

## Chap.4 Molecular Orbital Theory

The M.O. of a molecule is treated as the linear combination of atomic orbitals → LCAO-MO

$$\psi_i = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + \dots + c_n \phi_n = \sum_{i=1}^n c_i \phi_i$$

The energy of the M.O. system is obtained by solving equation.

$$\mathcal{H} \psi = \psi E$$

Hamiltonian operator
Eigen value

The energy of a molecule arises from electron motions, internal vibrations, rotations, translation.

The electron motion can be treated separately from nuclear motion.

Hamiltonian operator gives the energy of electrons, for  $2e^-$ , 2 nuclei

$$\mathcal{H}_e = -\frac{\hbar^2}{2m} \sum_{i=1}^2 \nabla_i^2 - \sum_{i=1}^2 \frac{z_1 e^2}{R_{1i}} - \sum_{i=1}^2 \frac{z_2 e^2}{R_{2i}} + \frac{e^2}{r_{12}}$$

distance between electron and nuclei
distance between 2 electron

$$\int \psi \mathcal{H} \psi d\tau = \int \psi E \psi d\tau \quad E = \frac{\int \psi \mathcal{H} \psi d\tau}{\int \psi^2 d\tau}$$

## § *Ab initio* Molecular Orbital Theory

Solve the Schrodinger equation with approximations, but no empirical parameters.

Born-Oppenheimer Approximation: separation of nuclei and electrons, keeping nuclei fixed.

The orbital approximation: the total wavefunction is considered as a product of one electron wavefunctions-orbital.

$$\Psi = \psi(1) \psi(2) \psi(3) \dots \psi(m)$$

Pauli Principle: the total wavefunction of an atom or molecule must be antisymmetric with respect to an exchange of the coordinates of any two electrons.

## § Semi-empirical Method

NDO, MNDO, AM1, PM3...

## § Density Functional Theory

Calculating the electron density  $\rho$  across the entire molecule, which correlates with the total energy of the molecule

$$E = E^T + E^V + E^J + E^{XC}$$

$E^T$ : electron kinetic energy term

$E^V$ : potential energy term

$E^J$ : Coulomb self-interaction term

$E^{XC}$ : exchange correlation term

## § Hückel Molecular Orbital Theory

- 1. only  $\pi$  -electrons are treated ( $\sigma$ - $\pi$  separation)
- 2. the basis set consists of N p orbitals, one on each of the N carbon atoms of the  $\pi$  system

e.g For ethene

$$\psi_{\pi} = c_1 \phi_1 + c_2 \phi_2$$

$$E = \frac{\int (c_1 \phi_1 + c_2 \phi_2)^* \mathcal{H} (c_1 \phi_1 + c_2 \phi_2) d\tau}{\int (c_1 \phi_1 + c_2 \phi_2)^2 d\tau}$$

define  $\int \phi_1 \mathcal{H} \phi_2 d\tau = \int \phi_2 \mathcal{H} \phi_1 d\tau$

$$\int \phi_1 \mathcal{H} \phi_1 d\tau \equiv H_{11} \quad \begin{array}{l} \text{Coulomb integral} \\ \text{energy of an electron in its own orbital} \end{array}$$

$$\int \phi_1 \mathcal{H} \phi_2 d\tau \equiv H_{12} \quad \begin{array}{l} \text{Resonance integral} \\ \text{interaction energy} \end{array}$$

$$\int \phi_1 \phi_1 d\tau \equiv S_{11} \quad \text{Normalization integral}$$

$$\int \phi_1 \phi_2 d\tau \equiv S_{12} \quad \text{Overlap integral for adjacent atoms}$$

$$\frac{\partial E}{\partial c_1} \equiv 0 \quad c_1(H_{11} - E S_{11}) + c_2(H_{12} - E S_{12}) = 0$$

by variation principle

$$\frac{\partial E}{\partial c_2} \equiv 0 \quad c_1(H_{12} - E S_{12}) + c_2(H_{22} - E S_{22}) = 0$$

to solve  $c_1, c_2$

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{21} - E S_{21} & H_{22} - E S_{22} \end{vmatrix} = 0$$

assume  $S_{ii}=1, S_{ij}=0$  for  $i \neq j$

$H_{ii} = \alpha, H_{ij} = \beta$  if  $i$  and  $j$  are  $\sigma$ -bonded

energy of an electron in  $i$  orbital. same for all  $i$

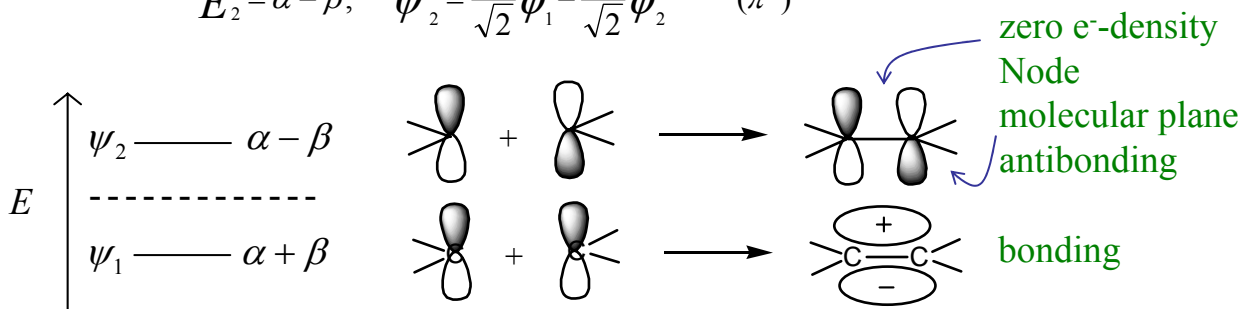
interaction energy of an  $e^-$  in basis orbital  $i$  and orbital  $j$ .

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

$$\begin{vmatrix} X & 1 \\ 1 & X \end{vmatrix} = 0 \quad X^2 - 1 = 0 \quad X = \pm 1 \quad \therefore E = \alpha \pm \beta$$

with  $E_1 = \alpha + \beta, \quad \psi_1 = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 \quad (\pi)$

$$E_2 = \alpha - \beta, \quad \psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_2 \quad (\pi^*)$$



### for 3 p-orbitals of allyl system

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

$$\begin{vmatrix} X & 1 & 0 \\ 1 & X & 1 \\ 0 & 1 & X \end{vmatrix} = 0 \quad X^3 - 2X = 0 \quad X = \pm\sqrt{2}, 0$$

$\therefore E_1 = \alpha + \sqrt{2}\beta$  bonding

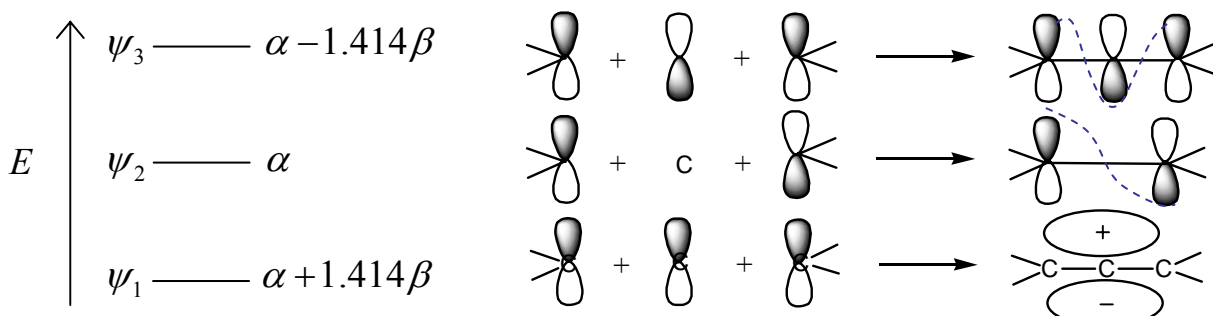
$$\psi_1 = \frac{1}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$$

$E_2 = \alpha$  non-bonding

$$\psi_2 = \frac{\sqrt{2}}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_3$$

$E_3 = \alpha - \sqrt{2}\beta$  anti-bonding

$$\psi_3 = \frac{1}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$$



## For four p-orbitals of butadiene

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

$$X \begin{vmatrix} X & 1 & 0 \\ 1 & X & 1 \\ 0 & 1 & X \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 \\ 0 & X & 1 \\ 0 & 1 & X \end{vmatrix} = 0$$

$$X(X^3 - 2X) - (X^2 - 1) = 0$$

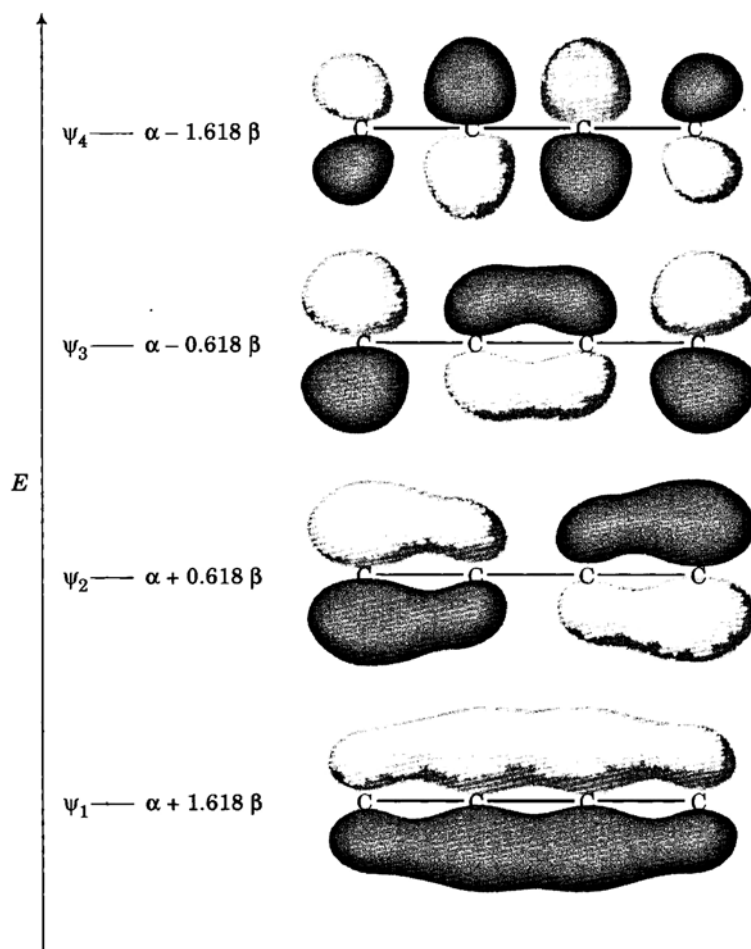
$$X^4 - 3X^2 + 1 = 0 \quad X = \pm 0.618 \text{ and } \pm 1.618.$$

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

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

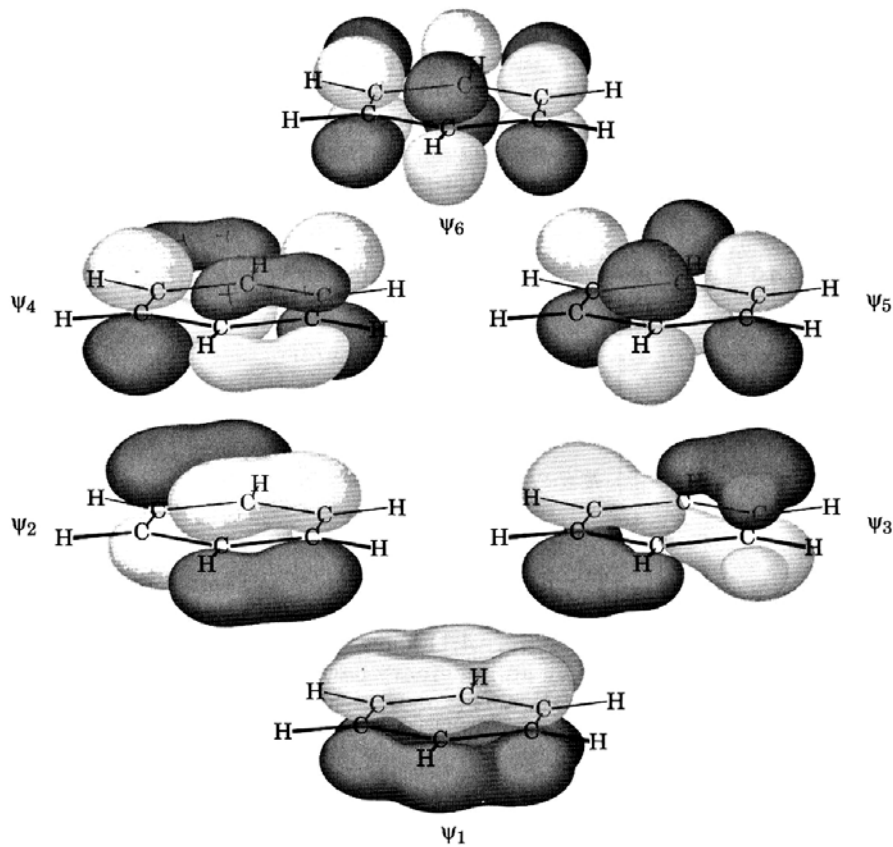
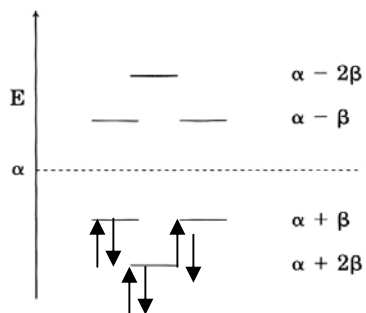
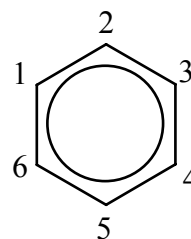
$$\psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$

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



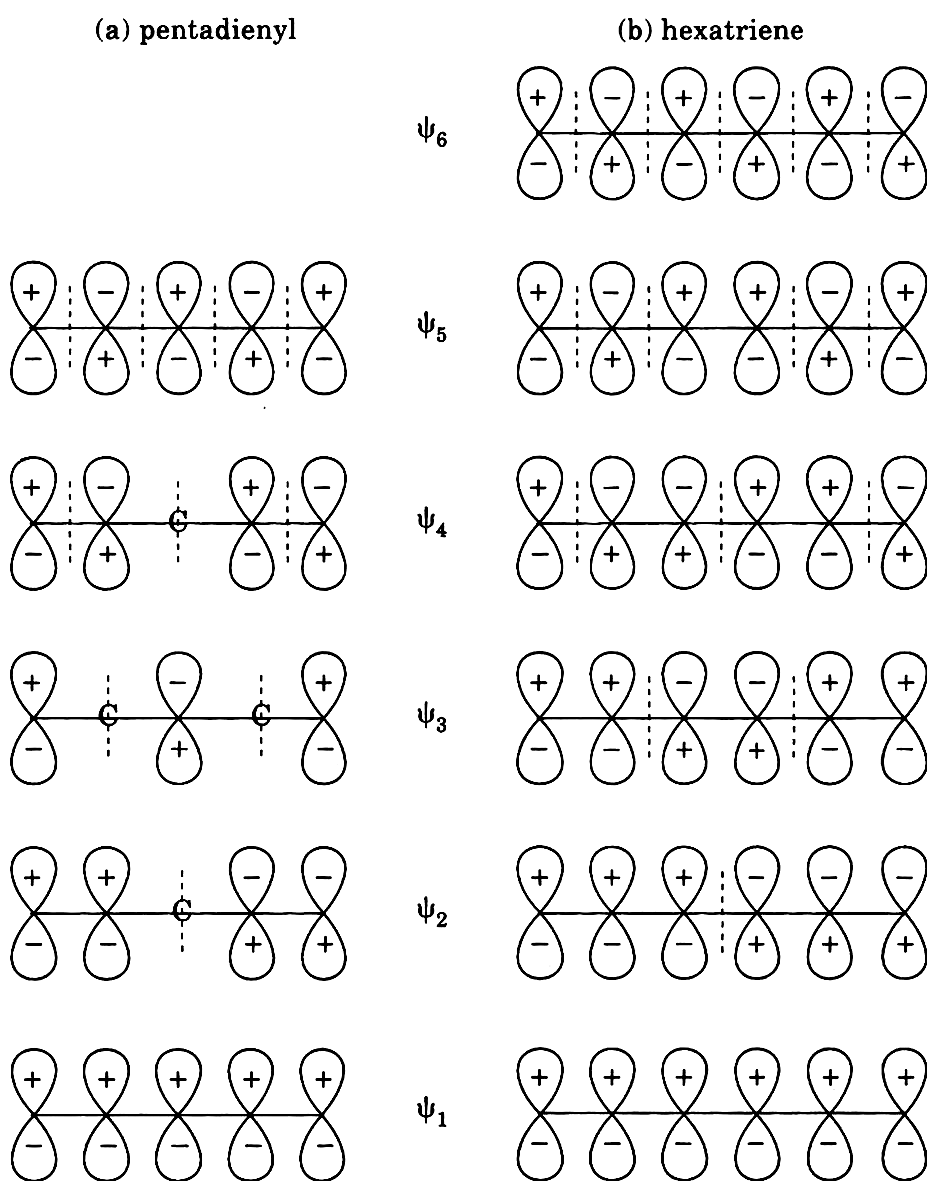
# Benzene HOMO

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



## Generalization :

1. The number of nodes increases from 0 to  $n-1$
2. The bonding and antibonding orbitals are symmetrically placed above and below  $E = \alpha$  (or non-bonding level)
3. Coefficients are symmetrical with respect to atomic orbital's  $c$ 's

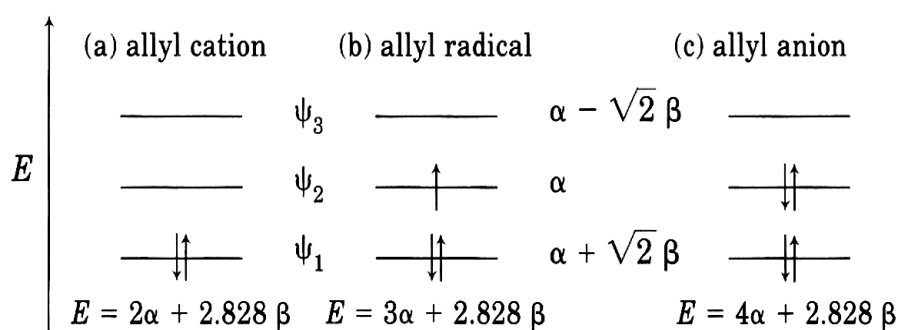


## § Correlation of Physical Properties with Results of HMO Calculations

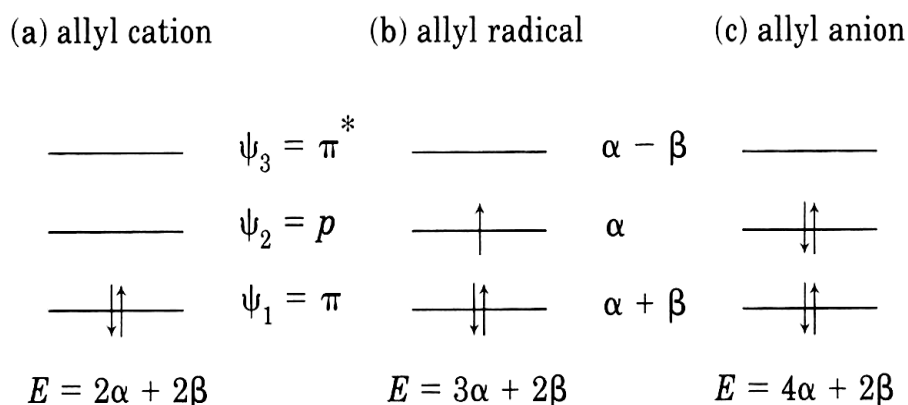
Energy

for ethylene,  $2e^-$  in  $\psi_1$ ,  $E_\pi = 2\alpha + 2\beta$

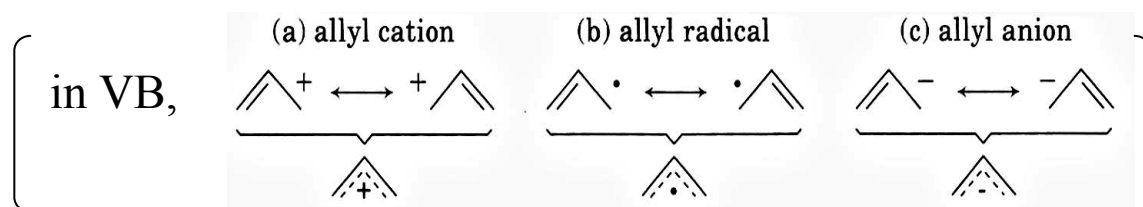
for allyl system (delocalized system)



Compare to localized reference system



delocalization energy =  $0.828\beta$



the extra stability is called resonance energy

For benzene  $E = 6\alpha + 8\beta$ , resonance energy 36kcal  $\rightarrow \beta = 18\text{kcal}$



$\pi$  -bond order

$$P_{ij} = \sum_{\text{occup'd } \psi} n c_i c_j$$

$n$  : no. of electron in a particular orbital

$c_i, c_j$  : the coefficient of  $i, j$  (bonded together) for the M.O.

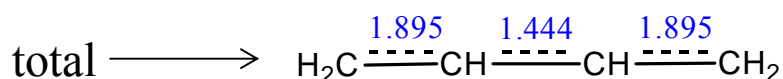
butadiene

$$2e^- \text{ in } \psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$

$$2e^- \text{ in } \psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$

$$P_{12} = 2 \times 0.372 \times 0.602 + 2 \times 0.602 \times 0.372 = 0.895$$

$$P_{23} = 2 \times 0.602 \times 0.602 + 2 \times 0.372 \times (-0.372) = 0.444$$



bond order =  $\sigma$  bond order +  $\pi$  -bond order

For excited state of butadiene

$$2e^- \text{ in } \psi_1$$

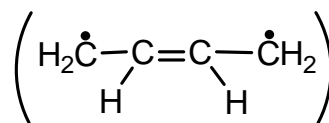
$$1e^- \text{ in } \psi_2$$

$$1e^- \text{ in } \psi_3$$

$$P_{12} = 2 \times 0.372 \times 0.602 + 1 \times 0.602 \times 0.372 + 0.602 \times (-0.372) = 0.448$$

$$P_{23} = 2 \times 0.602 \times 0.602 + 1 \times 0.372 \times (-0.372) + 1 \times (-0.372) \times (-0.372) = 0.725$$

total bond order



electron density

$$\psi = c_1\phi_1 + c_2\phi_2 + \dots + c_k\phi_k$$

to normalize  $\psi$ ,

$$c_1^2 + c_2^2 + c_3^2 + \dots + c_k^2 = 1$$

if one electron occupies the orbital,  $c_i^2$  is the fraction of electron density on  $i$ th carbon, or  $2c_i^2$  for  $2e^-$ /orbital

$$\rho_i = \sum_{\text{occ'd } \psi} nc_i^2$$

for allyl  $\psi_1 = \frac{1}{2}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$

$$\psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$$

$$\psi_3 = \frac{1}{2}\phi_1 - \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$$

charge density

for cation,  $e^-$ -density on  $c_1 = 2 \times \left(\frac{1}{2}\right)^2 = \frac{1}{2}$

$$\frac{1}{2}$$

$$c_2 = 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

$$0$$

$$c_3 = 2 \times \left(\frac{1}{2}\right)^2 = \frac{1}{2}$$

$$\frac{1}{2}$$

for radical, on  $c_1 = 2 \times \left(\frac{1}{2}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2 = 1$

$$0$$

$$c_2 = 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 + 0 = 1$$

$$0$$

$$c_3 = 2 \times \left(\frac{1}{2}\right)^2 + \left(-\frac{1}{\sqrt{2}}\right)^2 = 1$$

$$0$$

for anion, on  $c_1 = 2 \times \left(\frac{1}{2}\right)^2 + 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 = 1\frac{1}{2}$

$$-\frac{1}{2}$$

$$c_2 = 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 + 2 \times 0 = 1$$

$$0$$

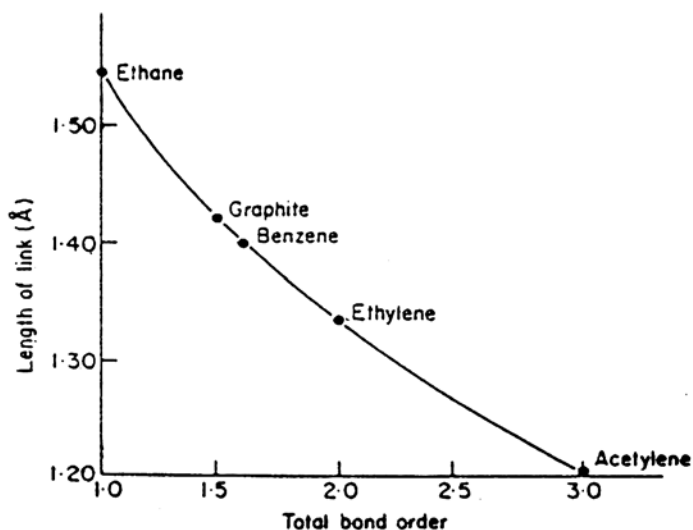
$$c_3 = 2 \times \left(\frac{1}{2}\right)^2 + 2 \times \left(-\frac{1}{\sqrt{2}}\right)^2 = 1\frac{1}{2}$$

$$-\frac{1}{2}$$

charge density on  $i$ th atom  $q_i = 1 - \rho_i$

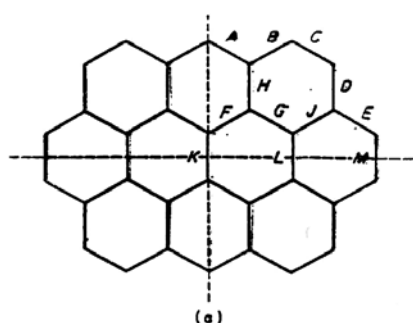
## Correlation of Bond Order and Bond length

C-C 1.54Å      C=C 1.34Å      C≡C 1.24Å



benzene bond order  
1.67 → 1.4Å

expt'l bond length  
1.397Å

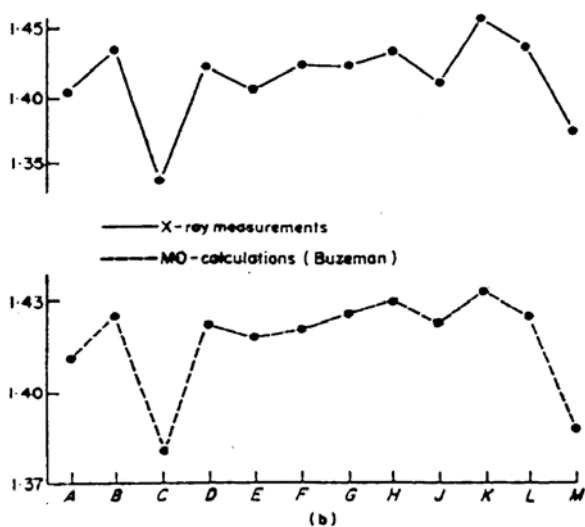


after  $n \rightarrow \pi^*$  excitation

$$(\psi_1)^2(\psi_2)^2 + 1e^- \rightarrow (\psi_1)^2(\psi_2)^2(\psi_3)^1$$

↑  
from Oxygen's  
non-bonding e<sup>-</sup>

bond length change upon  
 $n \rightarrow \pi^*$  transition



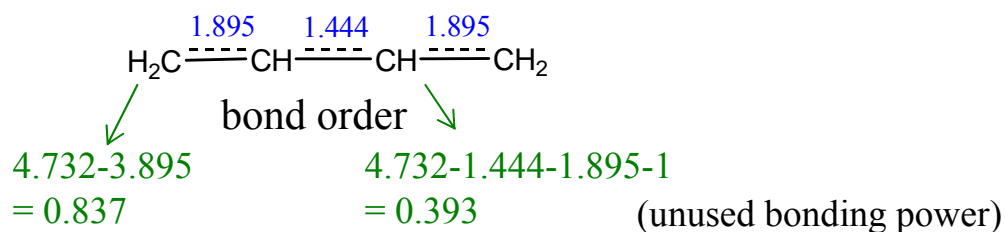
	calc'd	obs'd
$\Delta r_{12}$	0.04Å	0.06Å
$\Delta r_{23}$	-0.03Å	-0.04Å

FIG. 4-6 (a) Non-equivalent carbon-carbon bonds (A to H, J to M) in ovalene (b) Comparison of calculated and experimentally-observed bond-lengths in ovalene (Redrawn from A. J. Buzeman *Proc. Phys. Soc. London*, A63, 827, (1950).)

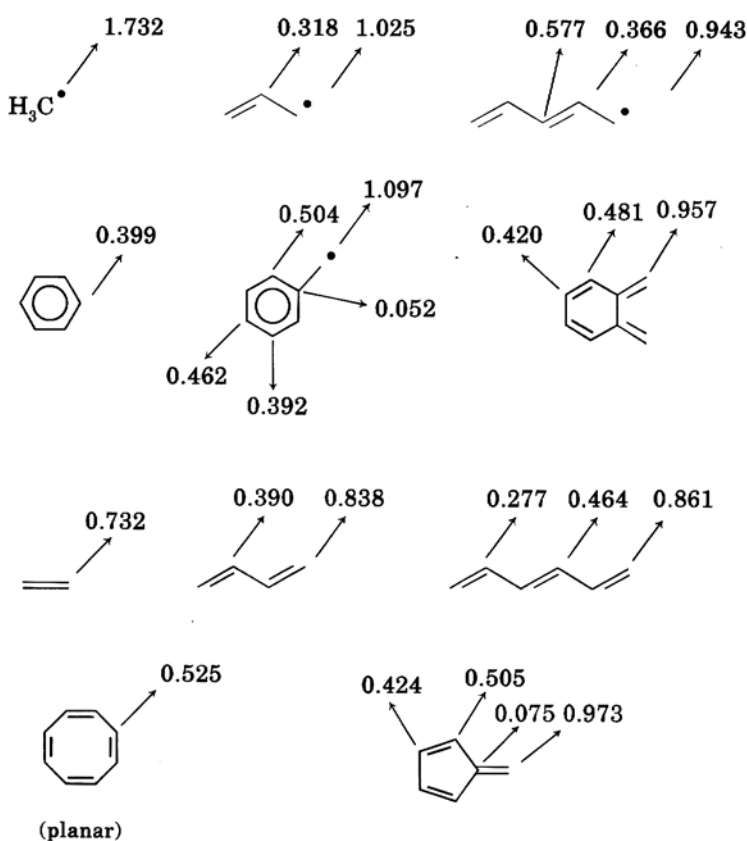
## Free Valence

maximum possible bond order for  $sp^2$ -C  
(obtained from trimethylene methane radical)

$$F = 4.732 - \sum_{\psi \text{ occ.}} P_{ij}$$



## Free valence values



free valence correlate the reactivity of radical rxns such as  $\text{CH}_3$ ,  $\text{CCl}_3$  toward conjugate molecules.

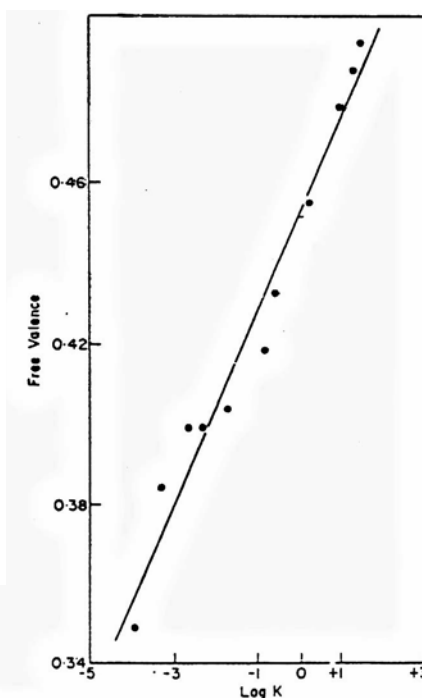


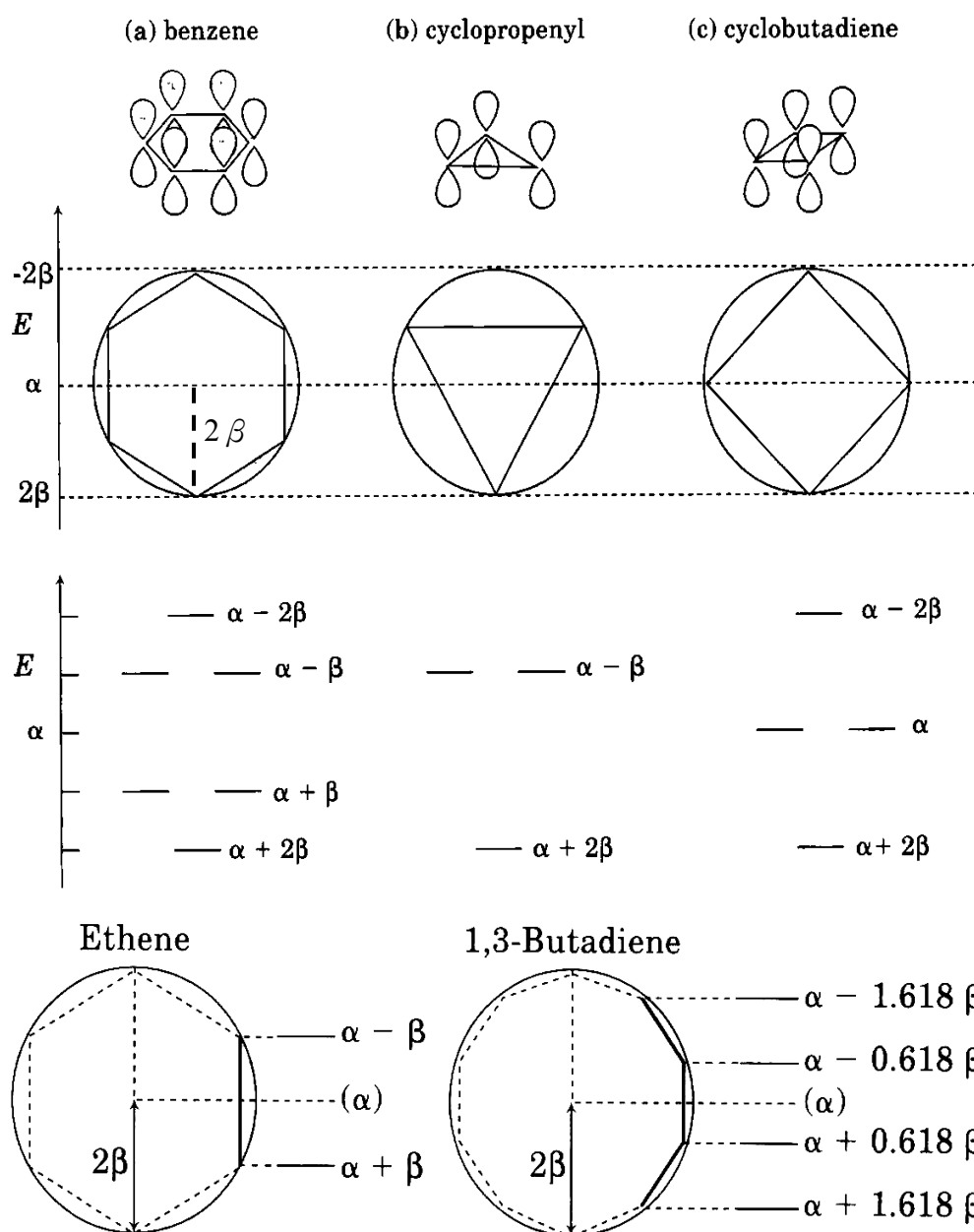
FIG. 4-11 Relation between  $\ln$  reaction-rate for  $\text{CCl}_3$ -addition and maximum free-valence, for a series of molecules. (Redrawn from E. C. Kooyman and E. Forenhorst, *Trans. Faraday Soc.*, 49, 58 (1953).)

### Hückel $4n+2$ Rule :

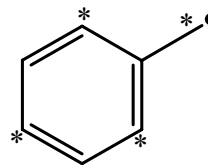
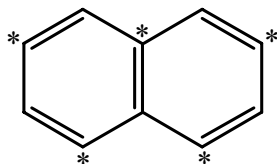
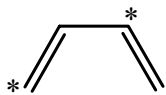
Planar cyclic system with  $4n+2$   $\pi$ -electron  $\rightarrow$  aromatic  
extra stability relative to acyclic analogs

Planar cyclic system with  $4n$   $\pi$ -electron  $\rightarrow$  antiaromatic  
less stable than acyclic analogues

Circle Method for arriving the energy levels for monocyclic  $\pi$ -system



## Alternate Hydrocarbon $\begin{cases} \text{even} \\ \text{odd} \end{cases}$



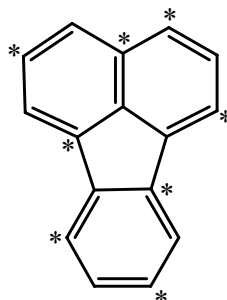
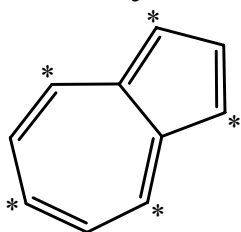
no. of starred positions  
= no. of unstarred positions

even

no. of starred positions  
 $\neq$  no. of unstarred positions

odd

## Non-alternate Hydrocarbon

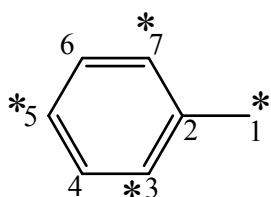


## Coulson-Rushbrooke Theorem

- In an alternate hydrocarbons, the MO energy levels are symmetrically paired above the  $E = \alpha$  level.  $\rightarrow E = \alpha + k\beta$   
 $E = \alpha - k\beta$
  - In an alternate hydrocarbon, the LCAO-coefficient of any pair of complementing orbitals are identical except for a change of sign in the coefficients of atomic orbitals centered on the unstarred atoms.
  - In a neutral alternate hydrocarbon or hydrocarbon-radical electron density on various C-atom are, in the ground state, all unity. (self-consistent)
- (Corollary : For odd alternate hydrocarbon, there is at least one non-bonding MO, at  $E = \alpha$ .(or odd number or NBMO))

more about NBMO :

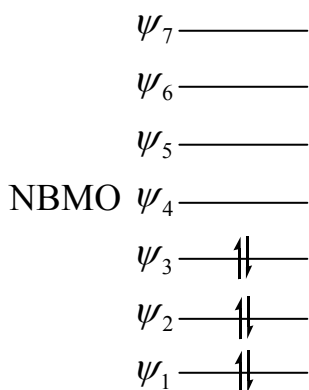
- The NBMO will have non-zero coefficients only at the starred position.
- The sum of the coefficients of the atomic orbitals of the starred atoms directly linked to a given non-starred atom is zero.



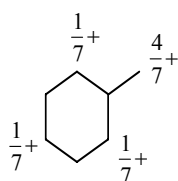
$$\begin{aligned}
 c_1 + c_3 + c_7 &= 0 & \text{let } c_5 &= c, & c_3 &= -c \\
 c_5 + c_7 &= 0 & & & c_7 &= -c \\
 c_3 + c_5 &= 0 & & & c_1 &= +2c \\
 c_1^2 + c_3^2 + c_5^2 + c_7^2 &= 1 \\
 \Rightarrow c &= \pm \frac{1}{\sqrt{7}}
 \end{aligned}$$

$$\psi_{NBMO} = \frac{2}{\sqrt{7}}\phi_1 - \frac{1}{\sqrt{7}}\phi_3 + \frac{1}{\sqrt{7}}\phi_5 - \frac{1}{\sqrt{7}}\phi_7$$

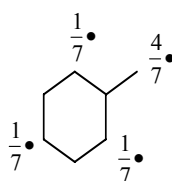
determine the unpaired electron density or the charge density in anion or cation



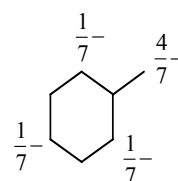
benzyl cation  
electron density



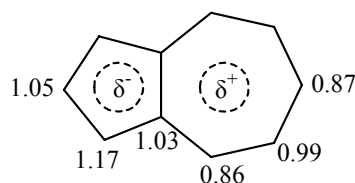
radical



anion



For non-alternate hydrocarbon, the electron density in each contributing carbon is not unity, not equivalent.

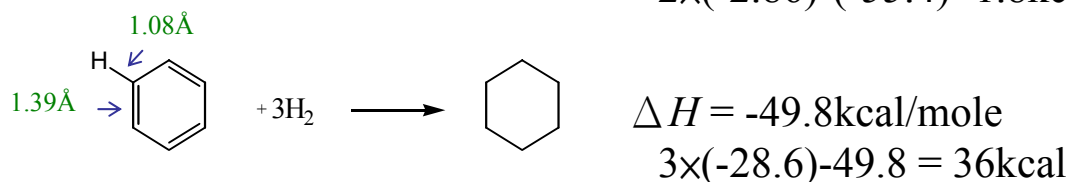
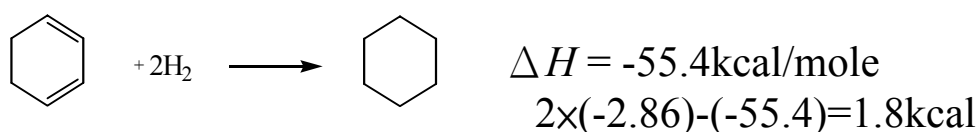
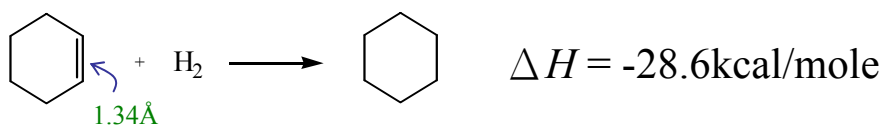


# Benzene and Aromaticity

Benzene (and derivatives) exhibit special properties

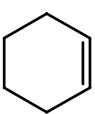

- aromatic {
- thermal stability
  - substitution reaction with electrophilic reagents
  - resistance to oxidation
  - different physical properties as analogous aliphatic compounds

resonance energy :



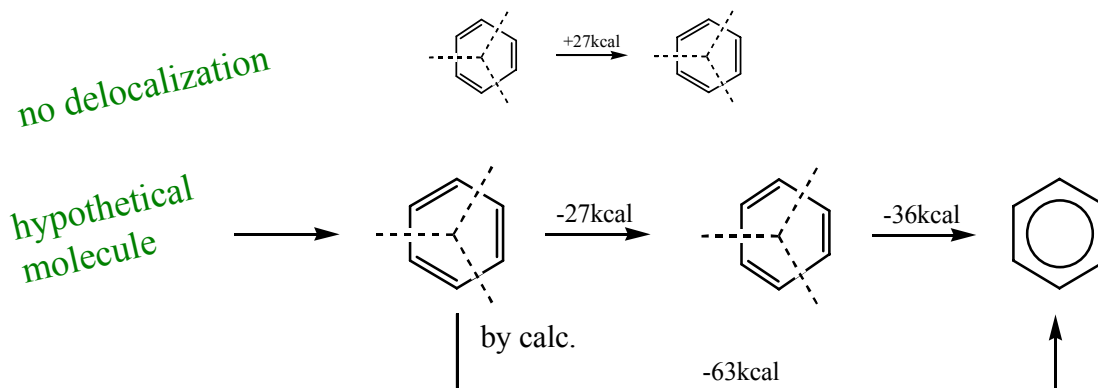
a criteria of aromaticity

$$\frac{2\beta}{}$$

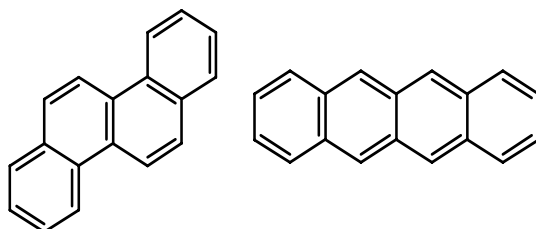
However, the double in  is different from the “double” bond in .


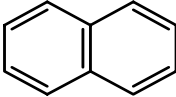
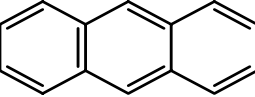
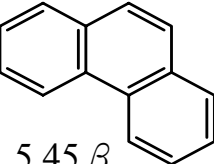


A true reference should be a cyclohexatriene with same bond lengths but no delocalization.

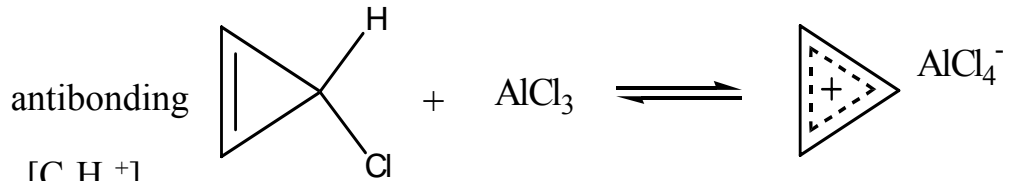
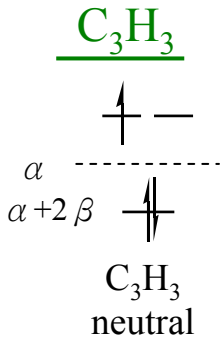


1. So R.E. increase with no. of rings
2. bent poly ring more stable in a linear



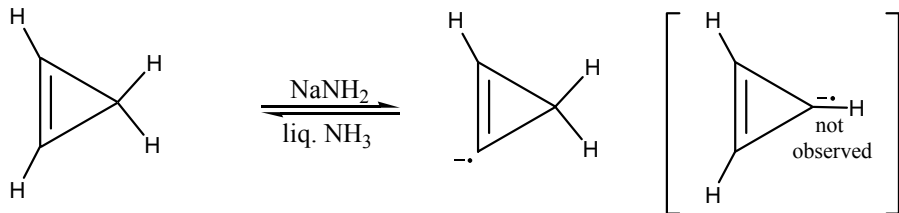
R.E. by HMO by Expt'l				
	$2\beta$	$3.68\beta$	$5.32\beta$	$5.45\beta$
	36kcal	61kcal	83.5kcal	91.3kcal

# Aromaticity in Small Rings

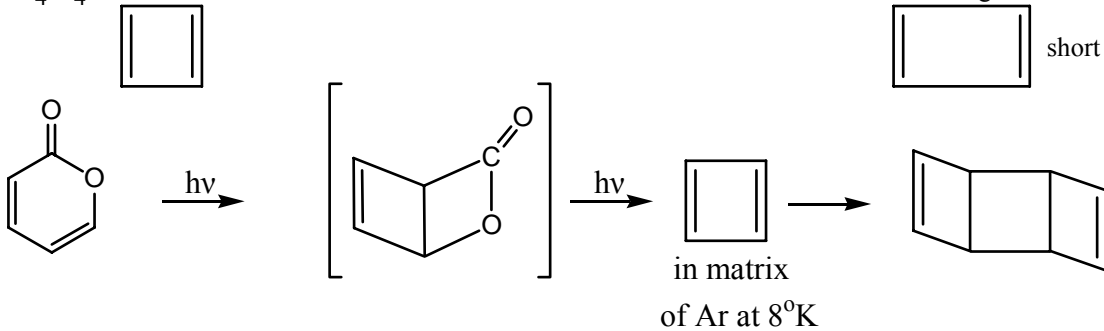
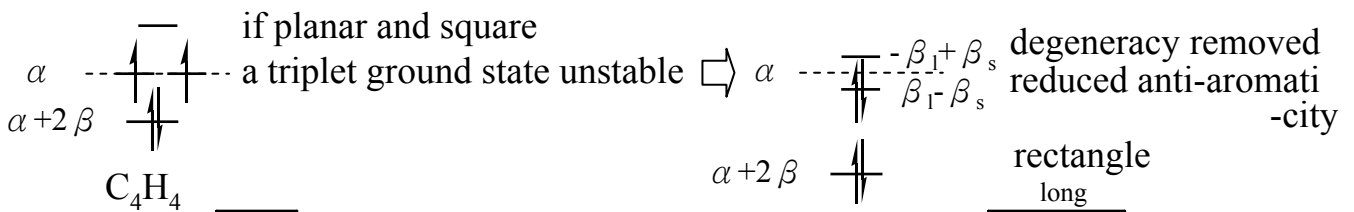


[C<sub>3</sub>H<sub>3</sub><sup>+</sup>]  
would be stable with  
2  $\beta$  resonance energy.

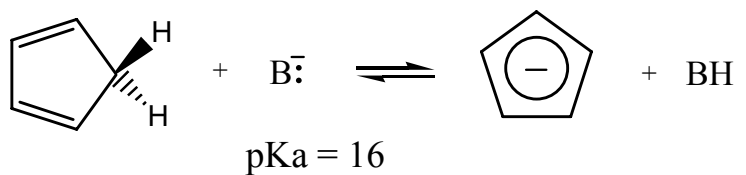
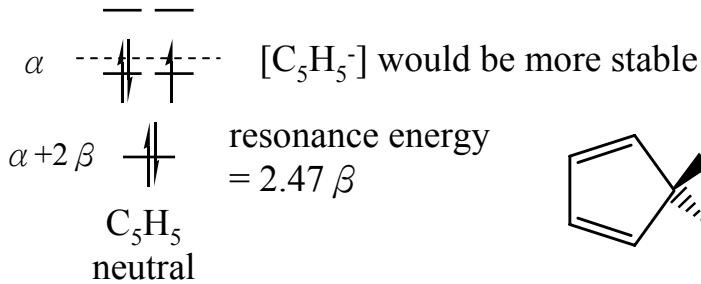
[C<sub>3</sub>H<sub>3</sub><sup>-</sup>] would be unstable



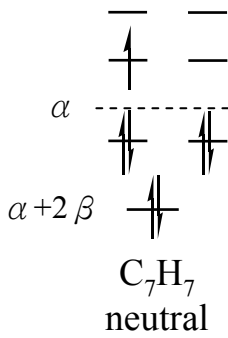
## C<sub>4</sub>H<sub>4</sub>



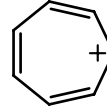
## C<sub>5</sub>H<sub>5</sub>



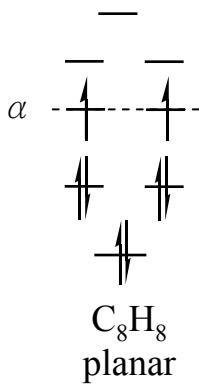
## C<sub>7</sub>H<sub>7</sub>



[C<sub>7</sub>H<sub>7</sub><sup>+</sup>] would be more stable  
resonance energy  
= 2.99 β



## C<sub>8</sub>H<sub>8</sub>

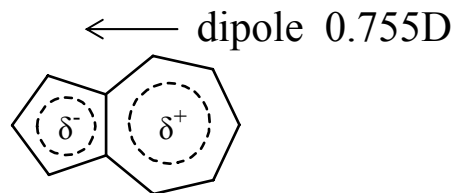


The planar structure involves severe angle strain (135°) that the molecule buckles → non-aromatic

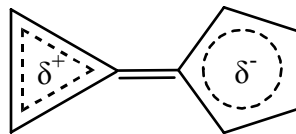


dianion → closed shell  
dication → aromatic exist

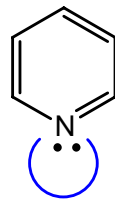
## Azulene



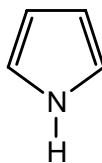
## Cyclotriapentafulvalene



→  
dipole (6.0D for hexaphenyl substituted derivative !)

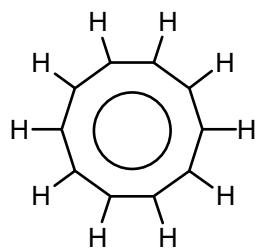


both  
6-e<sup>-</sup>

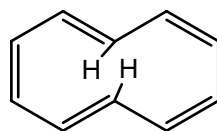


## Larger Annulenes

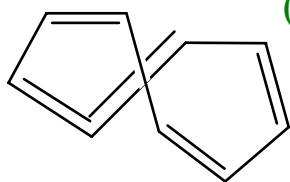
### [10] Annulene



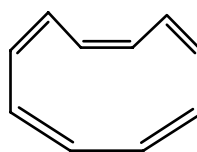
planar, severe angle strain  
(144°)



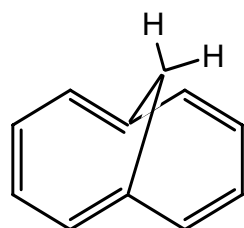
Severe non-bonded strain



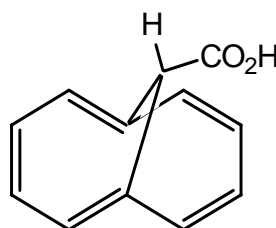
non-planar, more stable  
( 30kcal/mole more stable than all *cis*-planar )



The observed isomers are non-aromatic, due to non-planarity, not due to breakdown of Hückel's Rule.



show diamagnetic ring current



no significant bond alternation observed

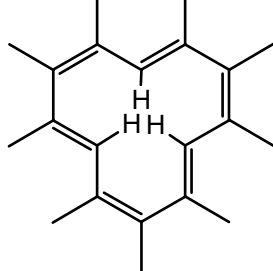
Experimental Evidence for aromaticity :

Bond length : Aromatic systems show C-C bond length 1.38~1.44 and uniform around the ring.

non-aromatic systems show  $sp^2$ - $sp^2$  single bond and  $sp^2$ - $sp^2$  double bond length.

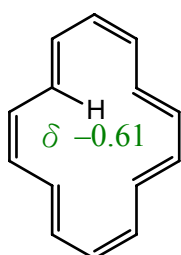
NMR chemical shift : shielding effect for nuclei above/below the ring → Upfield (by 6~11 ppm)  
due to diamagnetic anisotropy deshielding effect for nuclei attach to the ring → Down field (by 2~4 ppm)

## [12]-Annulene

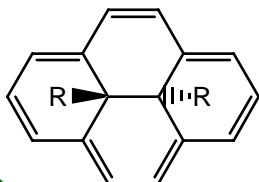


show paramagnetic current at  $-170^{\circ}\text{C}$

## [14]-Annulene

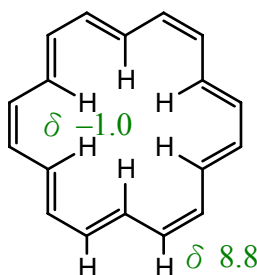


show diamagnetic current  
bond length  $1.35\sim 1.41\text{\AA}$ , no alternation  
distortion from planarity due to non-bonded strain of  
internal H.

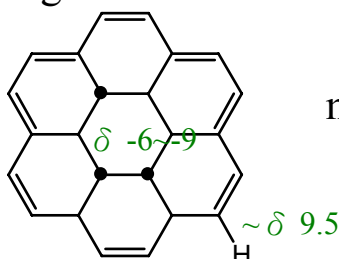


R = Et,  
show bond length  $1.39\sim 1.40\text{\AA}$

## [18]-Annulene

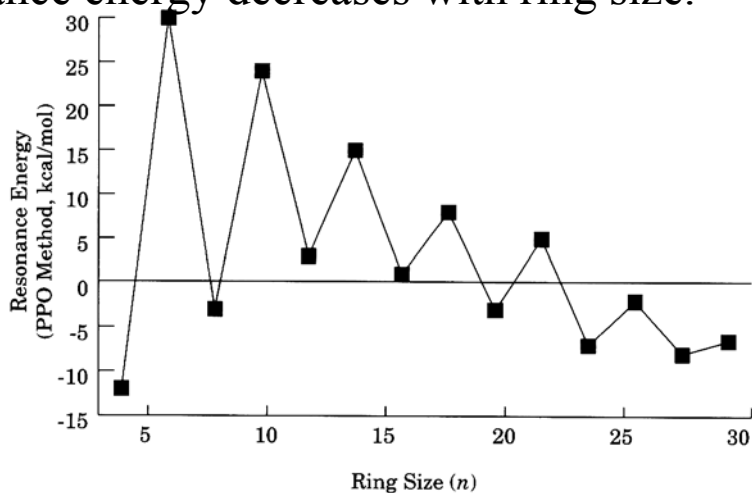


close to planar, bond length  $1.38\sim 1.42\text{\AA}$ , not alternating  
no angle strain. Aromatic



more effective than the  
flexible [18]-annulene

The resonance energy decreases with ring size.



## Other definitions of Aromaticity

$$\text{Resonance Energy} = \Delta H_f^\circ - \Delta H_{f \text{ ref}}^\circ$$

$\Delta H_f^\circ$  : heat of formation of an organic cpd

$\Delta H_{f \text{ ref}}^\circ$  : heat of formation calculated for

localized reference

$\Delta H_{f \text{ ref}}^\circ$  calculated from bond energies of C - H, C = C, C = O, C - O.

## Dewar Resonance Energy = DRE

**Table 4.2** DRE values for selected hydrocarbons.

Compound	Experimental RE <sup>a</sup>	Calculated DRE <sup>b</sup>
Cyclobutadiene <sup>c</sup>	—	- 17 kcal/mol
Benzene	+ 21 kcal/mol	+ 21
Cyclooctatetraene <sup>d</sup>	—	- 10
Cyclodecapentaene	+ 10	+ 6
Naphthalene	+ 33	+ 33
Anthracene	+ 43	+ 42
Phenanthrene	+ 49	+ 49

DRE > 0

aromatic

DRE < 0

antiaromatic

DRE  $\approx$  0

non-aromatic

<sup>a</sup>Calculated from the experimental heat of formation given in reference 113 and equation 4.63.

<sup>b</sup>Values taken from Tables 3 and 4 of reference 113.

<sup>c</sup>Experimental heats of formation are not available.

<sup>d</sup>Assumed to be planar.

## Absolute hardness

relate to e<sup>-</sup>-affinity

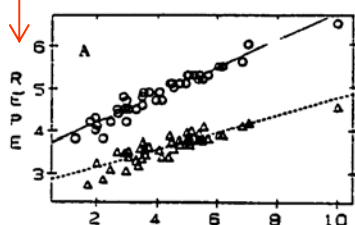
$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$$

relate to ionization potential

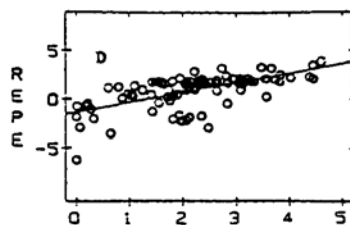
the wider the gap, the lower the chemical reactivity,

the higher the aromaticity

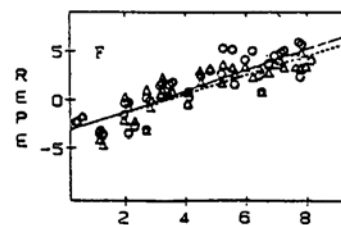
resonance energy per  $\pi$ -electron



for benzenoids



for non-alternate hydrocarbons



for heterocycles

aromatic for Hückel hardness < -0.2  $\beta$

antiaromatic for Hückel hardness > -0.15  $\beta$

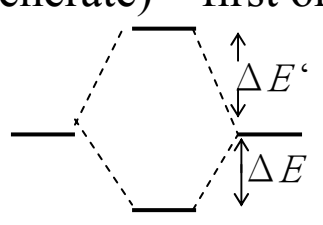
## Perturbation MO Theory (Orbital mixing rules)

The interaction of two orbitals (atomic or molecular) can be seen as a perturbation on the original orbital.

new orbitals and energies are resulted.

1. Symmetry: only orbitals of like symmetry can interact.
2. Overlap: orbitals must overlap in order to interact, the greater the overlap, the stronger the interaction.
3. Relative energy: the closer the energy, the stronger the interaction.

— if the two interacting orbitals are of the same energy, (degenerate) --- first order perturbation

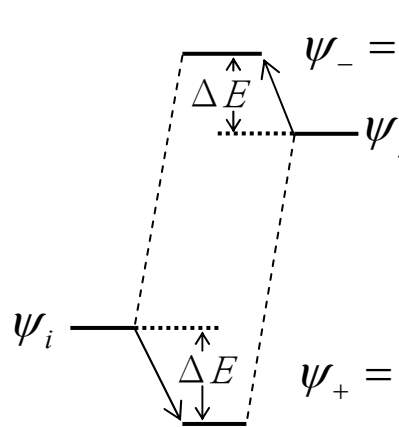


$$\psi_- = \psi_1 - \psi_2 \quad \Delta E = \frac{H_{ii}S + H_{ij}}{1 + S}$$

$$\psi_+ = \psi_1 + \psi_2 \quad \Delta E' = \frac{H_{ii}S - H_{ij}}{1 - S}$$

The antibonding orbital is destabilized more than the bonding orbital is stabilized.

— if the two interacting orbitals are of different energy (non-degenerate) --- second order perturbation



$$\psi_- = \psi_j - \lambda \psi_i \quad E'_j = E_j^\circ + \frac{|H'_{ij}|^2}{E_j^\circ - E_i^\circ}$$

$$\psi_+ = \psi_i + \lambda \psi_j \quad E'_i = E_i^\circ + \frac{|H'_{ij}|^2}{E_i^\circ - E_j^\circ}$$

$$H'_{ij} = \int \psi_i^\circ \mathcal{H}' \psi_j^\circ d\tau$$

1. The lower orbital, mixing with the upper orbital, gives a bonding orbital, between the interacting region.

The upper orbital, mixing with the lower orbital, gives an anti-bonding orbital, between the interacting region.

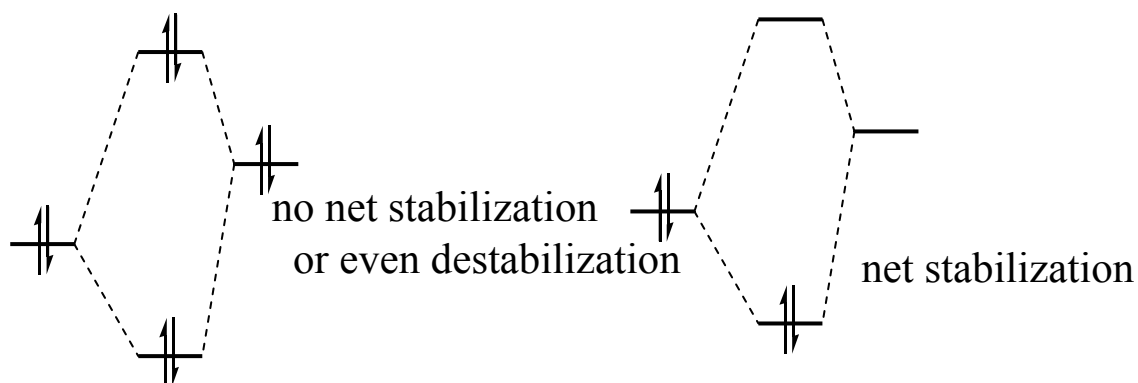
2. The perturbation causes the lower energy orbital to be even lower in energy and vice versa.

The energy changes are larger for larger overlap, and smaller if the initial difference is larger.

3. The orbital initially of lower energy is altered by adding in (mixing) a portion of the higher one in a bonding way.

The orbital initially of higher energy is altered by adding in (mixing) a portion of lower one in an anti-bonding way.

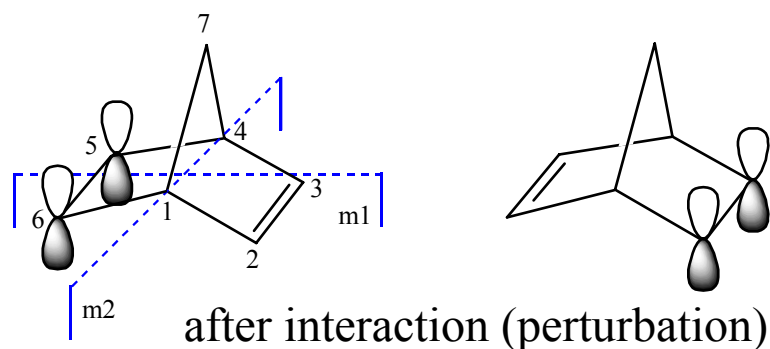
The mixing is larger the larger the overlap, and smaller the larger the initial energy difference.



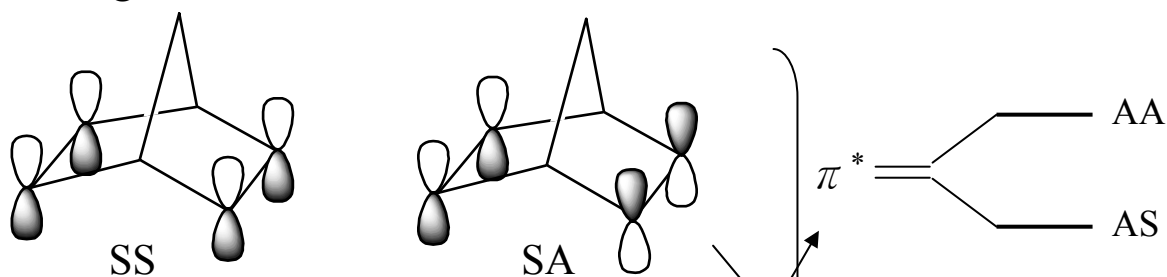
useful interaction usually involves one filled orbital and one empty orbital, such as a HOMO of one system and the LUMO of the other system.



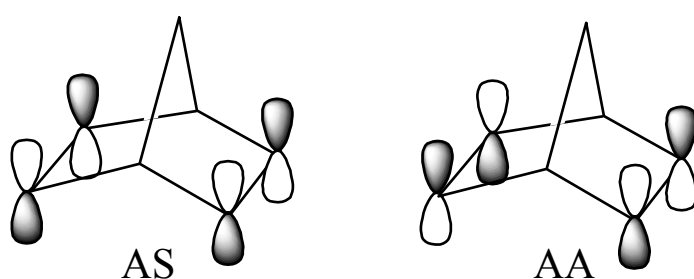
# Norbornadiene

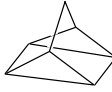


the mixing of  $\pi$



the mixing of  $\pi^*$

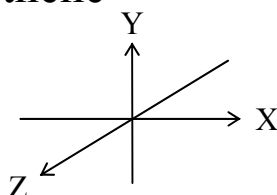
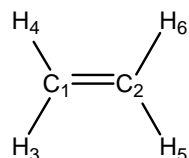


- Consequences :
1. the ionization potential of norbornadiene should be smaller than the model compound norbornene.
  2.  $\pi$ ,  $\pi^*$  transition (SA $\rightarrow$ AS) should be red-shifted, but it is also a forbidden transition.
  3. The  $\pi$ ,  $\pi^*$  excitation promote an  $e^-$  from an orbital which is 2-6 and 3-5 anti-bonding to one which is bonding in the same region.  
( $\therefore$  photochemical closure to  is promoted.)
  4. removing one  $e^-$  (from SA) or adding one  $e^-$  (to AS) promote the bond formation between C<sub>2</sub>-C<sub>6</sub> and C<sub>3</sub>-C<sub>5</sub>.

## Extended Hückel Theory

Take into account of all atomic orbitals 2s, 2p

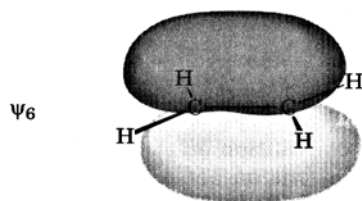
e.g. the basis set for ethene



$$2s_{C1}, 2s_{C2}, 1s_{H3}, 1s_{H4}, 1s_{H5}, 1s_{H6},$$

$$2p_{xC1}, 2p_{xC2}, 2p_{yC1}, 2p_{yC2},$$

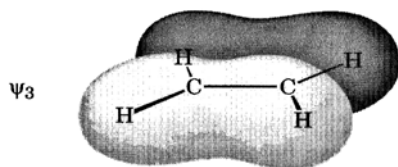
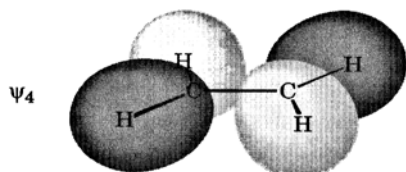
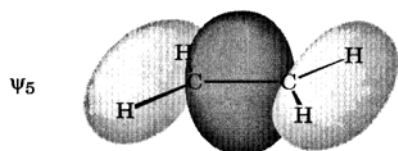
$$2p_{zC1}, 2p_{zC2}$$



$$\psi_6 = +0.0 2s_{C1} + 0.0 2p_{xC1} - 0.612 2p_{yC1} + 0.0 2p_{zC1}$$

$$+ 0.0 2s_{C2} + 0.0 2p_{xC2} - 0.612 2p_{yC2} + 0.0 2p_{zC2}$$

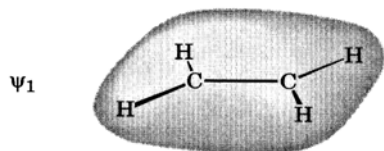
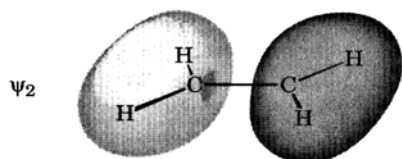
$$+ 0.0 1s_{H3} + 0.0 1s_{H4} + 0.0 1s_{H5} + 0.0 1s_{H6}$$



$$\psi_3 = +0.0 2s_{C1} + 0.0 2p_{xC1} + 0.0 2p_{yC1} - 0.355 2p_{zC1}$$

$$+ 0.0 2s_{C2} + 0.0 2p_{xC2} - 0.0 2p_{yC2} - 0.355 2p_{zC2}$$

$$+ 0.267 1s_{H3} - 0.267 1s_{H4} + 0.267 1s_{H5} - 0.267 1s_{H6}$$



$$\psi_1 = -0.419 2s_{C1} + 0.042 2p_{xC1} + 0.0 2p_{yC1} + 0.0 2p_{zC1}$$

$$- 0.419 2s_{C2} - 0.042 2p_{xC2} + 0.0 2p_{yC2} + 0.0 2p_{zC2}$$

$$- 0.153 1s_{H3} - 0.153 1s_{H4} - 0.153 1s_{H5} - 0.153 1s_{H6}$$

All MO's must be symmetric or anti-symmetric to the symmetry element of the molecule.

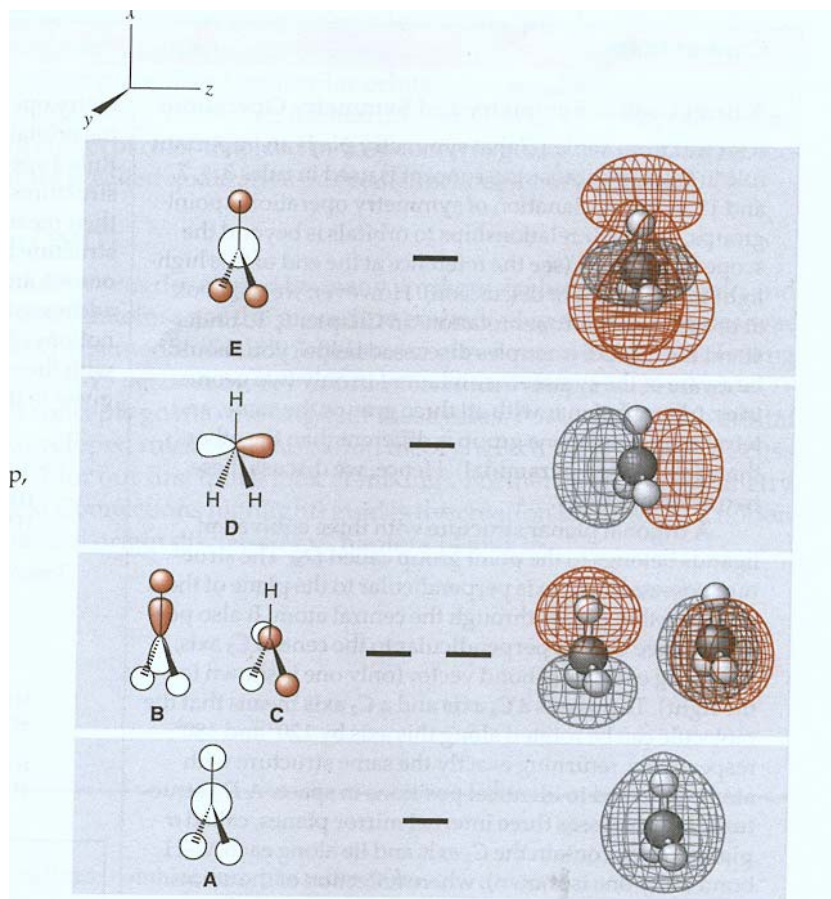
# Qualitative Molecular Orbital Theory

Table 1.7  
The Rules of QMOT\*

1. Consider valence orbitals only.
2. Form completely delocalized MOs as linear combinations of  $s$  and  $p$  AOs.
3. MOs must be either symmetric or antisymmetric with respect to the symmetry operations of the molecule.
4. Compose MOs for structures of high symmetry and then produce orbitals for related but less symmetric structures by systematic distortions of the orbitals for higher symmetry.
5. Molecules with similar molecular structures, such as  $\text{CH}_3$  and  $\text{NH}_3$ , have qualitatively similar MOs, the major difference being the number of valence electrons that occupy the common MO system.
6. The total energy is the sum of the molecular orbital energies of individual valence electrons.
7. If the two highest energy MOs of a given symmetry derive primarily from different kinds of AOs, then mix the two MOs to form hybrid orbitals.
8. When two orbitals interact, the lower energy orbital is stabilized and the higher energy orbital is destabilized. The out-of-phase or antibonding interaction between the two starting orbitals always raises the energy more than the corresponding in-phase or bonding interaction lowers the energy.
9. When two orbitals interact, the lower energy orbital mixes into itself the higher energy one in a bonding way, while the higher energy orbital mixes into itself the lower energy one in an antibonding way.
10. The smaller the initial energy gap between two interacting orbitals, the stronger the mixing interaction.
11. The larger the overlap between interacting orbitals, the larger the interaction.
12. The more electronegative elements have lower energy AOs.
13. A change in the geometry of a molecule will produce a large change in the energy of a particular MO if the geometry change results in changes in AO overlap that are large.
14. The AO coefficients are large in high energy MOs with many nodes or complicated nodal surfaces.
15. Energies of orbitals of the same symmetry classification cannot cross each other. Instead, such orbitals mix and diverge.

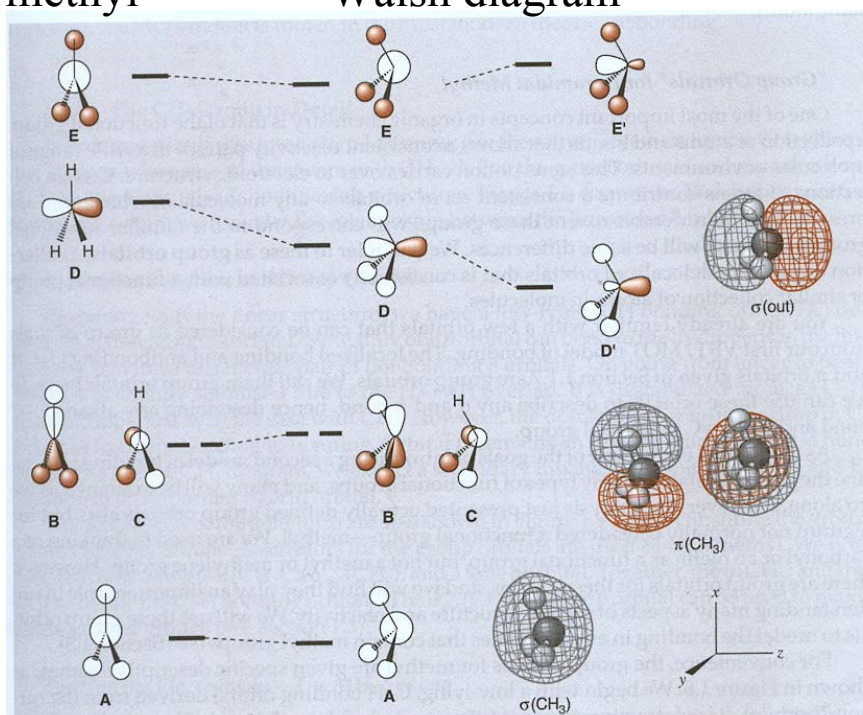
\*Adapted, with modifications, from Gimarc, B. M. (1979). *Molecular Structure and Bonding: The Qualitative Molecular Orbital Approach*, Academic Press, New York.

# Group orbitals from qualitative molecular orbital theory(QMOT) planar methyl

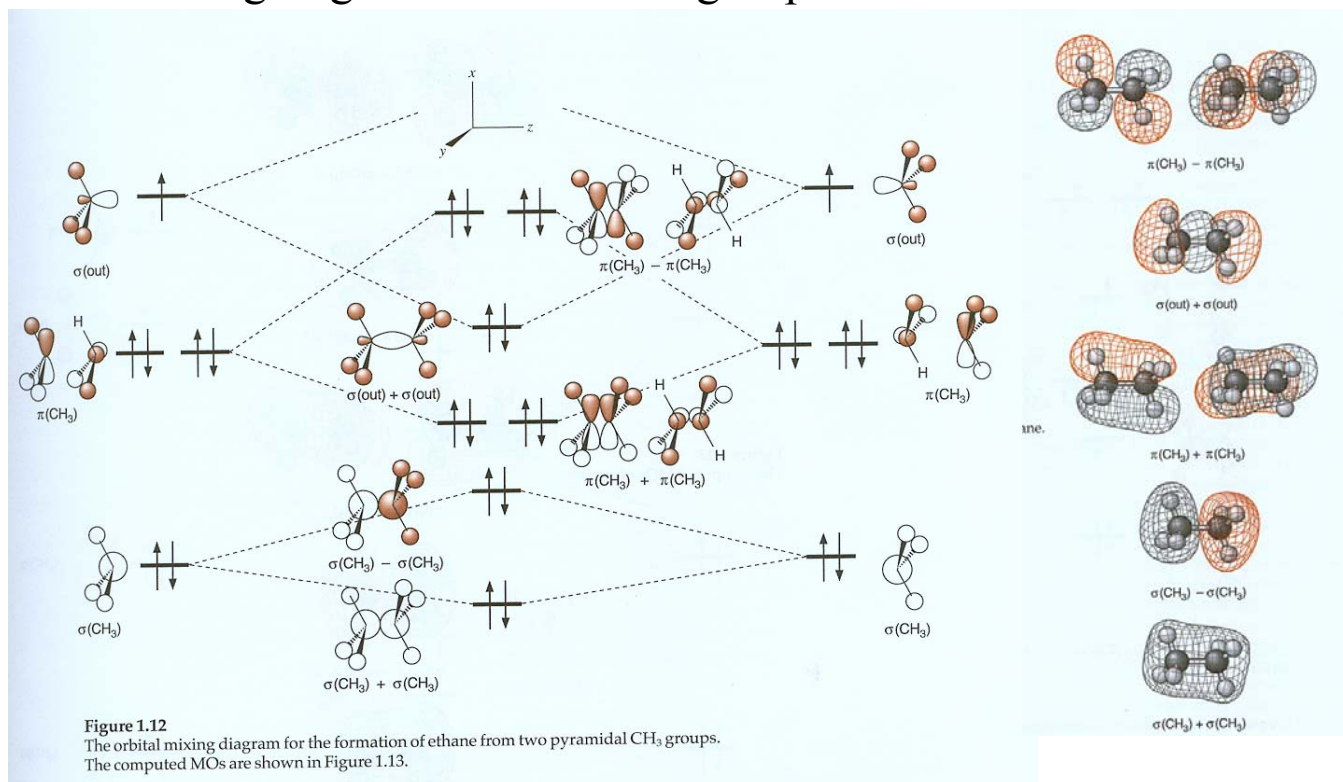


pyramidal methyl

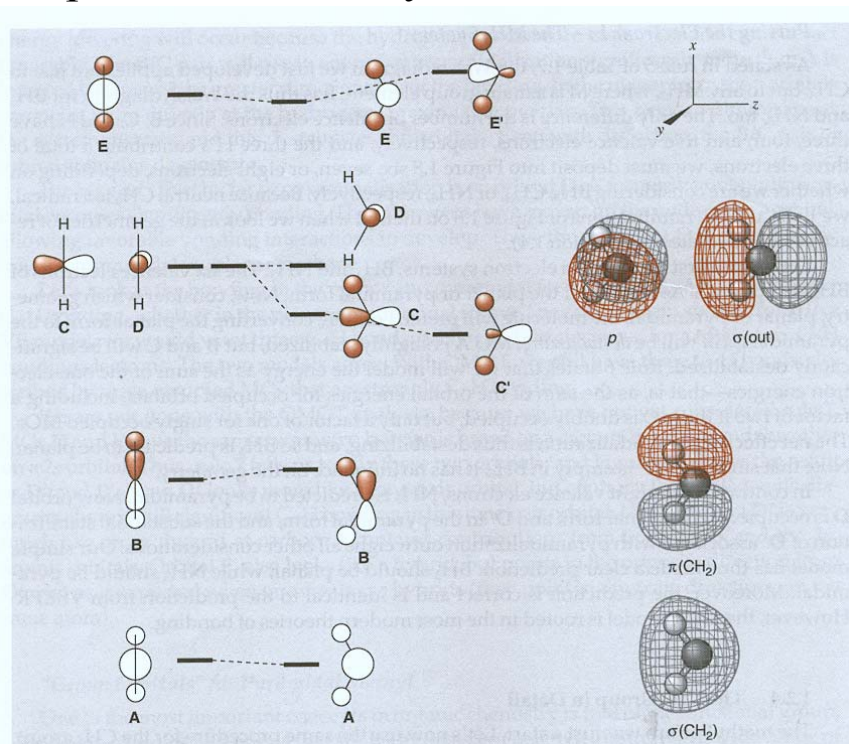
Walsh diagram



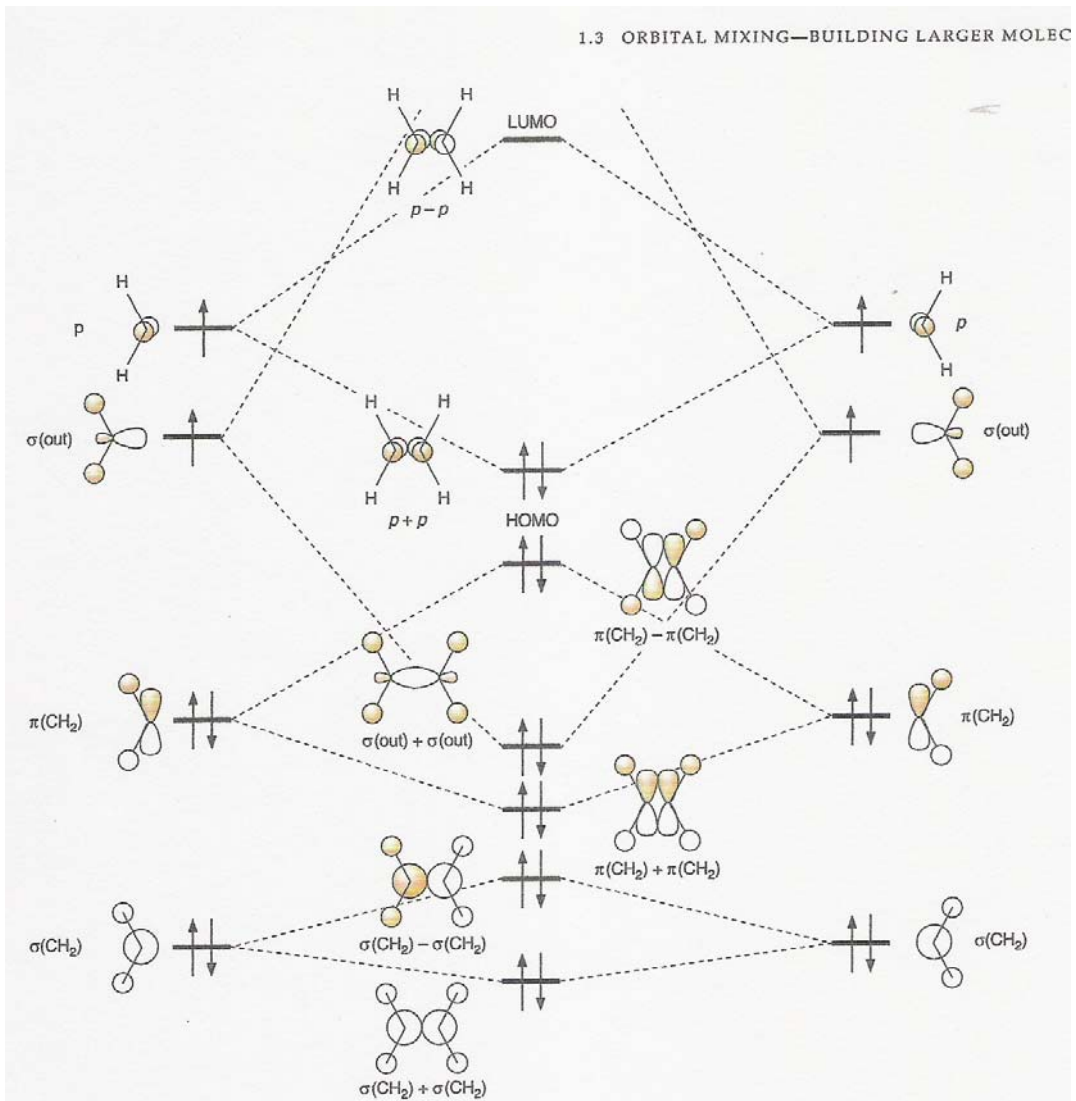
## Building larger molecule from group orbitals



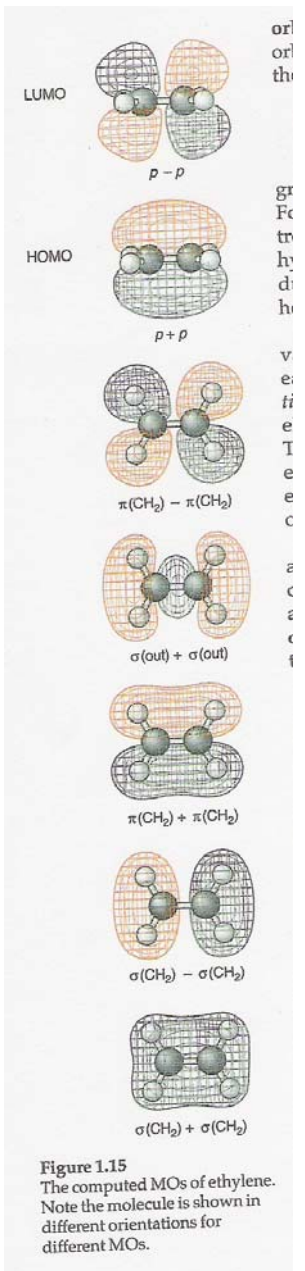
## The group orbital for methylene



# Formation of ethylene by mixing of two CH<sub>2</sub> group orbitals



**Figure 1.14**  
Orbital mixing diagram for the formation of ethylene by mixing two CH<sub>2</sub> groups. The computed MOs are shown in Figure 1.15.



## The effect of heteroatoms

Similar molecules have similar MO diagrams, with altered orbital energies.

