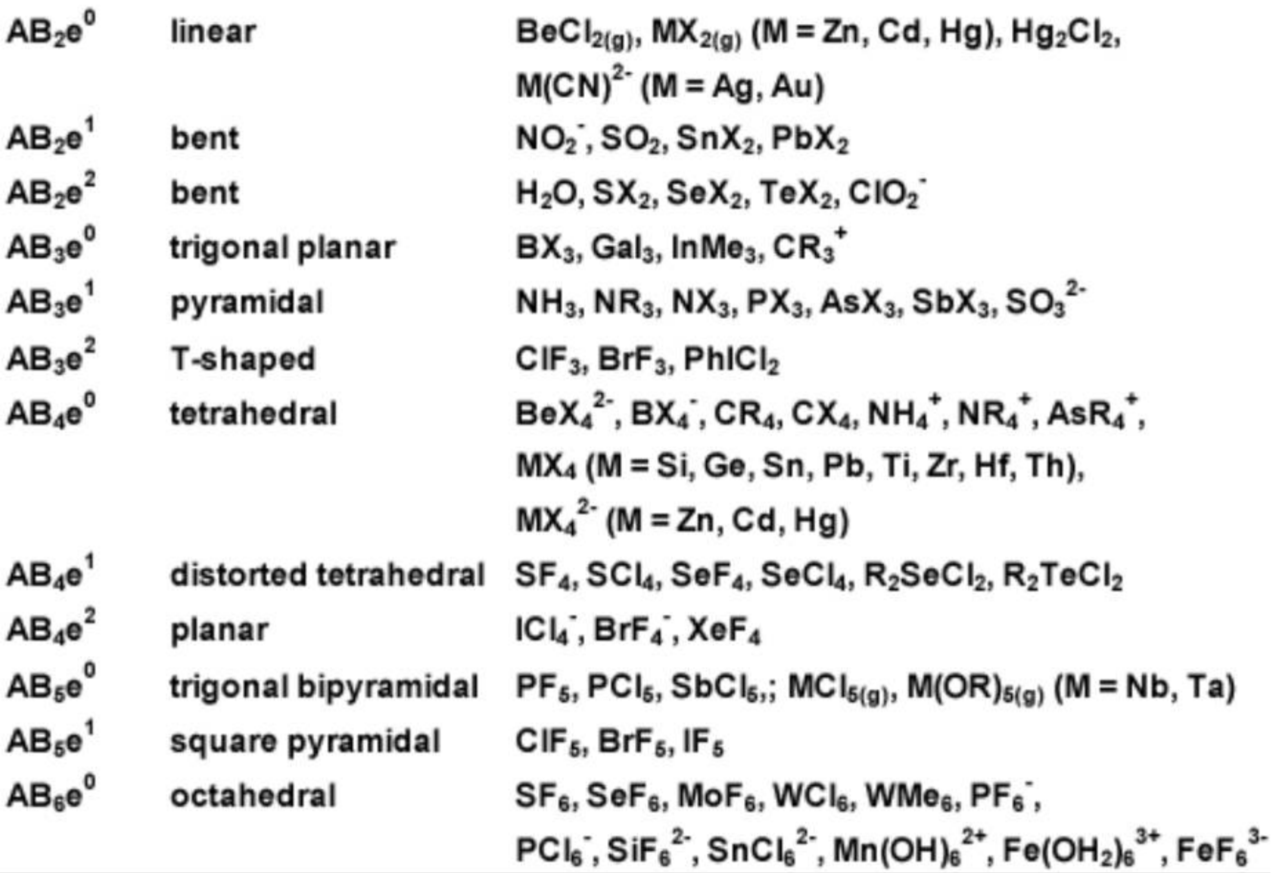
possible structures:



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

VSEPR Example





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 Hückel molecular orbital theory and conjugated system

---

§ 3 Huckel molecular orbital theory and conjugated system

1. HMO method

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

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

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

(4)*seqular equation*

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

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

Modified Hückel molecular orbital theory (R. Hoffmann, Nobel prize)

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

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

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

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

---

2. The HMO treatment for butadiene

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

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

Secular equation

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

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

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

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

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

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

$$x_1^2 = 0.38 \qquad \mathrm{x}_1 = \pm 0.618$$

$$x_2^2 = 2.62 \qquad \mathrm{x}_2 = \pm 1.618$$

thus,

$E_1 = \alpha + 1.618\beta$ Bonding

$E_2 = \alpha + 0.618\beta$ Bonding

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

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

---

solve seqular equation :

$$\mathrm{c}_1\mathrm{x} + \mathrm{c}_2 = 0$$

$$\mathrm{c}_1 + \mathrm{c}_2 x + \mathrm{c}_3 = 0$$

$$\mathrm{c}_2 + \mathrm{c}_3 x + \mathrm{c}_4 = 0$$

$$\mathrm{c}_3\mathrm{x} + \mathrm{c}_4 = 0$$

and,

$$\mathrm{c}_1^2 + \mathrm{c}_2^2 + \mathrm{c}_3^2 + \mathrm{c}_4^2 = 1$$

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

➡

substituting $\mathrm{x} = -1.618$

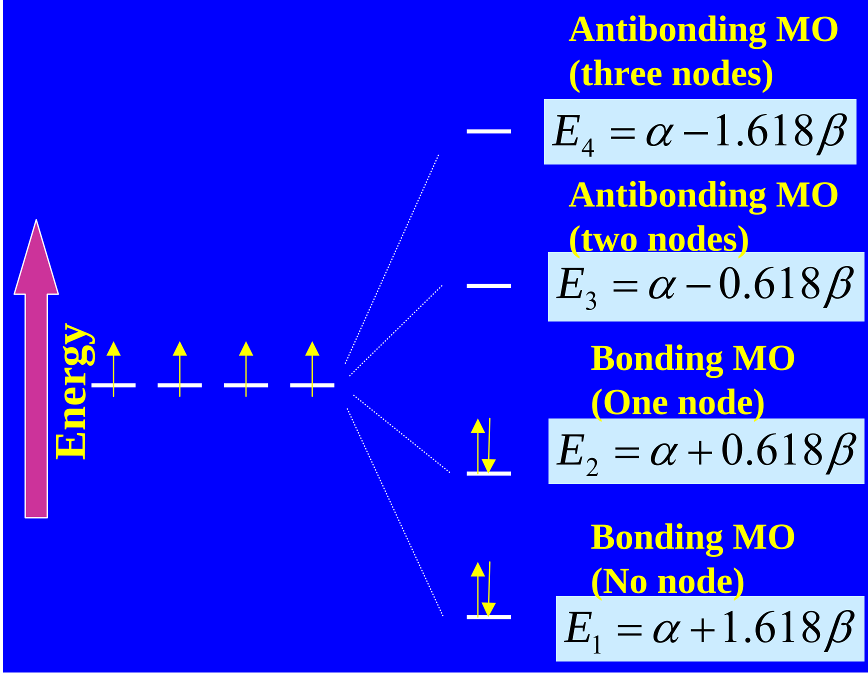
$$\mathrm{c}_1 = c_4 = 0.372$$

$$\mathrm{c}_2 = c_3 = 0.602$$

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

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

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



Antibonding MO (three nodes)

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

Antibonding MO (two nodes)

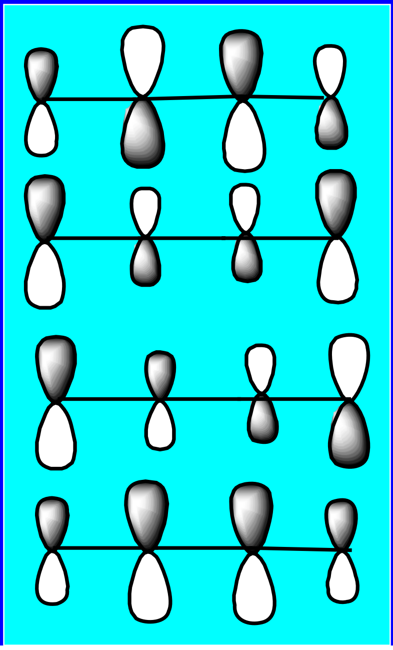
$$E_3 = \alpha - 0.618\beta$$

Bonding MO (One node)

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

Bonding MO (No node)

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

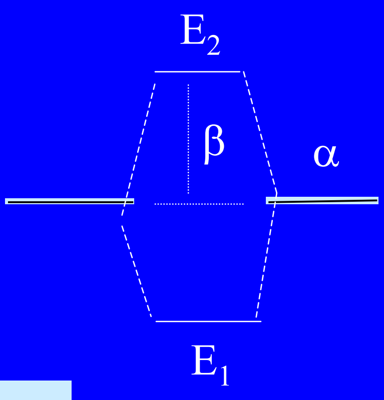


Delocalized energy

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

if forms two lacalized π orbitals

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



thus, delocalized energy or resonance energy

$$\mathrm{E}_{\pi d} = 0.48\beta$$

3. Population analysis and molecular diagrams of conjugated system

i. Charge density --- the probability of π electrons on the ith atom

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

$$\rho_1 = 2\times0.372^2 + 2\times0.602^2 = 1.000$$
$$\rho_2 = 2\times0.602^2 + 2\times0.372^2 = 1.000$$
$$\rho_3 = \rho_4 = 1.000$$

$$\psi_\pi^1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$
$$\psi_\pi^2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$
$$\psi_\pi^2 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$
$$\psi_\pi^4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4$$

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

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

$$p_{12} = 2\times0.372\times0.602 + 2\times0.602\times0.372 = 0.896 = p_{34}$$
$$p_{23} = 2\times0.602^2 + 2\times0.372^2\times(-1) = 0.448$$

---

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

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

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

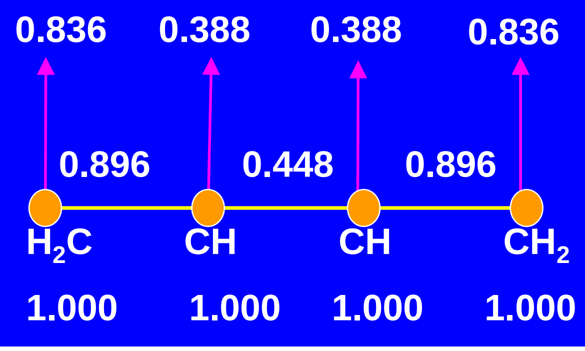
$$F_1 = \sqrt{3} - 0.896 = 0.836 = F_4$$

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

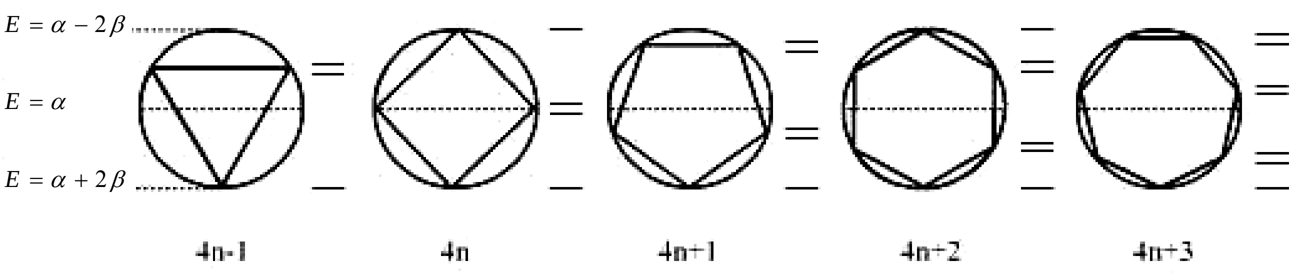
Example: 1,4 addition reaction of butadiene

$H2C{=}CH{-}CH{=}CH2 + Br2 \rightarrow BrH2C{-}CH{=}CH{-}CH2Br$

iv. Molecular diagram.



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



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

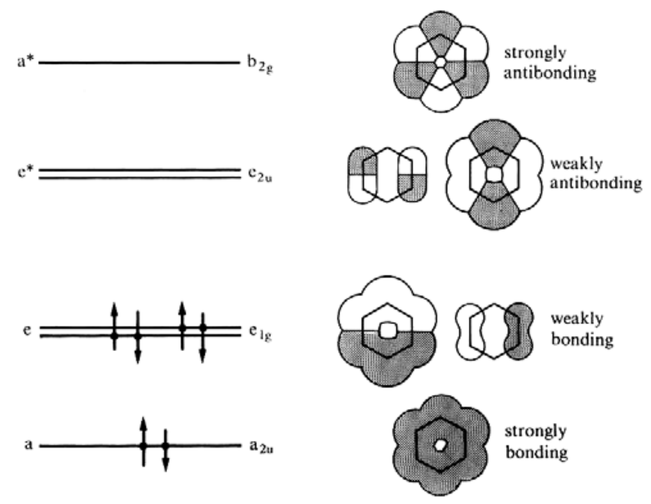
$$\psi_5(e_{2u}) = \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

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

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

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

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

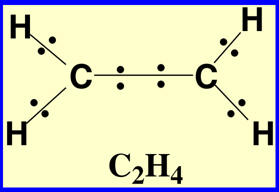


---

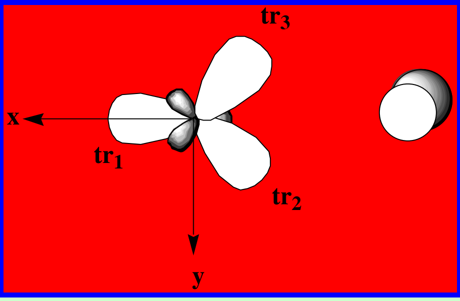
§ 5.4 Delocalized molecular orbital theory

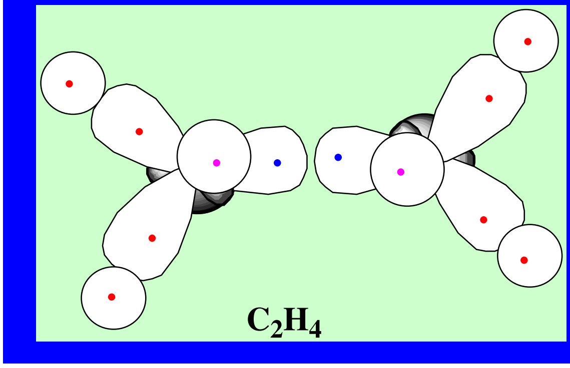
1. Normal π bond

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.

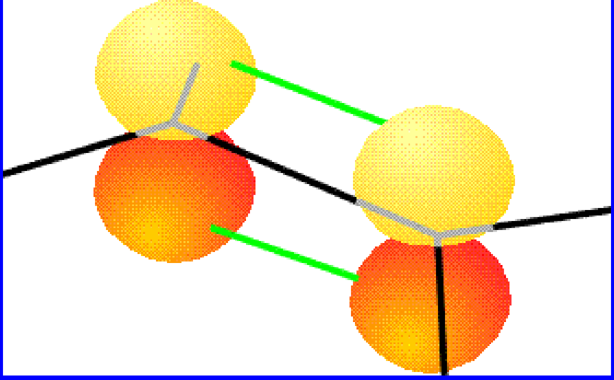


C_2H_4





C_2H_4



---

2. Delocalized π bond

$$\prod_{n}^{m}$$

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

Conditions for the formation of delicalized 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.

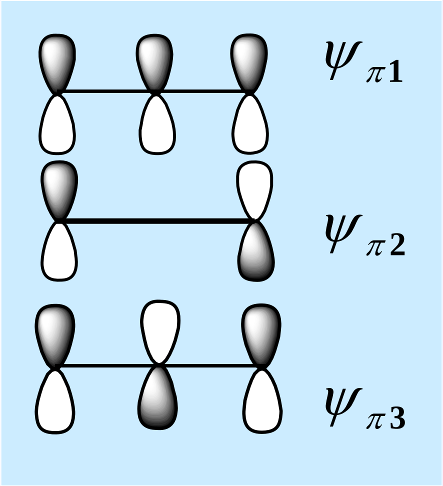
A. Some Inorganic conjugated molecules

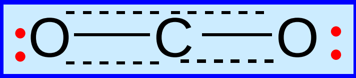
i. Linear type (AB_2 16 valence electron) C: sp hybridization $+p_x$ $+p_y$,

$$\psi_{\pi 1} = \frac{1}{2}[\phi_O(1) + \sqrt{2}\phi_C + \phi_O(2)] \qquad \text{bonding}$$

$$\psi_{\pi 2} = \frac{1}{\sqrt{2}}[\phi_O(1) - \phi_O(2)] \qquad \text{non-bonding}$$

$$\psi_{\pi 3} = \frac{1}{2}[\phi_O(1) - \sqrt{2}\phi_C + \phi_O(2)] \qquad \text{anti-bonding}$$





π electrons : 16 - 4 - 4 = 8

$2\Pi_3^4$: $\Pi_{x\,3}^{\,4}$, $\Pi_{y\,3}^{\,4}$

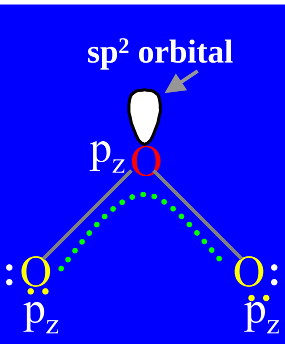
Isoelectron analogy : CO_2, NO_2^+, N_2O, N_3^-, COS, $BeCl_2$, $HgCl_2$

---

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

ex. 18 O_3 (valence electron)

O: sp^2 hybridization + p_z



Π_3^4

π electrons : 18 - 6 - 8 = 4 Π_3^4

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

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

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

Isoelectron analogy: SO_2 Π_3^4
17 valence electron NO_2 Π_3^3
19 valence electron ClO_2 Π_3^5

↑ anti-bonding
↑↓ non-bonding
↑↓ bonding

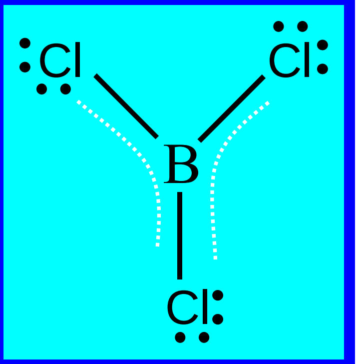
iii. Equilateral angular type BCl_3 D_{3h}

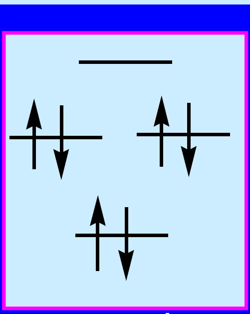
24 valence electrons

Centric atom B: sp^2 hybridization

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

24
-6
18
-12
6





anti-bonding

non-bonding

bonding

π electrons : Π_4^6

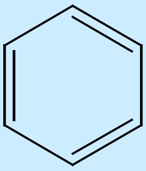
Isoelectron analogy: AlF_3, NO_3^-, CO_3^{2-}, SO_3, Cl_2CO, $(H_2N)_2C{=}O$, $Cl_2C{=}S$

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

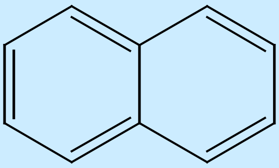
While, for four atom linear type moleculars, forming two bonding and two antibonding orbitals,

---

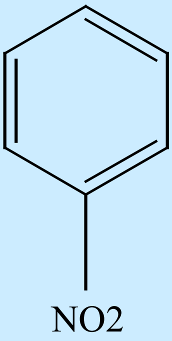
B. Some organic conjugated molecules



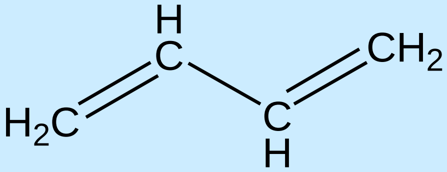
Π_6^6



Π_{10}^{10}



Π_9^{10}

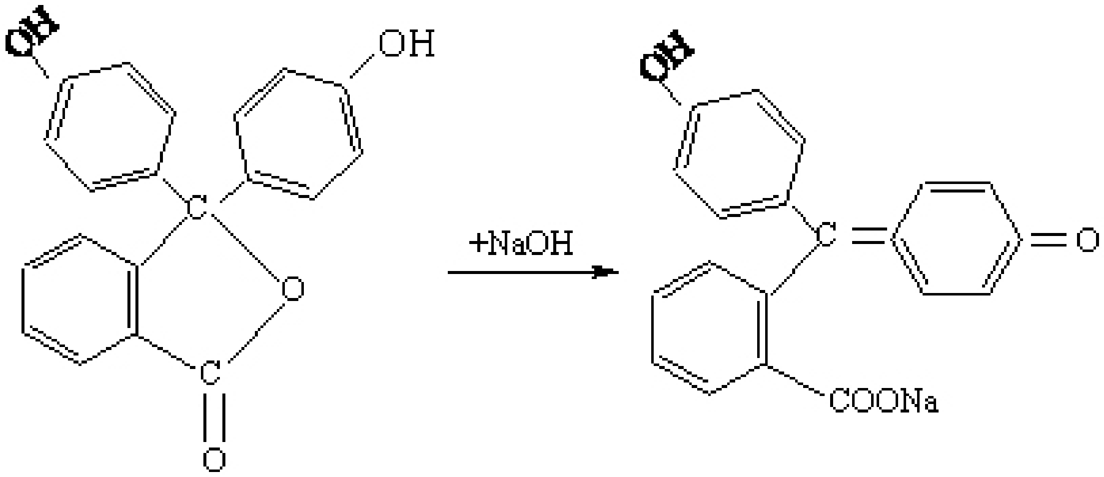


Π_4^4

3. The conjugation effect.

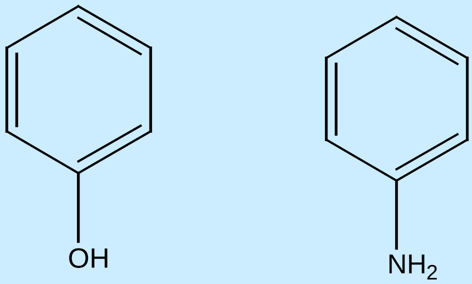
i. The electrical conductivity is enhanced by the delocalization of π bond.

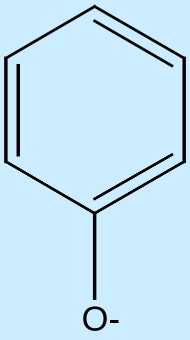
ii. Color. The formation of delocalized π bond increases the delocalized extent of the π electrons and causes the energy of the system to decrease.



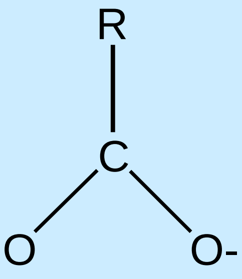
---

iii. Acidity and basicity.

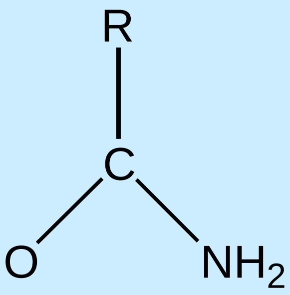




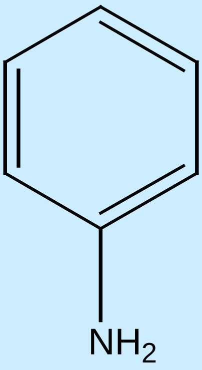
Π_7^8



Π_3^4



Π_3^4

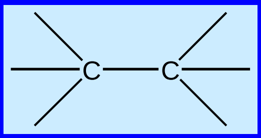
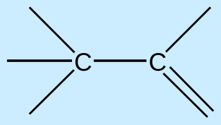
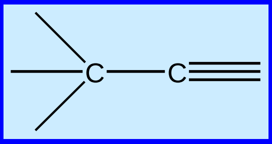


Π_7^8

iv. Chemical reactivity.

e.g. $H2C=CH-Cl$ 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 (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

5.5 Defined method of AO coefficient in molecular orbitals

5.4 Defined method of AO coefficient in molecular orbitals

(AO = atomic orbital, MO = molecular orbital)

- Principle

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

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

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

……

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

……

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

---

let $x=-\dfrac{\alpha-E}{\beta}$ $\quad E=\alpha+x\beta$

let $x=2\cos\theta$ $\quad E=\alpha+2\beta\cos\theta$

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

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

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

……

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

……

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

$\Rightarrow$

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

$C_1-2\cos\theta\, C_2+C_3=0$

$C_2-2\cos\theta\, C_3+C_4=0$

……

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

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

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

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

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

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

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

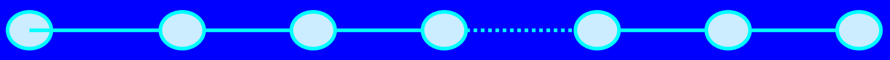
let $\quad C_1 = \sin\theta \qquad C_2 = 2\cos\theta\sin\theta = \sin 2\theta$

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

....

thus :

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



$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \qquad \sin(n-1)\theta \quad \sin n\theta$

$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \qquad \sin(n-1)\theta \quad \sin n\theta$

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

$$(n+1)\theta = m\pi \qquad \Rightarrow \theta = \frac{m\pi}{n+1} \qquad (\mathrm{m}=1,2,3,\ldots,\mathrm{n})$$

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

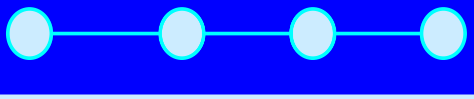
$$E = \alpha + x\beta = \alpha + 2\beta\cos\frac{m\pi}{n+1} \qquad (\mathrm{m}=1,2,3,\ldots,\mathrm{n})$$

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

Normalization coefficents

Example

i) butadiene (n=4)



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

$$\sin 5\theta = 0$$

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	$\alpha + 1.618\beta$	$\alpha + 0.618\beta$	α - 0.618β	$\alpha - 1.618\beta$

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

$$(\mathrm{m}=1,2,3,4)$$

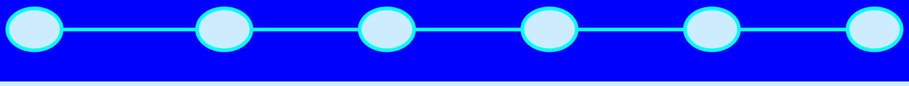
$$\psi_\pi^1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$

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

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

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

ii) hexatriene n=6



sin θ sin 2θ sin 3θ sin 4θ sin 5θ sin 6θ

$$\sin 7\theta = 0$$

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

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

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.

---

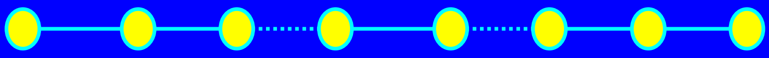
iii) Symmetry classification

a. Molecules with even carbon atoms

Symmetric:

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

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



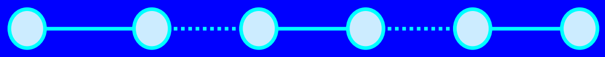
$\cos\frac{n-3}{2}\theta,\quad \cos\frac{n-1}{2}\theta$

The boundary condition:

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

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

asymmetric:



$$-\sin\frac{\theta}{2},\ \sin\frac{\theta}{2}$$

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

The boundary condition:

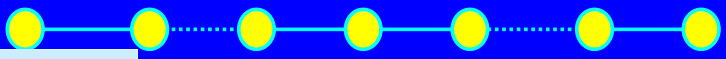
$$\sin\frac{n+1}{2}\theta = 0 \qquad \Rightarrow \theta = \frac{2\mathrm{m}}{\mathrm{n}+1}\pi \quad (m = 1,2,\ldots,<\frac{n}{2})$$

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

---

b. Molecules with odd carbon atoms

Symmetric:



$$\cos\theta,\ 1,\ \cos\theta$$

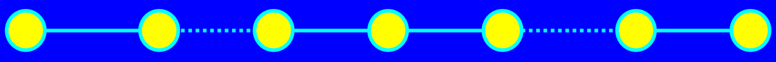
$$\cos\frac{n-1}{2}\theta,\ \ \cos\frac{n-3}{2}\theta \qquad \cos\frac{n-3}{2}\theta,\ \ \cos\frac{n-1}{2}\theta$$

Boundary conditions:

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

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

Asymmetric:



$-\sin\theta,\ 0,\ \sin\theta$

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

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

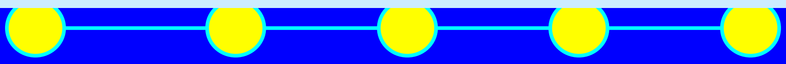
Boundary condition:

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

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

Example:

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



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

symmetric

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

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

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

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

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

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

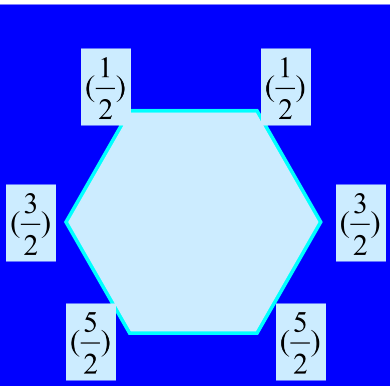
asymmetry:

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

$E=\alpha-\beta \quad (\mathrm{m}=1) \quad$ anti-bonding

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

c. Cyclic conjugated molecules
Example 1： benzene ---solution I



i) symmetry

Boundary condition:

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

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

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

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

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

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

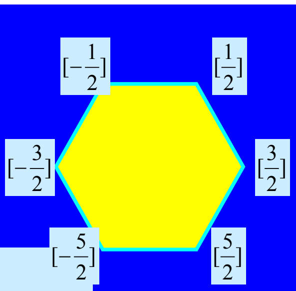
$$\psi_1 = N(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$
$$= \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_2 = N(0 + \frac{\sqrt{3}}{2}\phi_2 + \frac{\sqrt{3}}{2}\phi_3 + 0 - \frac{\sqrt{3}}{2}\phi_5 - \frac{\sqrt{3}}{2}\phi_6)$$
$$= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

$$\psi_3 = N(-\phi_1 + \frac{1}{2}\phi_2 + \frac{1}{2}\phi_3 - \phi_4 + \frac{1}{2}\phi_5 + \frac{1}{2}\phi_6)$$
$$= \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)$$

ii) asymmetry

Boundary condition：



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

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

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

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

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

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

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

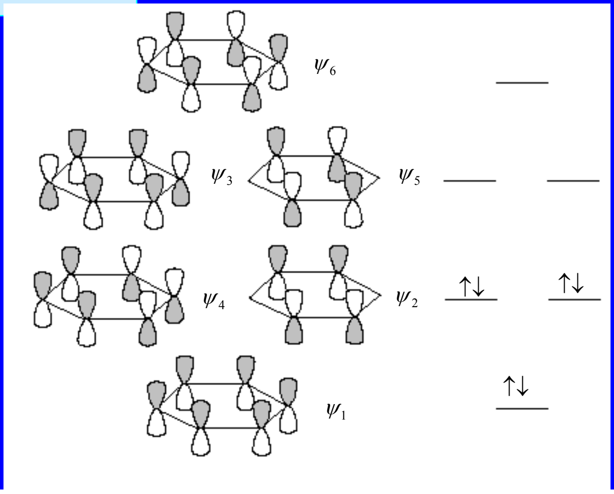
$$= \frac{1}{\sqrt{6}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

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

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

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

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



α -2β

α -β

α +β

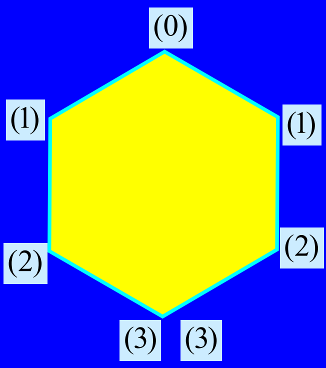
α +2β

Example 2： benzene ---solution II

i)symmetric

Boundary condition:

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



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

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

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

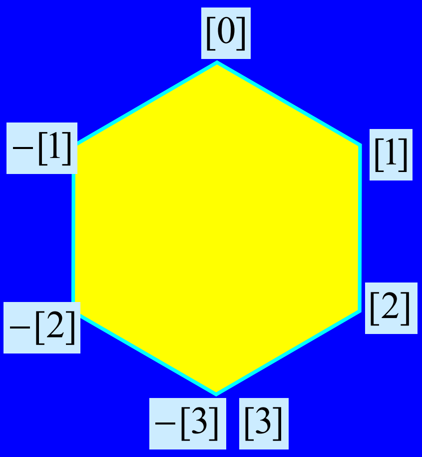
θ	0°,	60°	120°	180°
$\cos\theta$	1	1/2	-1/2	-1
$2\cos\theta$	2	1	-1	-2
E	$\alpha+2\beta$	$\alpha+\beta$	$\alpha-\beta$	$\alpha-2\beta$
	ψ_1	ψ_2	ψ_3	ψ_4
	bonding		anti-bonding	

ii)asymmetric

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

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

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



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

---

§ 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)

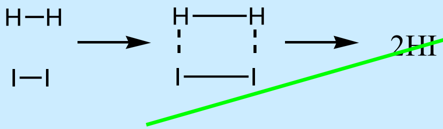
- A deeper understanding of chemical reactivity can be gained by focusing on the *frontier orbitals* of the reactants.

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 6ev).*
3. *When the HOMO and LUMO to 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.

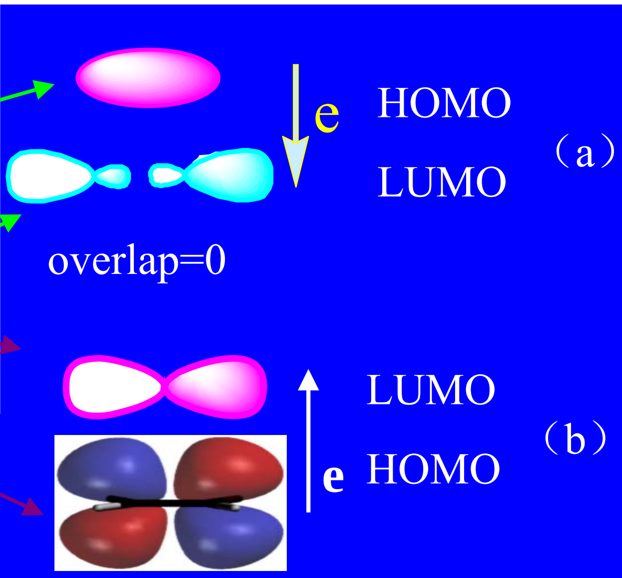
---

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



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

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



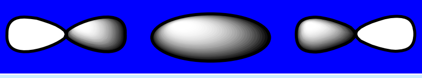
Its mechanics

$I_2 \rightarrow 2I$

$I + H_2 \rightarrow HI + H$

$H + I \rightarrow HI$

$H_2 + I_2 \rightarrow 2HI$

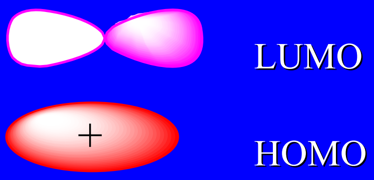


$\mathbf{H_2 : (\sigma_{1s})^2 (\sigma_{1s} *)^2}$

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

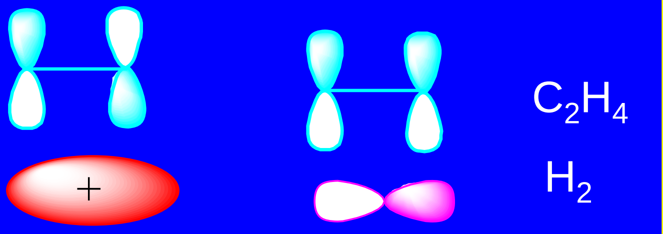
Example B: $C_2H_4 + H_2$

The π MOs of Ethylene



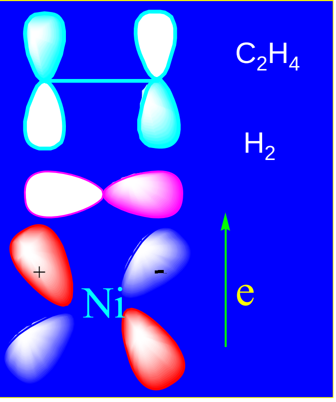
The MOs of Hydrogen

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



Overlap=0, Not compatible in symmetry

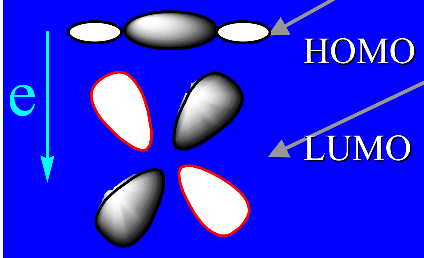
The reaction requires catalyst



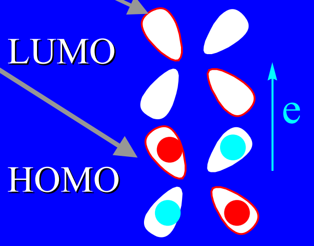
Example C, $N_2 + O_2 \underset{\times}{\rightarrow} 2NO$

$N_2:(\sigma_{2s})^2(\sigma_{2s}^{*})^2(\pi_{2px})^2(\pi_{2py})^2(\sigma_{2pz})^2(\pi_{2p}{*})^0$

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



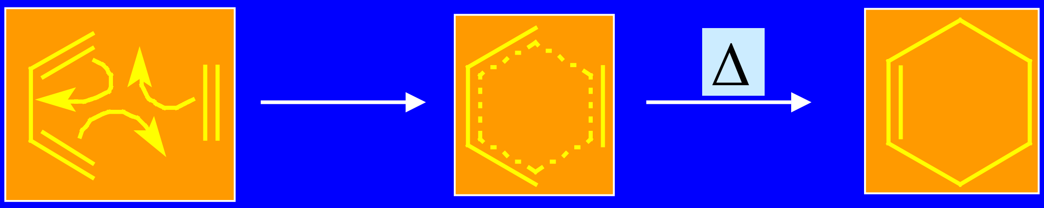
overlap=0



Electron transfering is not reasonable

Example D: $C_4H_6 + C_2H_4$

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

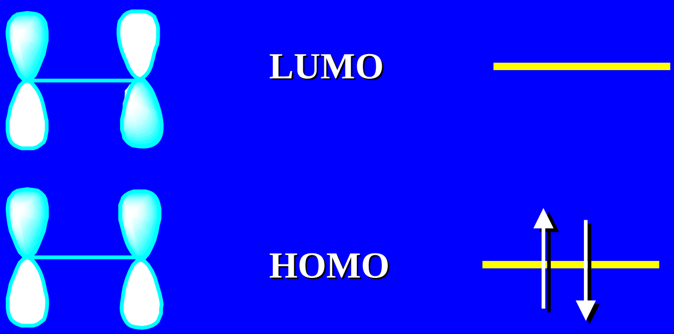


- We can illustrate HOMO-LUMO interactions by way of the Diels-Alder reaction between ethylene and 1,3-butadiene.
- We need only consider the π electrons of ethylene and 1,3-butadiene. We can ignore the framework of σ bonds in each molecule.

The π MOs of Ethylene

Antibonding π orbital of ethylene;

no electrons in this orbital



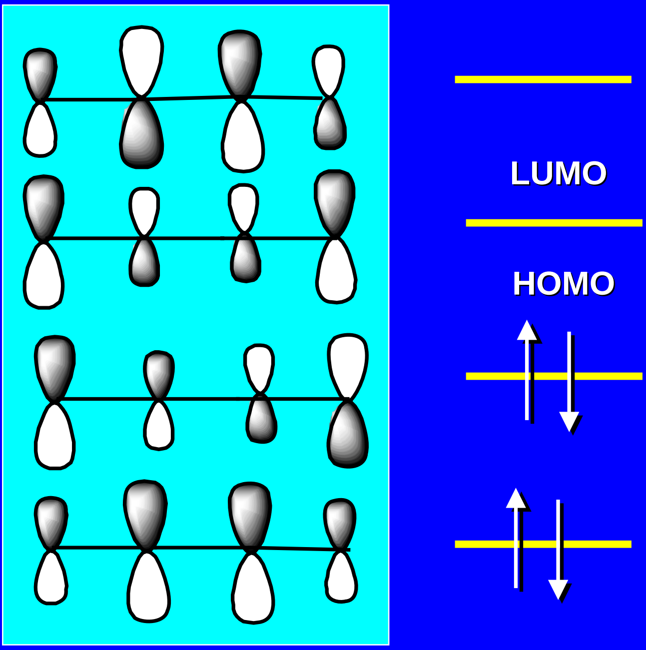
LUMO

HOMO

Bonding π orbital of ethylene;

two electrons in this orbital

π MOs of 1,3-Butadiene



LUMO

HOMO

Highest energy orbital

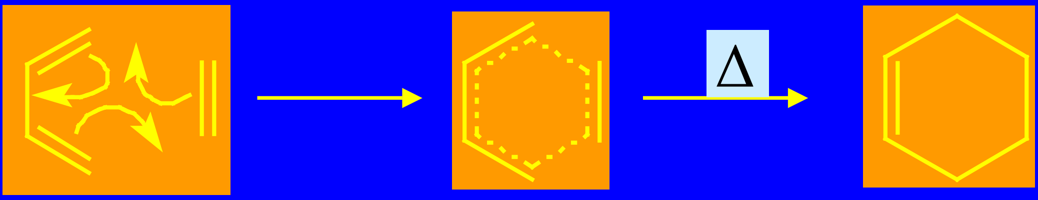
Both antibonding

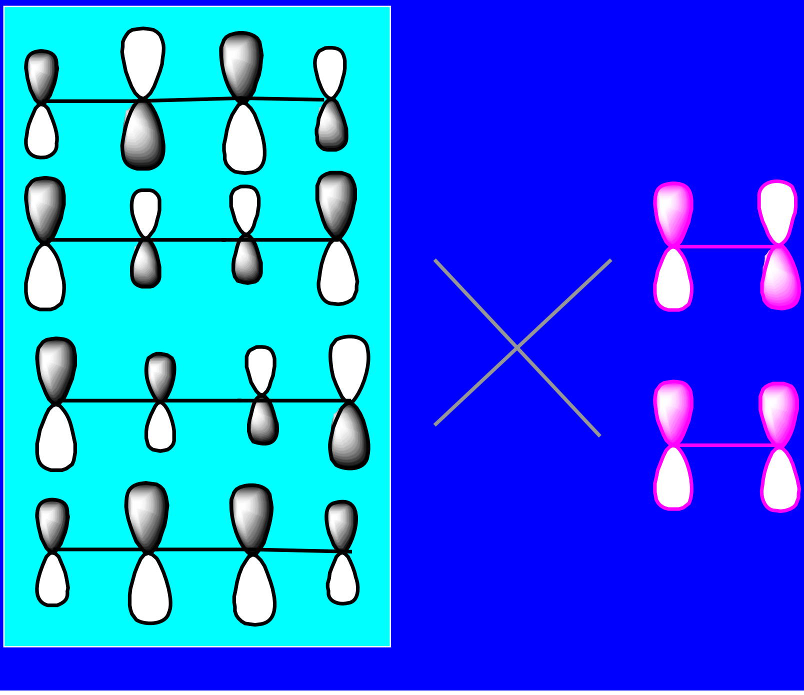
orbitals are vacant

4 π electrons; 2 in

each orbital

Lowest energy orbital



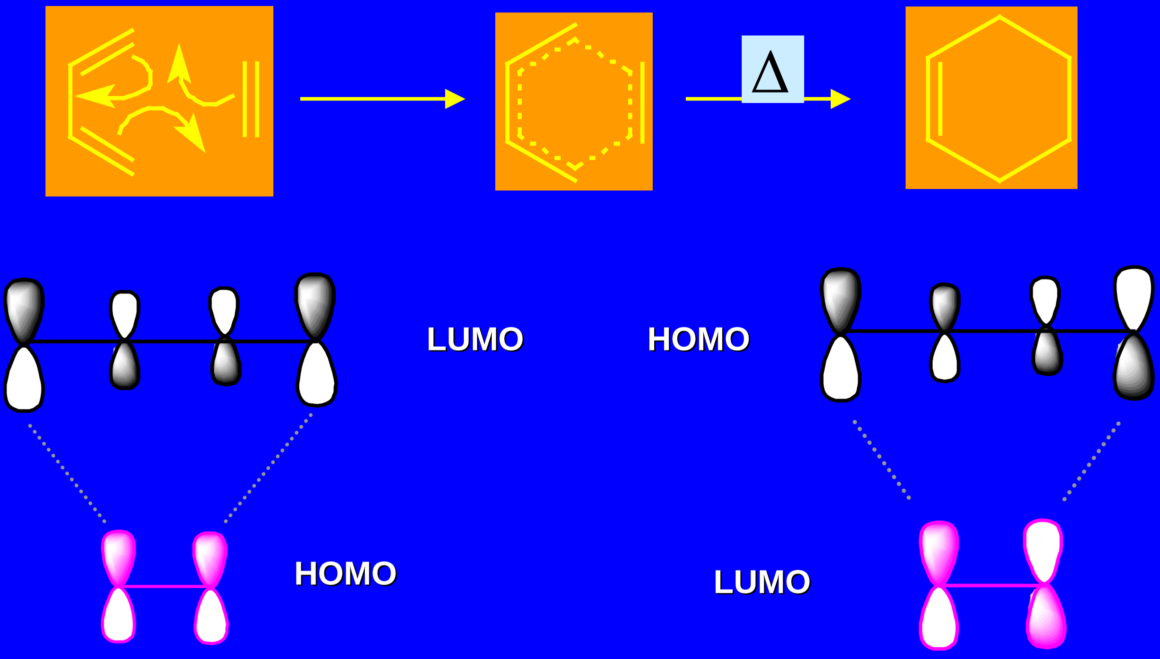


LUMO

HOMO

LUMO

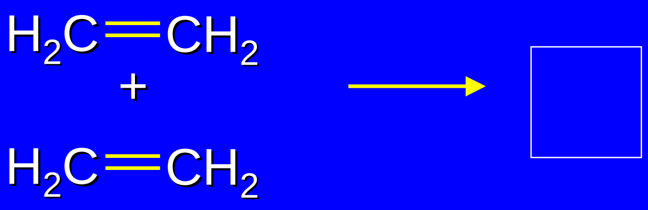
HOMO



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

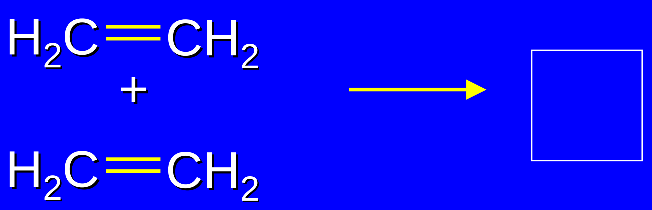
Example E:

A "forbidden" reaction

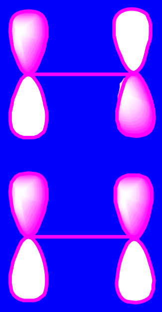


- The dimerization of ethylene to give cyclobutane does not occur under conditions of typical Diels-Alder reactions. Why not?

A "forbidden" reaction


$$H_2C{=}CH_2 + H_2C{=}CH_2 \longrightarrow \square$$

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

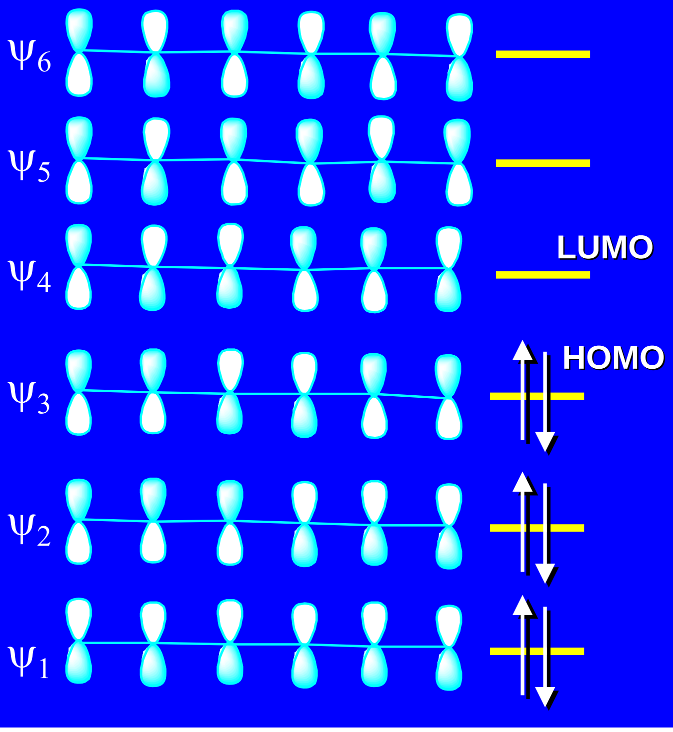


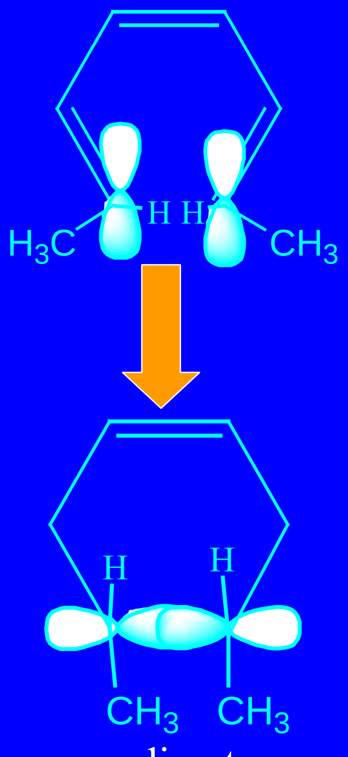
HOMO of one ethylene molecule

LUMO of other ethylene molecule

Example E: Octatriene

Thermal Electrocyclic Reactions

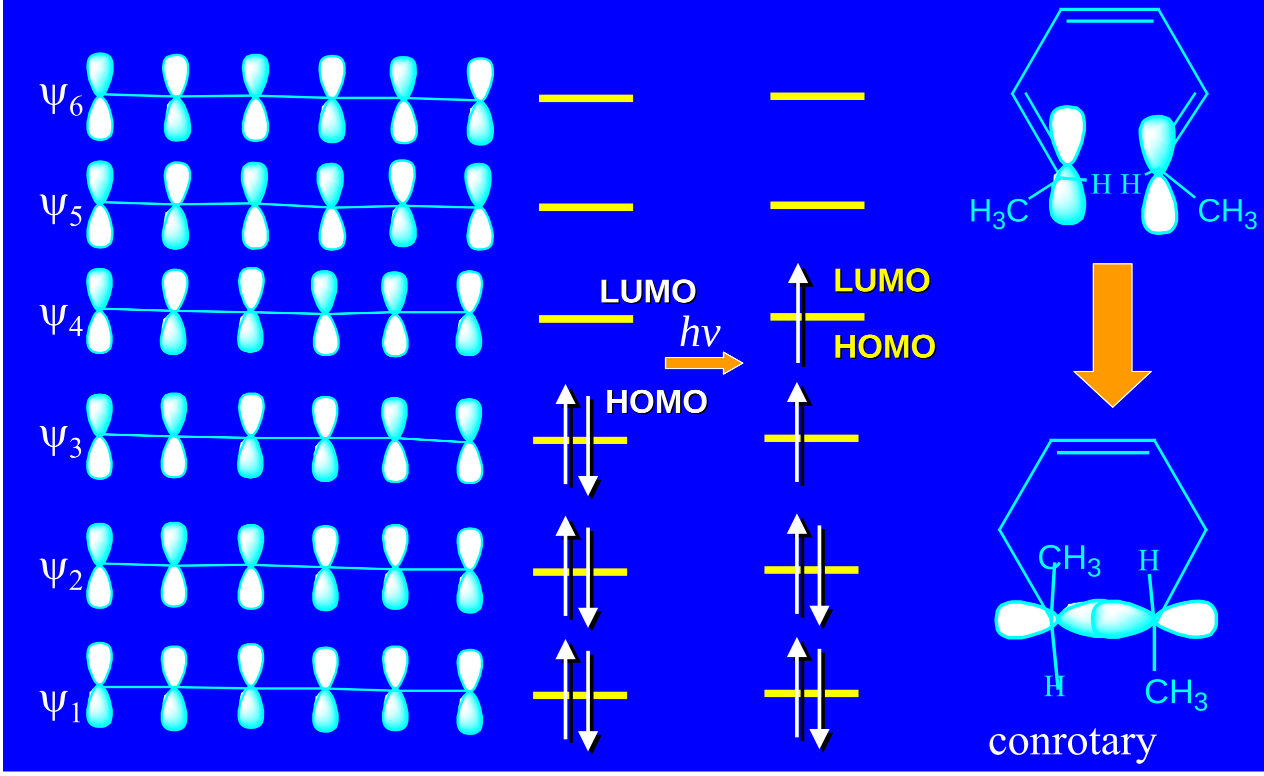




disrotary

Example E: Octatriene

Photochemical Electrocyclic Reactions



conrotary

Sterochemical 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.

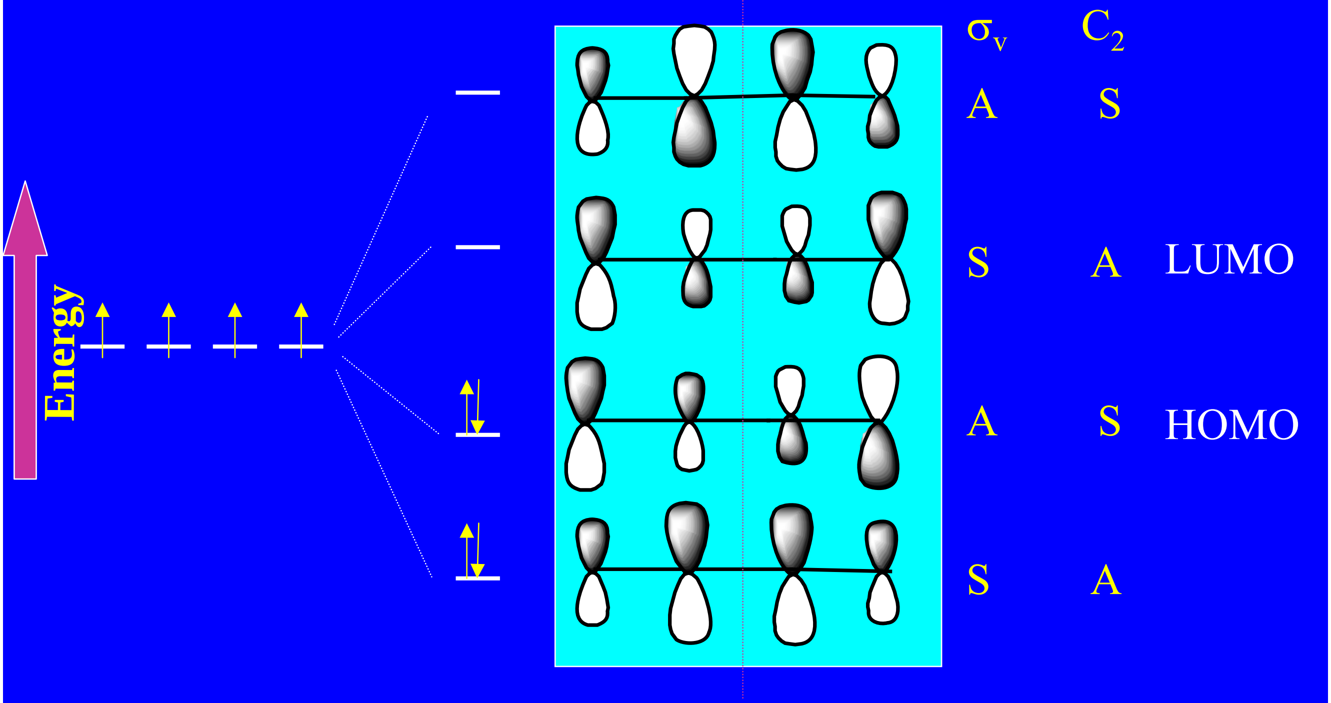
iii. The correlated orbitals should have comparable energies.

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

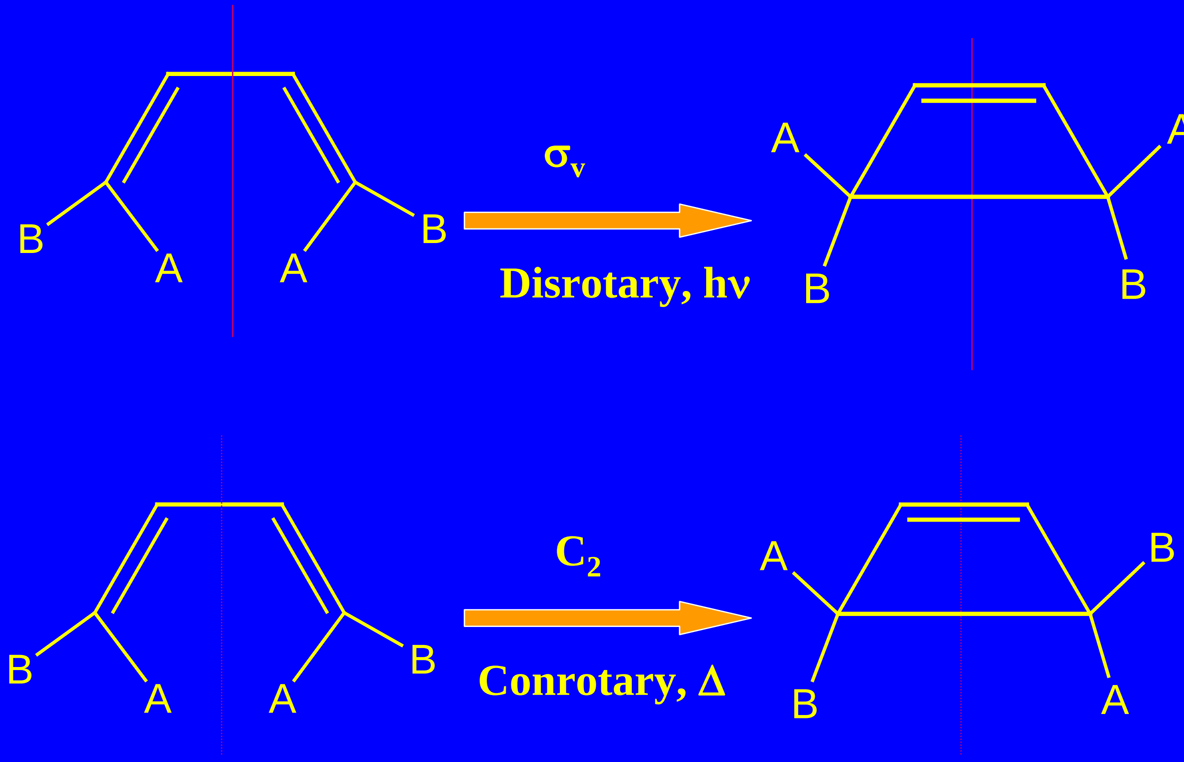
Example A:

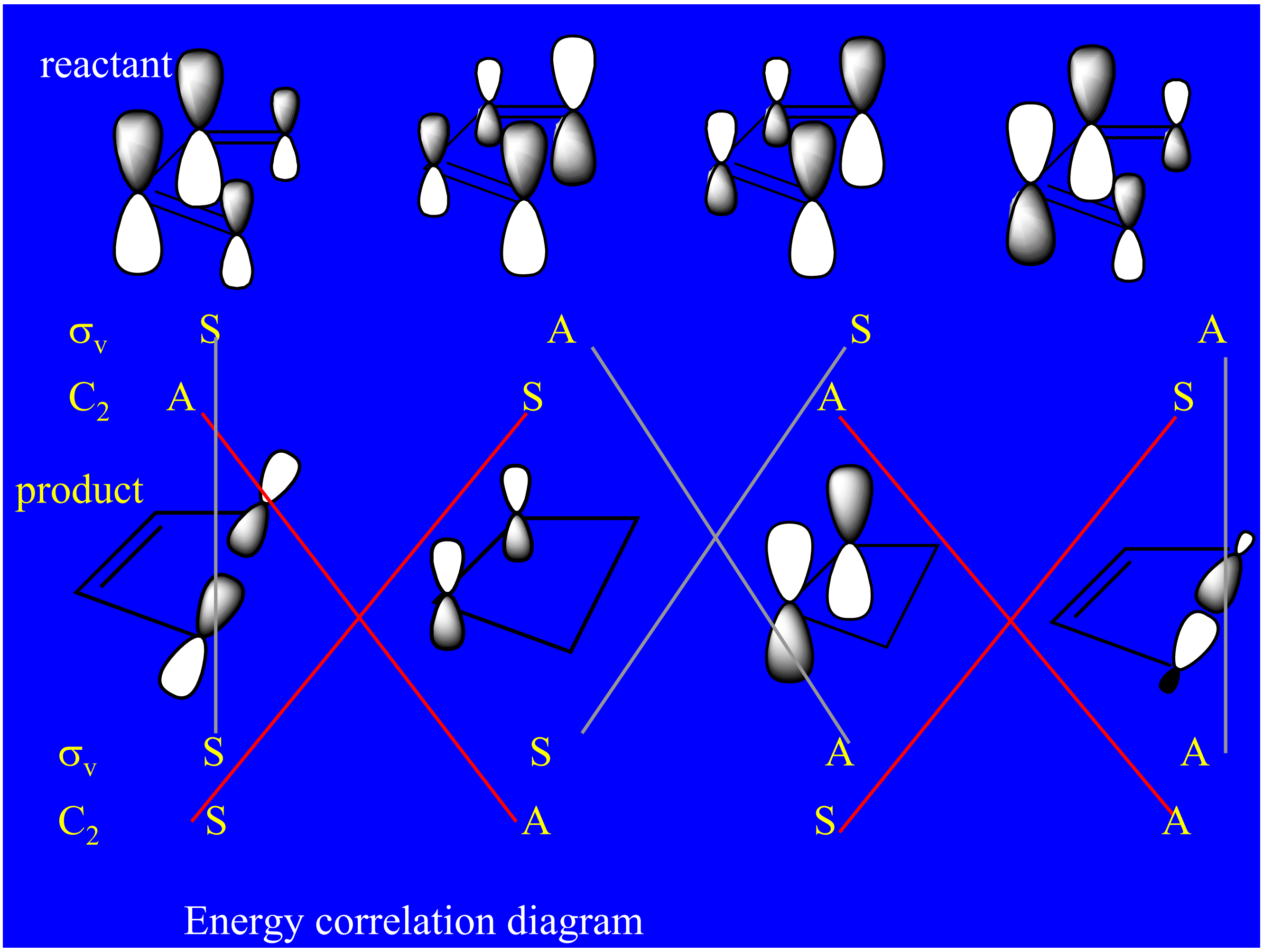
Electrocyclic Reactions of butadiene

π MOs of butadiene

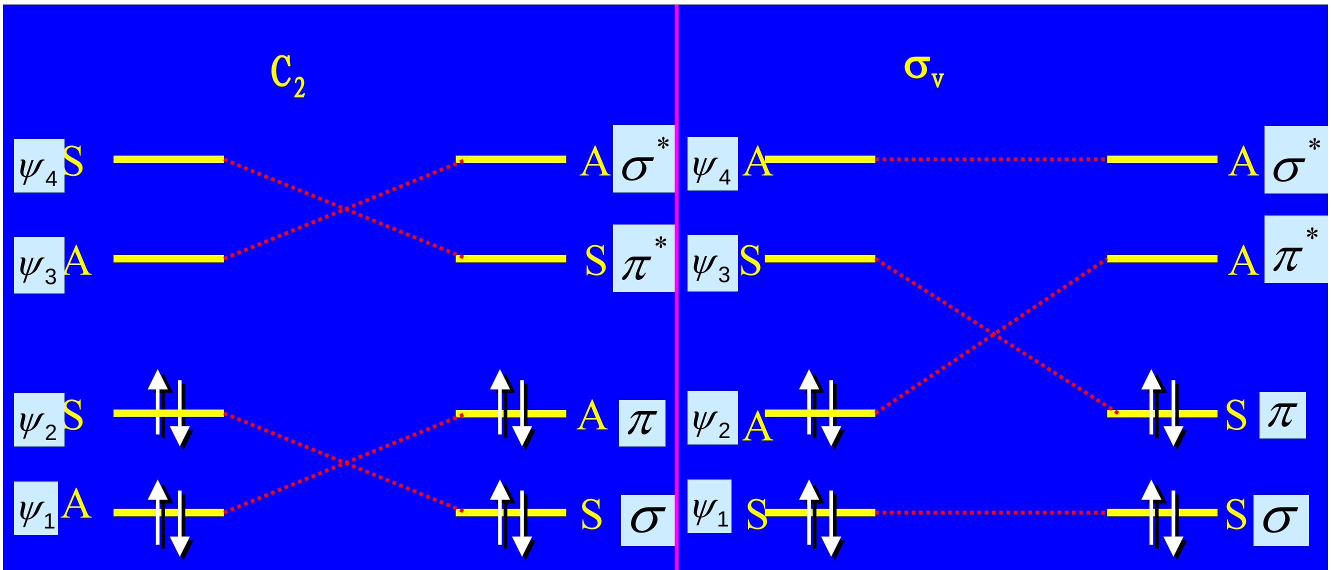


Orbital Symmetry Conservation





Energy correlation diagram



Conrotary mode
Thermal reaction

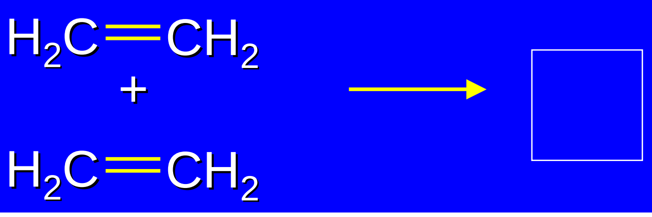
Disrotary mode
Photochemical reaction

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

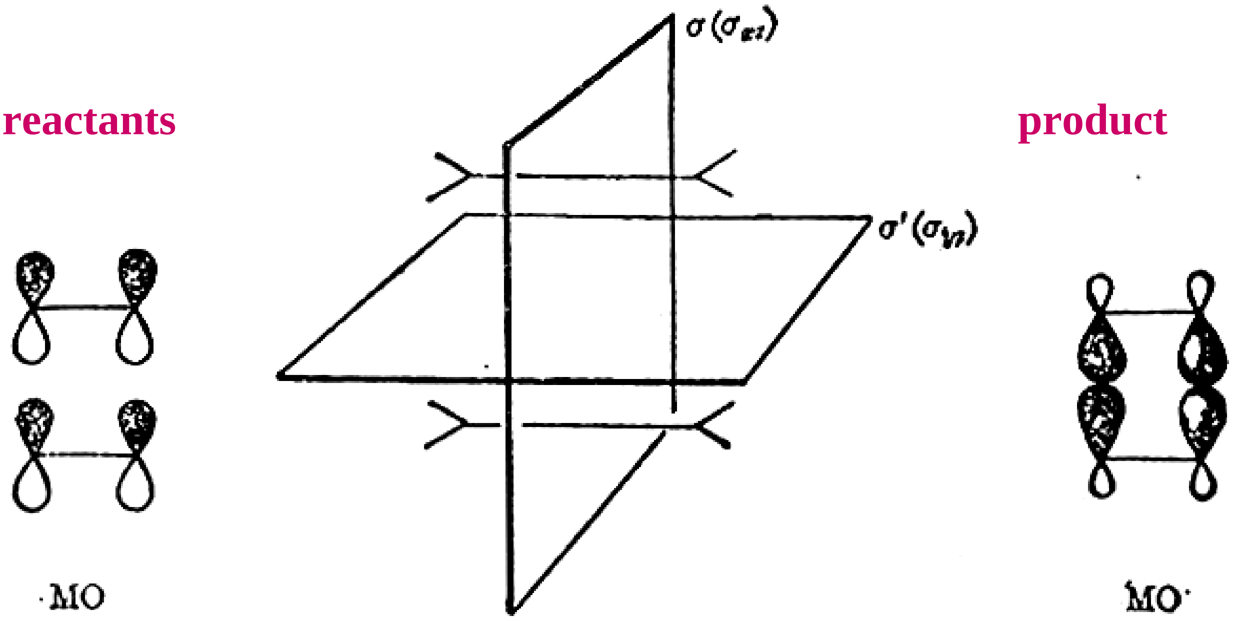
---

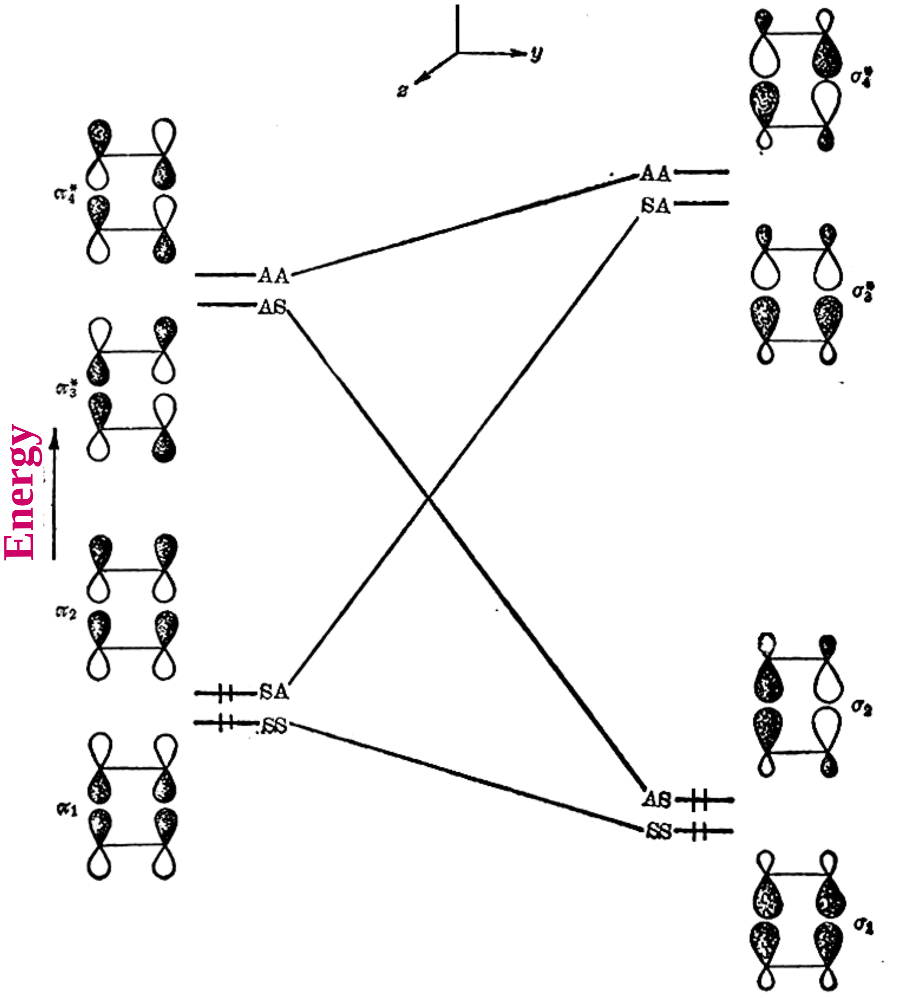
Example B:

Cycloaddition of ethylene



$H_2C{=}CH_2 + H_2C{=}CH_2 \rightarrow$





In photochemical reaction mode