Computational Material Science
Part I

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Qualitative Molecular Orbital Theory (QMOT)

How to get the energy of the system?

Shrödinger equation: $$\boldsymbol{H}\psi = \boldsymbol{E}\psi$$

$$\int \psi H \psi d\tau = \int \psi E \psi d\tau$$

⇒ $$E = \frac{\int \psi H \psi d\tau}{\int \psi \psi d\tau}$$

H: Hamiltonian operator ψ: wavefunction E: system energy

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

- What is in the Hamiltonian?

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}$$

Operator for kinetic energy of electron

For kinetic energy of nucleus

For attraction of the electrons to the nuclei

For the interelectronic repulsions

For the internuclear repulsions

Under the ***Born-Oppenheimer approximation*** (electrons respond to the motion of nucleus instantaneously, so assume fixed nuclear geometry when electronic energy is evaluated), this term is zero!

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

- What is the electronic wave function of a system?

In the so-called molecular orbital theory

ψ : linear combination of atomic orbitals

$$\psi_1 = c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 + \cdots c_{1N}\phi_N$$

$$\psi_2 = c_{21}\phi_1 + c_{22}\phi_2 + c_{23}\phi_3 + \cdots c_{2N}\phi_N$$

$$\vdots$$

$$\psi_N = c_{N1}\phi_1 + c_{N2}\phi_2 + c_{N3}\phi_3 + \cdots c_{NN}\phi_N$$

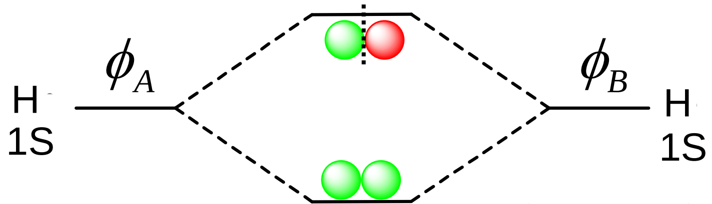
$$\boxed{\psi_i = \sum_{j=1}^{N} c_{ij}\phi_j}$$

ψ: molecular orbital

ϕ : atomic orbital wave function

Ex：H_2^+

$$\psi_- = N_-(\phi_A - \phi_B)$$



$$\psi_+ = N_+(\phi_A + \phi_B)$$

N：normalization const.

$$\int \psi_+^2 d\tau = 1 = N_+^2 \int (\phi_A + \phi_B)^2 d\tau$$

$$\Rightarrow \frac{1}{N_+^2} = \int \phi_A^2 d\tau + 2\boxed{\int \phi_A \phi_B d\tau} + \int \phi_B^2 d\tau = 2 + 2S_{AB}$$

Overlap integral S_{AB}

$$\therefore N_+ = \frac{1}{\sqrt{2+2S_{AB}}}$$

$$\int \psi_-^2 d\tau = 1$$

$$\Rightarrow N_- = \frac{1}{\sqrt{2-2S_{AB}}}$$

if $\psi = \psi_+$

$$E_+ = \frac{\int \psi^+ H \psi^+ d\tau}{\int \psi^+ \psi^+ d\tau} = N^2 \int (\phi_A + \phi_B) H (\phi_A + \phi_B) d\tau$$

$$= \frac{1}{2+2S}\left[\overset{\boldsymbol{H_{AA}}}{\underline{\int \phi_A H \phi_A d\tau}} + \overset{\boldsymbol{H_{AB}}}{\underline{\int \phi_A H \phi_B d\tau}} + \overset{\boldsymbol{H_{BA}}}{\underline{\int \phi_B H \phi_A d\tau}} + \overset{\boldsymbol{H_{BB}}}{\underline{\int \phi_B H \phi_B d\tau}}\right]$$

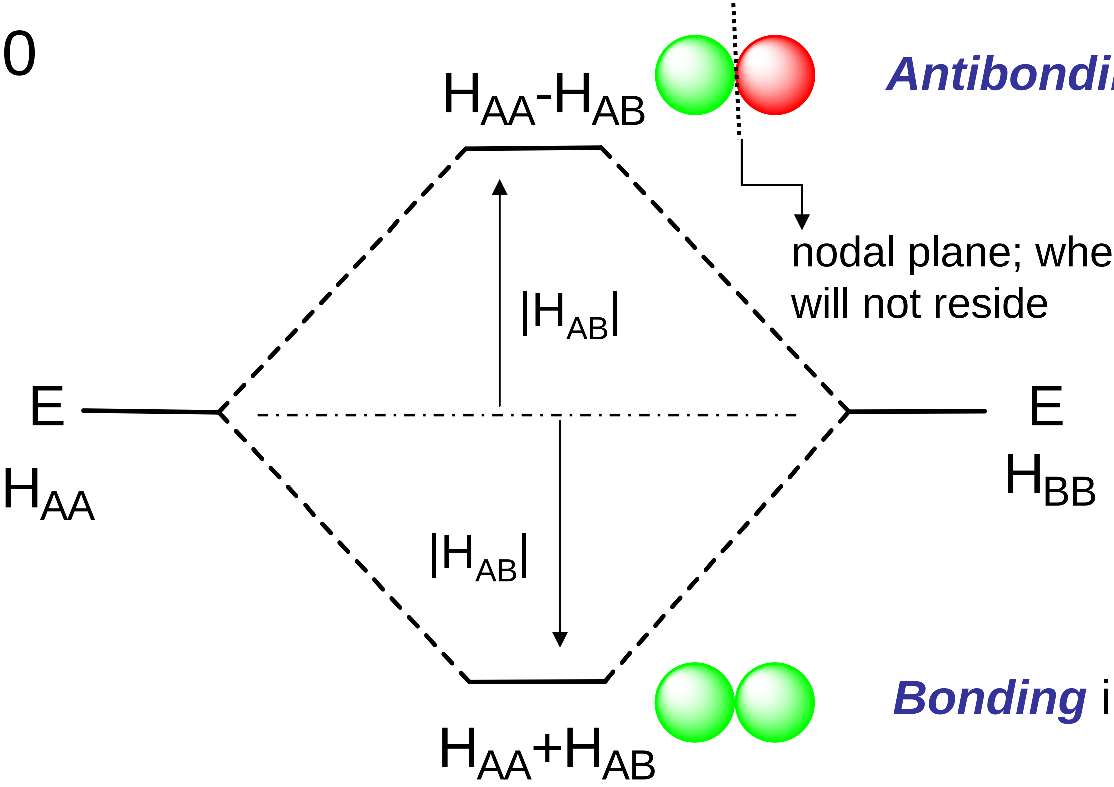
let $H_{AB} = \int \phi_A H \phi_B d\tau$

$$H_{AB} = H_{BA}$$

$$\therefore\ E_+ = \frac{2H_{AA} + 2H_{AB}}{2+2S} = \frac{\overset{<0}{H_{AA}} + \overset{<0}{H_{AB}}}{1+\underset{>0}{S}} \qquad E_- = \frac{2H_{AA} - 2H_{AB}}{2-2S} = \frac{H_{AA} - H_{AB}}{1-S}$$

$$E_{+} = \frac{2H_{AA} + 2H_{AB}}{2 + 2S} = \frac{H_{AA} + H_{AB}}{1 + S} \qquad E_{-} = \frac{2H_{AA} - 2H_{AB}}{2 - 2S} = \frac{H_{AA} - H_{AB}}{1 - S}$$

If S=0



H_{AA}-H_{AB}

Antibonding interaction

nodal plane; where electrons will not reside

$|H_{AB}|$

E

H_{AA}

E

H_{BB}

$|H_{AB}|$

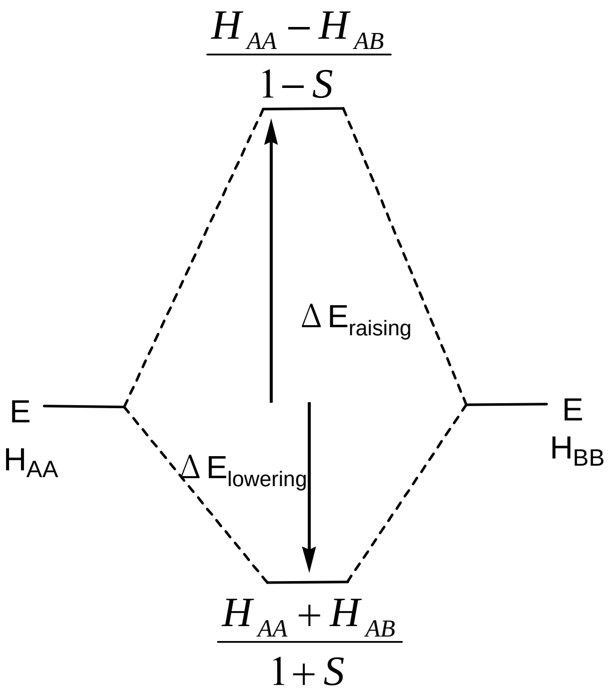
Bonding interaction

H_{AA}+H_{AB}

$$\Delta E_{\text{raising}} = \Delta E_{\text{lowering}}$$

In reality $S \neq 0$

☆ For two degenerate orbitals



$\Delta E_{raising} > 0$, $1-S > 0$
$\Rightarrow SH_{AA}-H_{AB} > 0$

$$\Delta E_{\text{raising}} = \frac{H_{AA}-H_{AB}}{1-S} - H_{AA}$$

$$= \frac{H_{AA}-H_{AB}-H_{AA}+SH_{AA}}{1-S} = \frac{SH_{AA}-H_{AB}}{1-S}$$

$$\Delta E_{lowering} = H_{AA} - \frac{H_{AA}+H_{AB}}{1+S}$$

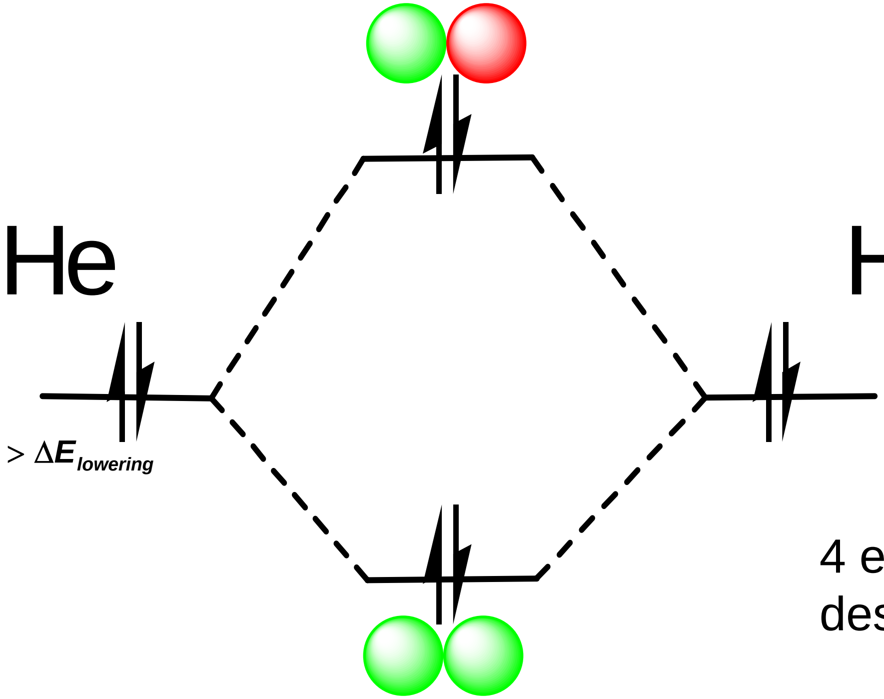
$$= \frac{H_{AA}+SH_{AA}-H_{AA}-H_{AB}}{1+S} = \frac{SH_{AA}-H_{AB}}{1+S}$$

$$\Delta E_{\text{raising}} - \Delta E_{lowering} = \frac{SH_{AA}-H_{AB}}{1-S} - \frac{SH_{AA}-H_{AB}}{1+S}$$

$$= \left(SH_{AA}-H_{AB}\right)\left(\frac{1}{1-S} - \frac{1}{1+S}\right)$$

$$= \underbrace{\left(SH_{AA}-H_{AB}\right)}_{>0}\underbrace{\left(\frac{2S}{1-S^2}\right)}_{>0}$$

$$\therefore \Delta E_{raising} > \Delta E_{lowering}$$



$\because \Delta \boldsymbol{E}_{raising} > \Delta \boldsymbol{E}_{\boldsymbol{lowering}}$

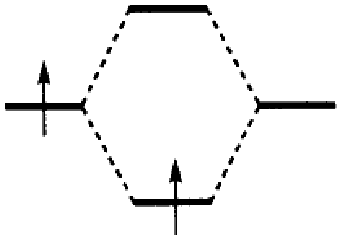
4 electron
destabilization

“close shell repulsion”

It is known that inert gas does not dimerize.

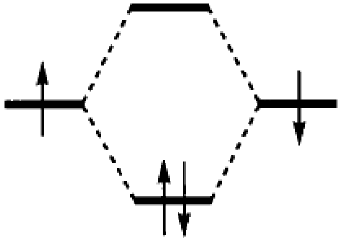
Consequence of filling electrons into ***bonding*** and ***antibonding*** orbitals:

H_2^+



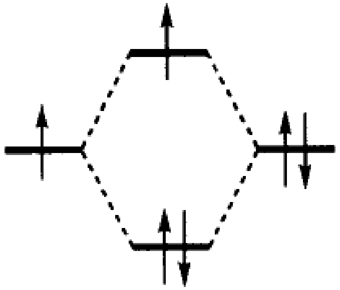
One-electron stabilization
R = 1.06 Å
Bond Energy = 61 kcal/mol

H_2



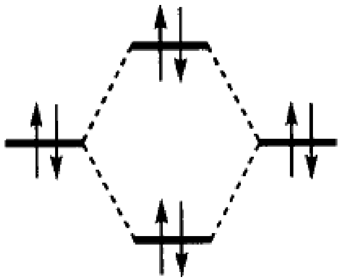
Two-electron stabilization
R = 0.74 Å
Bond Energy = 103 kcal/mol

He_2^+



Three-electron stabilization
R = 1.08 Å
Bond Energy ≈ 50 kcal/mol

He_2



Nonexistent

Repulsive four electron interaction

Notice the trends:

1. Electron in **bonding** orbital — bond length decreases; bond energy increases

2. Electron in **antibonding** orbital — bond length increases; bond energy decreases

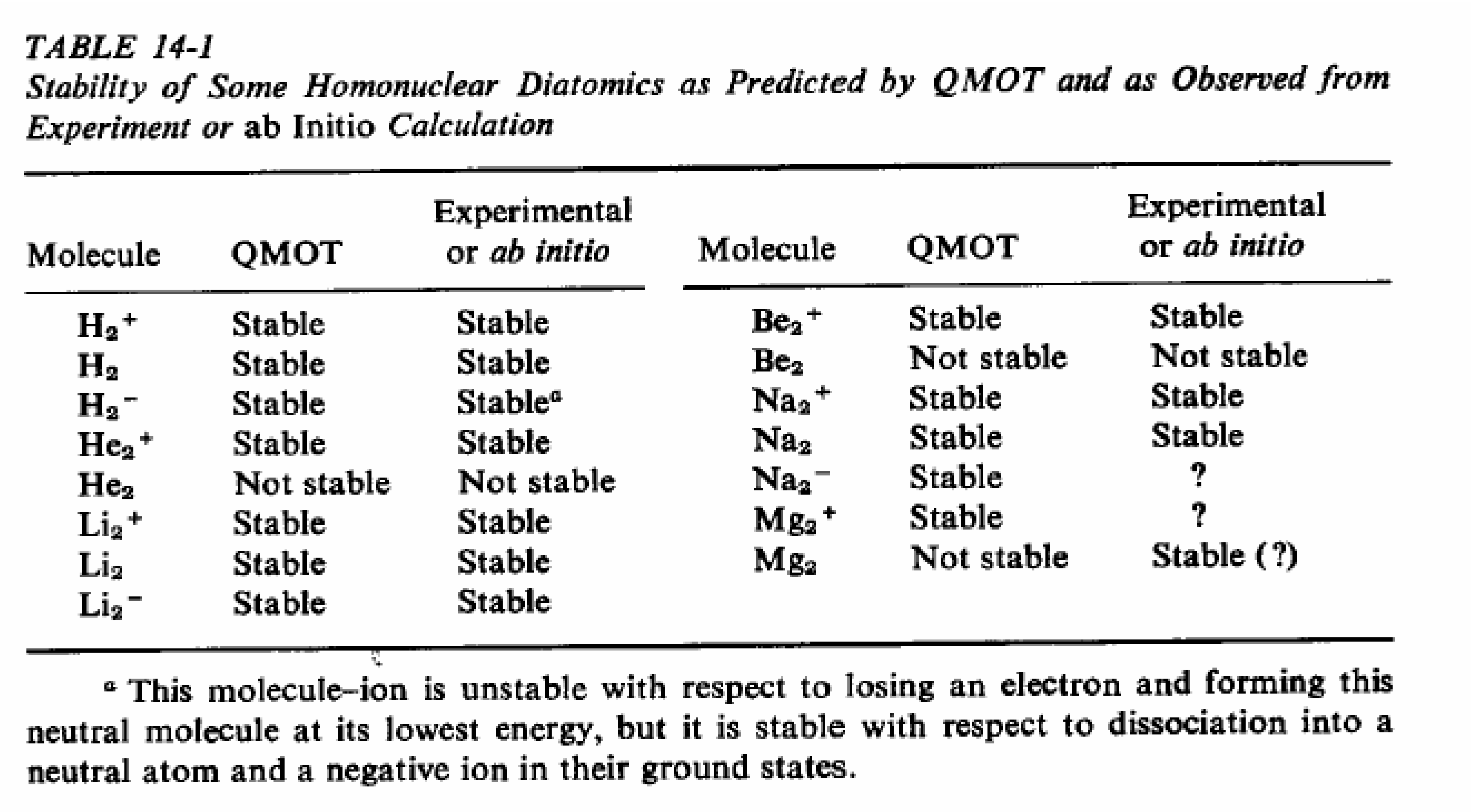


TABLE 14-1

Stability of Some Homonuclear Diatomics as Predicted by QMOT and as Observed from Experiment or ab Initio *Calculation*

Molecule	QMOT	Experimental or *ab initio*	Molecule	QMOT	Experimental or *ab initio*
H_2^+	Stable	Stable	Be_2^+	Stable	Stable
H_2	Stable	Stable	Be_2	Not stable	Not stable
H_2^-	Stable	Stable[a]	Na_2^+	Stable	Stable
He_2^+	Stable	Stable	Na_2	Stable	Stable
He_2	Not stable	Not stable	Na_2^-	Stable	?
Li_2^+	Stable	Stable	Mg_2^+	Stable	?
Li_2	Stable	Stable	Mg_2	Not stable	Stable (?)
Li_2^-	Stable	Stable			

[a] This molecule–ion is unstable with respect to losing an electron and forming this neutral molecule at its lowest energy, but it is stable with respect to dissociation into a neutral atom and a negative ion in their ground states.

For Na and Mg, 3s and 3p orbitals are very close in energy, unrealistic to treat as pure 3s cases.

Notice energies of bonding and antibonding orbitals may crossover. Therefore, simple QMOT results with limited molecular orbital interactions may not be correct!

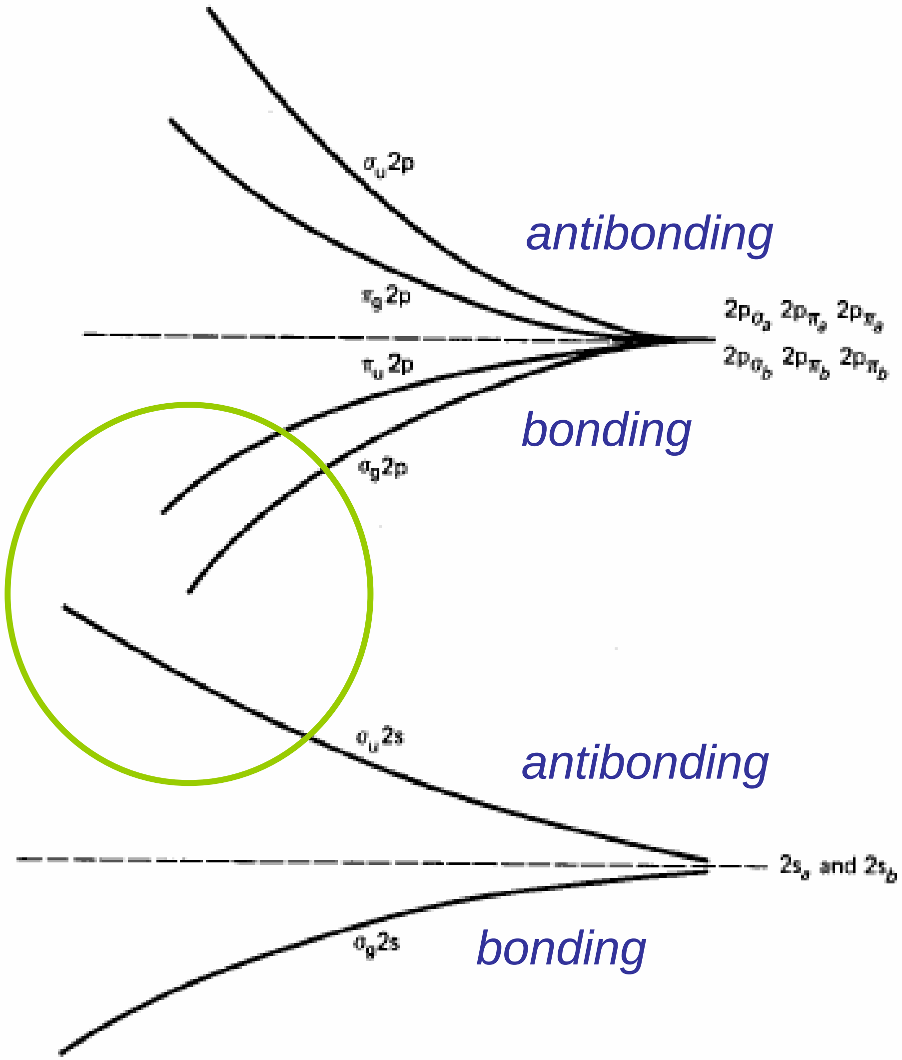
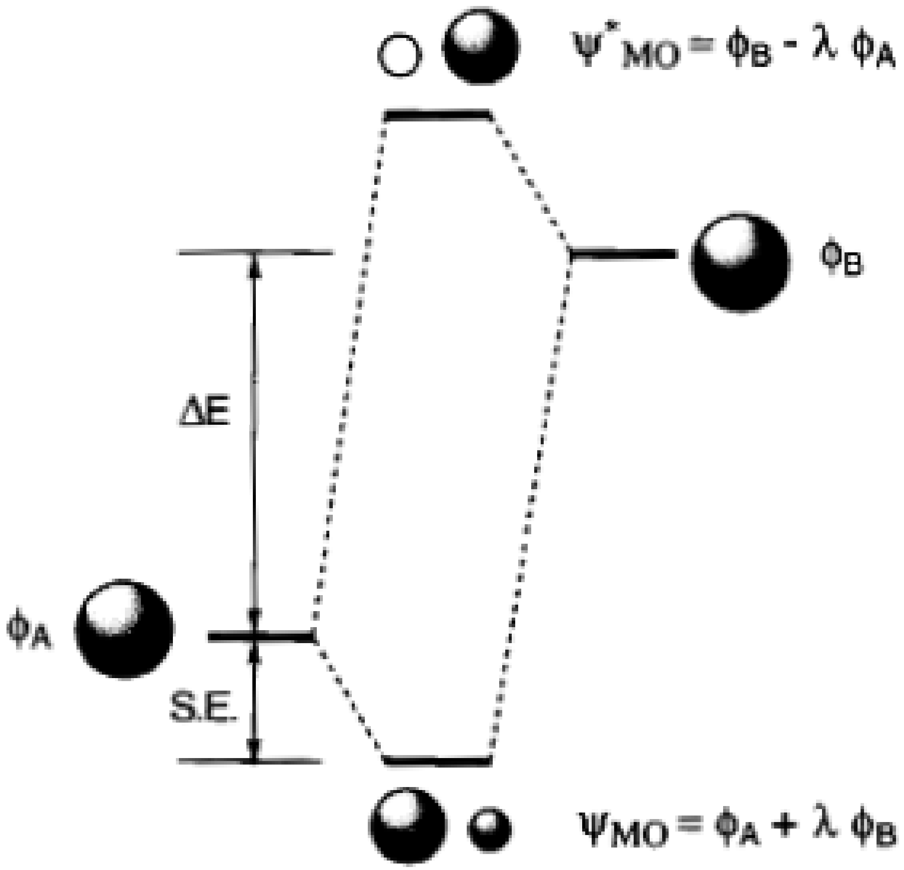


FIG. 14-5 Qualitative sketches of homonuclear diatomic MO energies as a function of *R* based on QMOT rules.

☆ For two nondegenerate orbitals

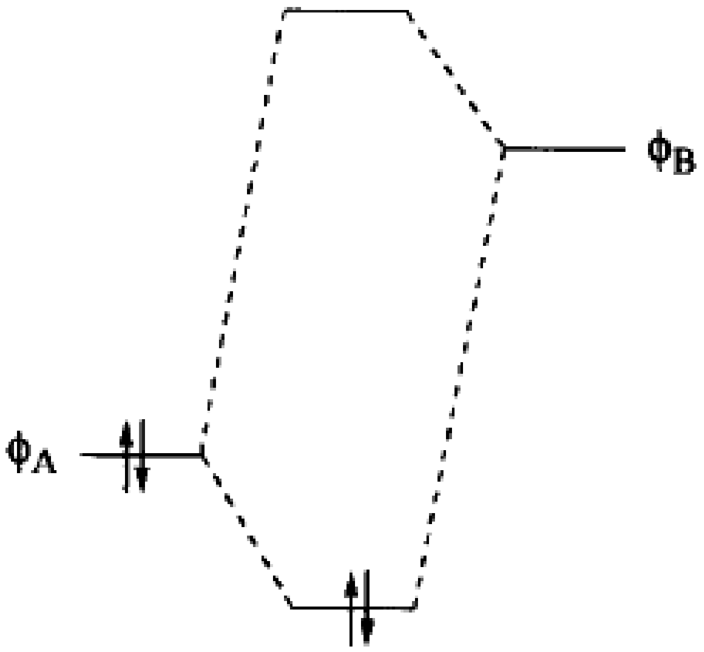


$$\lambda \propto \frac{S_{AB}}{\Delta E}$$

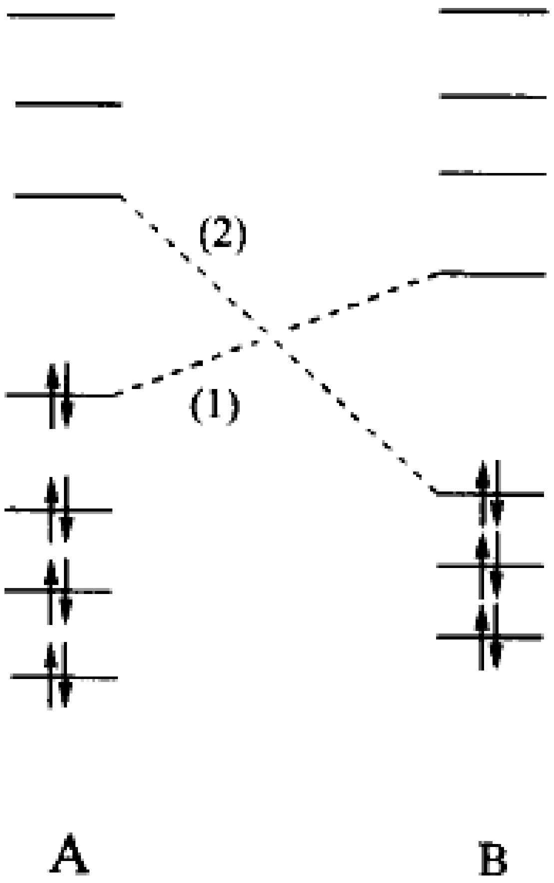
$$SE \propto \frac{S_{AB}^2}{\Delta E}$$

Rules in QMOT：

1) **occupied orbital repel occupied orbital**
2) **S↑, SE (Stabilization Energy)↑**
3) **closer in energy, SE↑**



2.2



LUMO
Lowest
Unoccupied

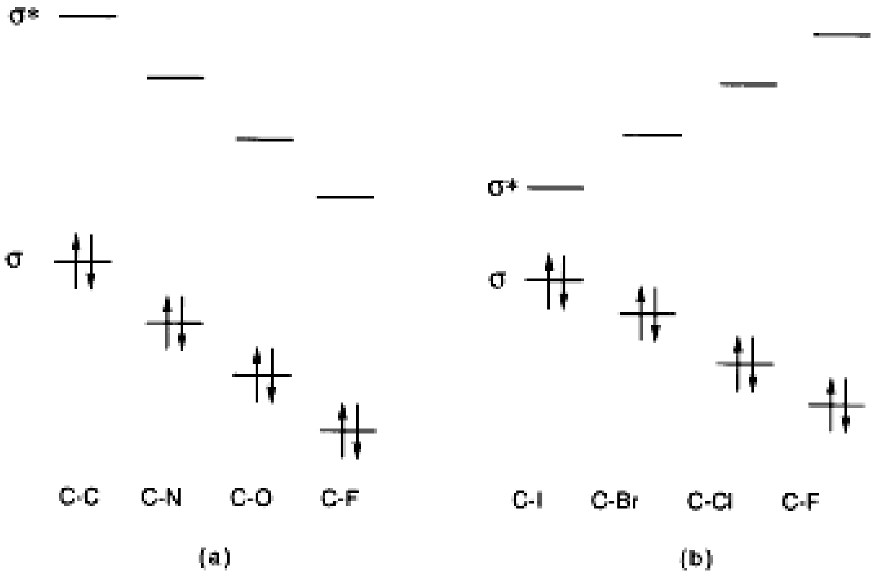
HOMO
Highest
Occupied

2.3

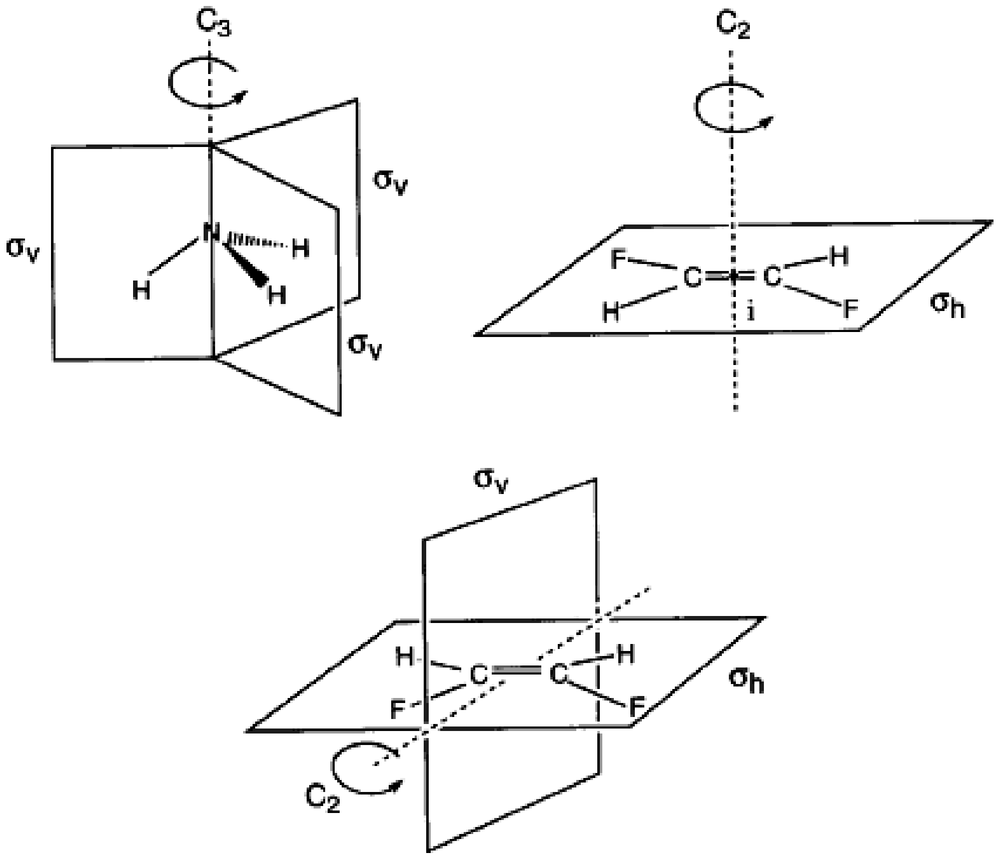
Occupied orbital interacts with unoccupied orbital => Lowering energy
HOMO–LUMO interaction important!

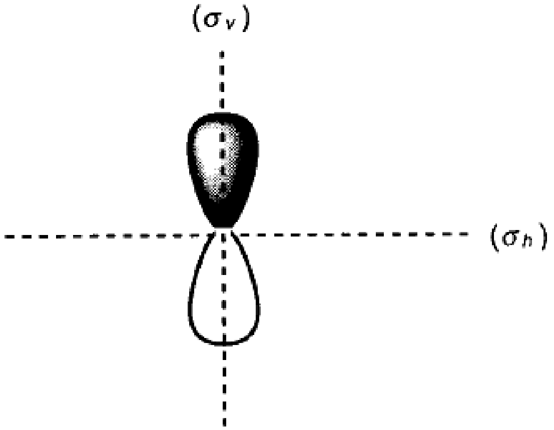
- **General rules for determining relative orbital energies**

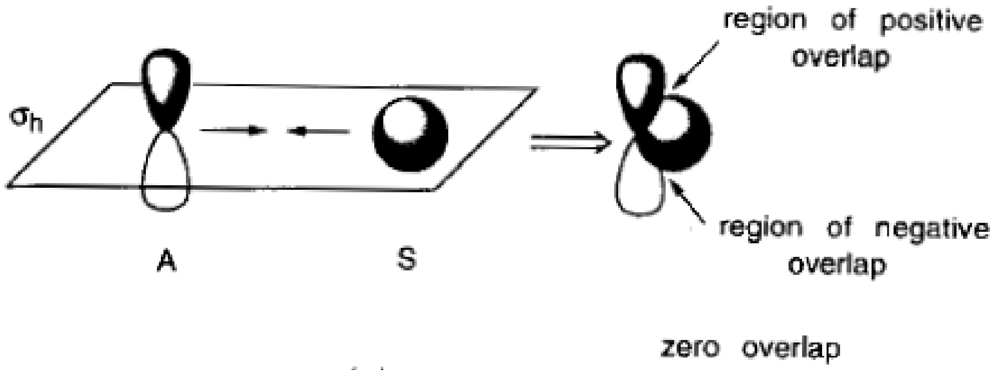
1. bonding < nonbonding < antibonding
2. σ orbitals < π orbitals < π^* orbitals < σ^* orbitals
3. AO energies decrease along a row of the periodic table. C 2p > N 2p > O 2p > F 2p =>
   $\sigma_{C-C} > \sigma_{C-N} > \sigma_{C-O} > \sigma_{C-F}$; $\sigma^*_{C-C} > \sigma^*_{C-N} > \sigma^*_{C-O} > \sigma^*_{C-F}$
4. $\sigma_{C-I} > \sigma_{C-Br} > \sigma_{C-Cl} > \sigma_{C-F}$; $\sigma^*_{C-F} > \sigma^*_{C-Cl} > \sigma^*_{C-Br} > \sigma^*_{C-I}$



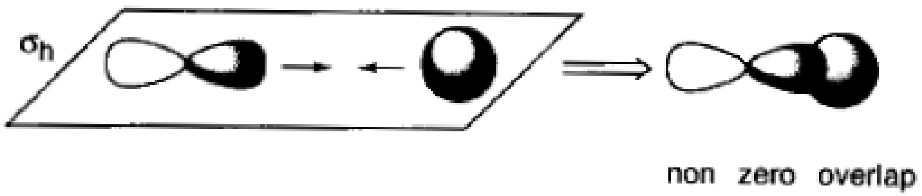
➢ Symmetry and orbital overlap





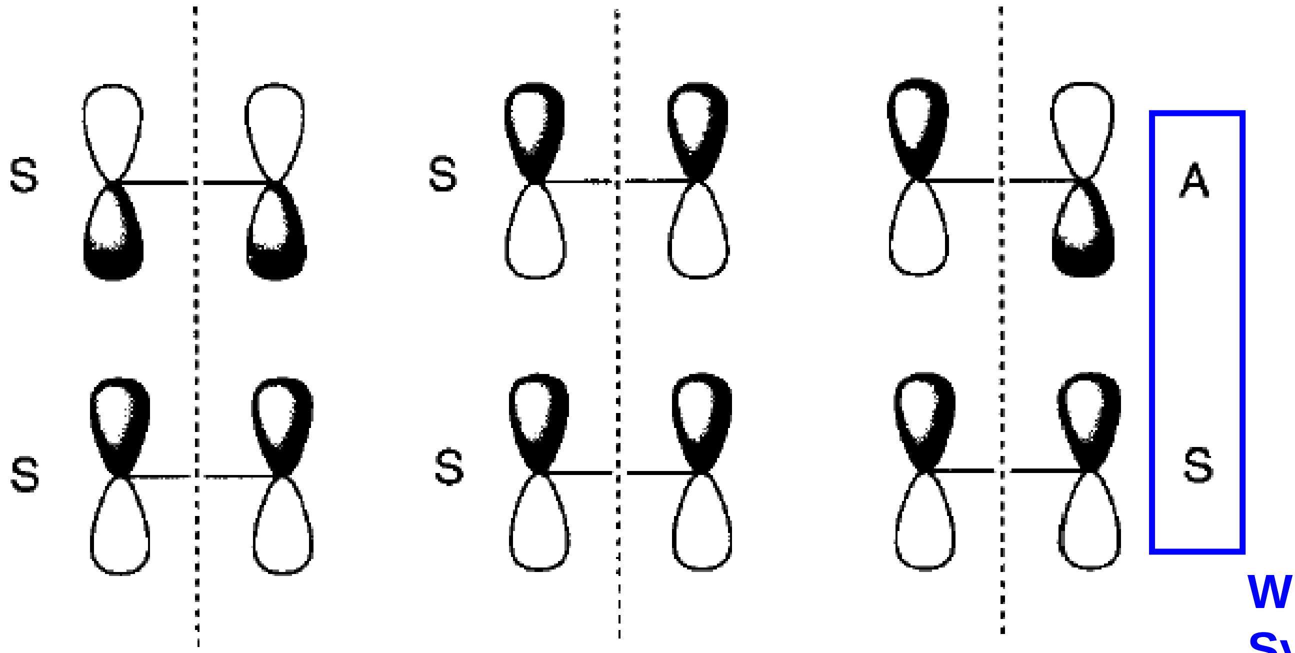


(a)



A: antisymmetric **S: symmetric**

Wrong symmetry will result in zero overlap!



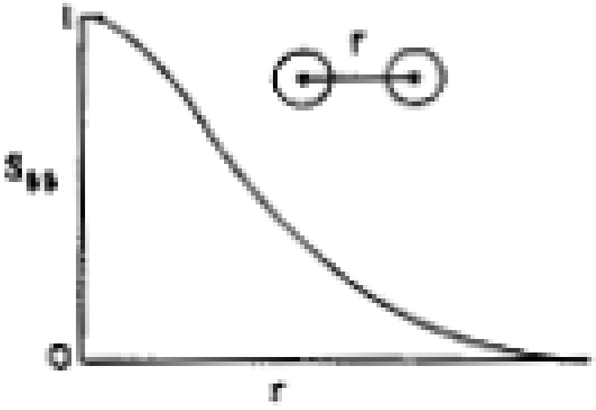
nonzero overlap
(a)

nonzero overlap
(b)

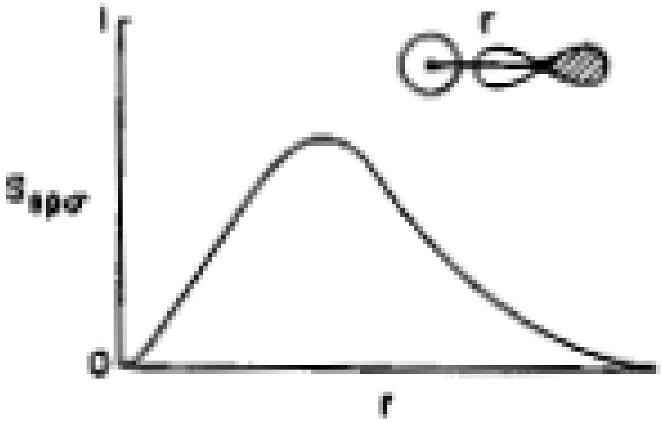
zero overlap
(c)

Wrong Symmetry!

- Overlap integral S *vs* r

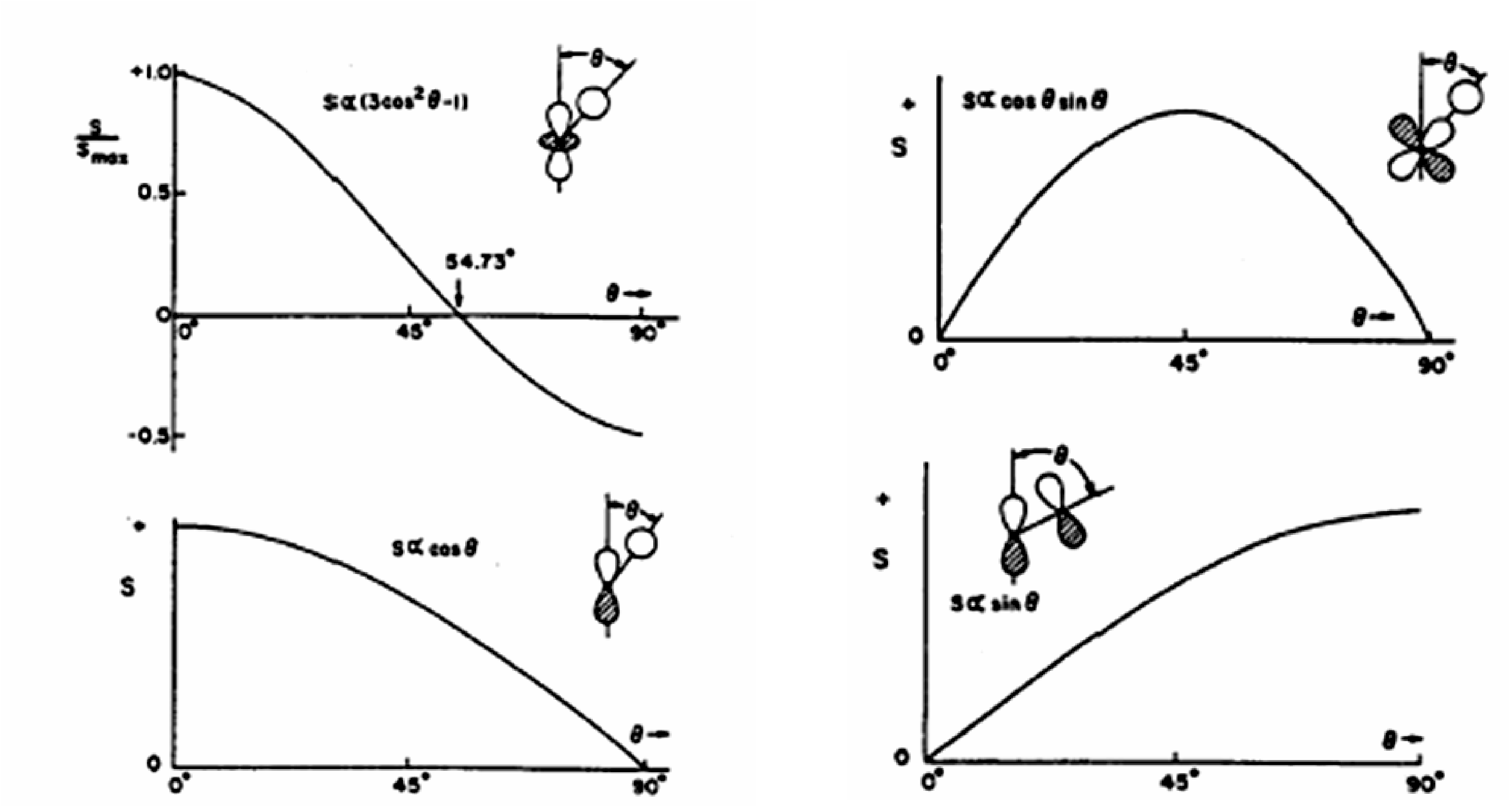


1.11

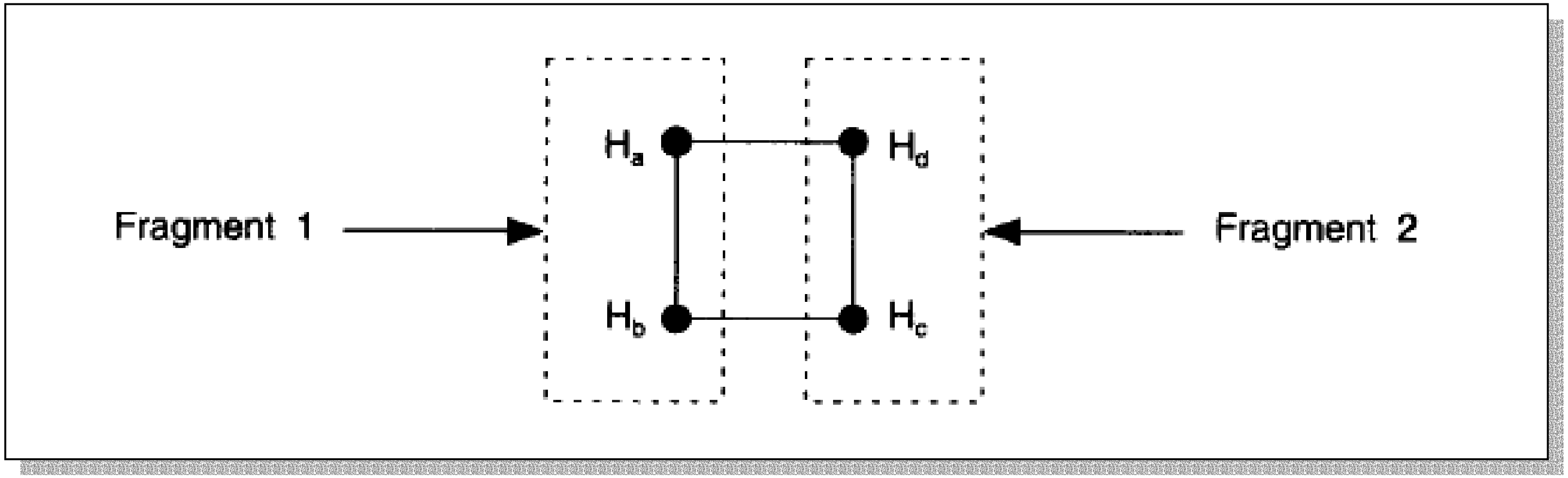


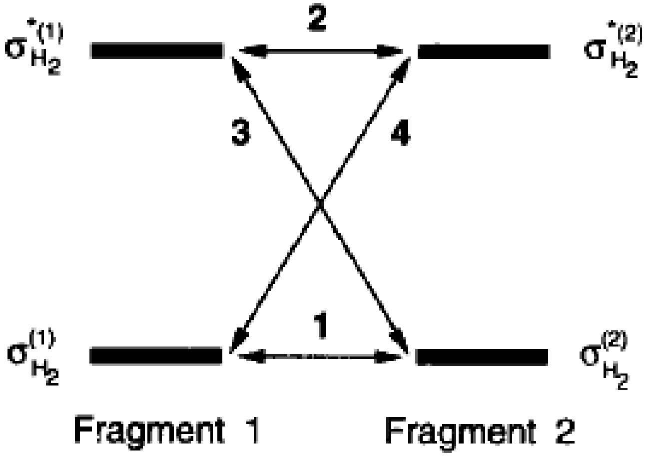
1.12

- Overlap integral *S* *vs* *angle*

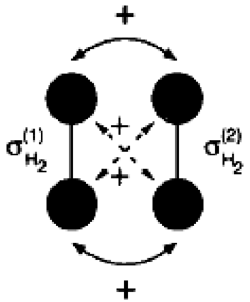


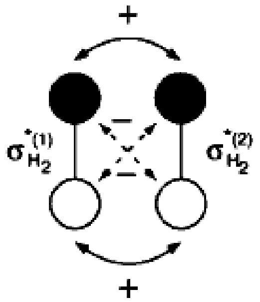
Ex: $H_{4\ (square)}$





Among interactions 1, 2, 3, and 4, which ones are valid?

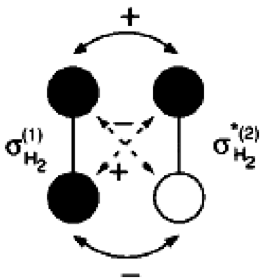


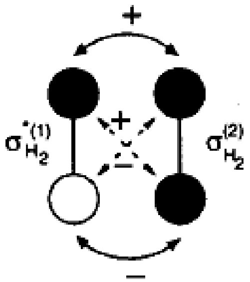


Interactions 1 and 2 $S \neq 0$ $S \neq 0$

4-3a **4-3b**

Will result in energy splitting!





Interactions 3 and 4 $S = 0$ $S = 0$

4-3c **4-3d**

No interaction!

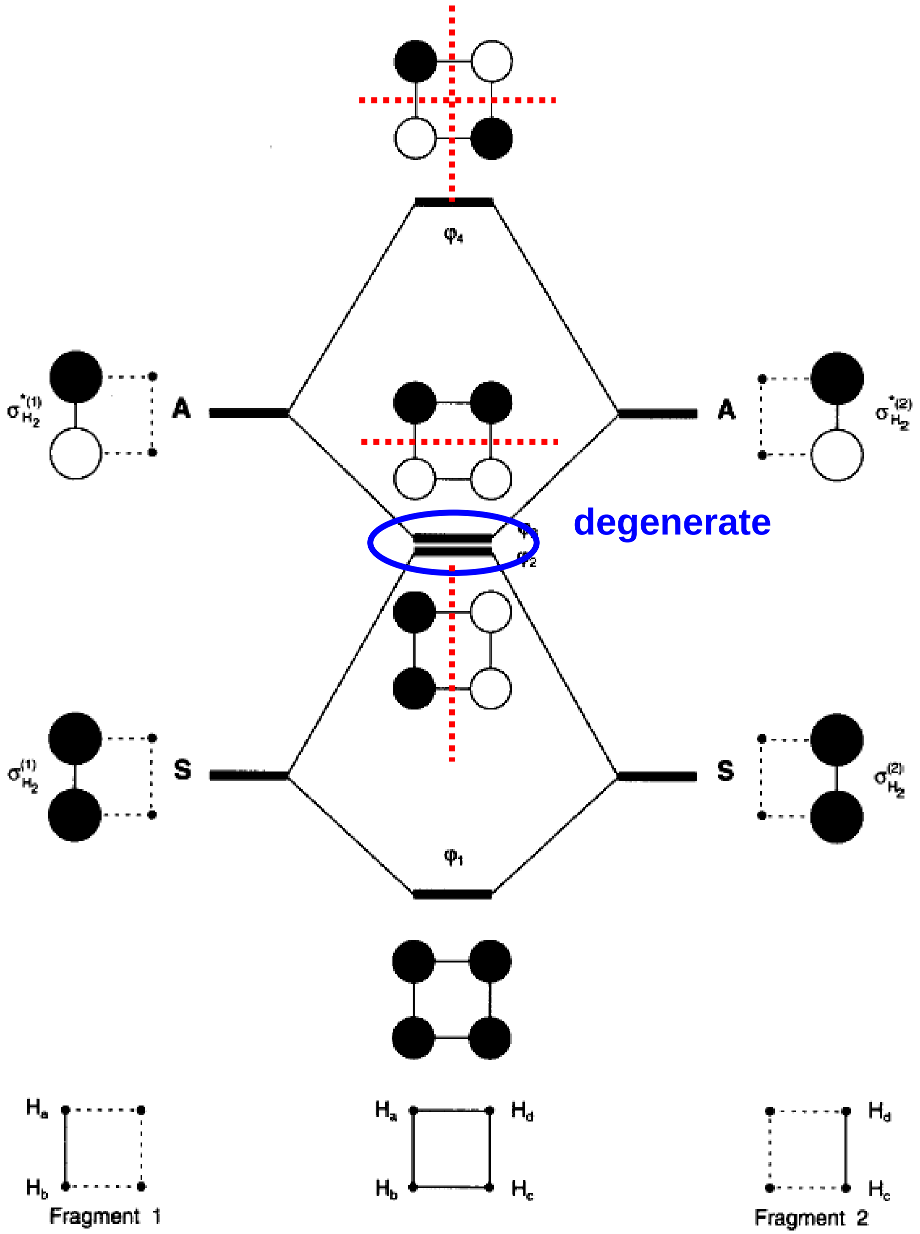


Figure 4.1. Construction of the MOs of square planar H_4.

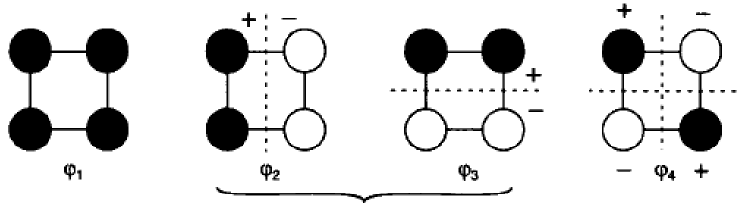
$$\phi_1 = \sigma_{H_2}(1) + \sigma_{H_2}(2)$$

$$\phi_2 = \sigma_{H_2}(1) - \sigma_{H_2}(2)$$

$$\phi_3 = \sigma^*_{H_2}(1) + \sigma^*_{H_2}(2)$$

$$\phi_4 = \sigma^*_{H_2}(1) - \sigma^*_{H_2}(2)$$

More nodal plane, higher in energy



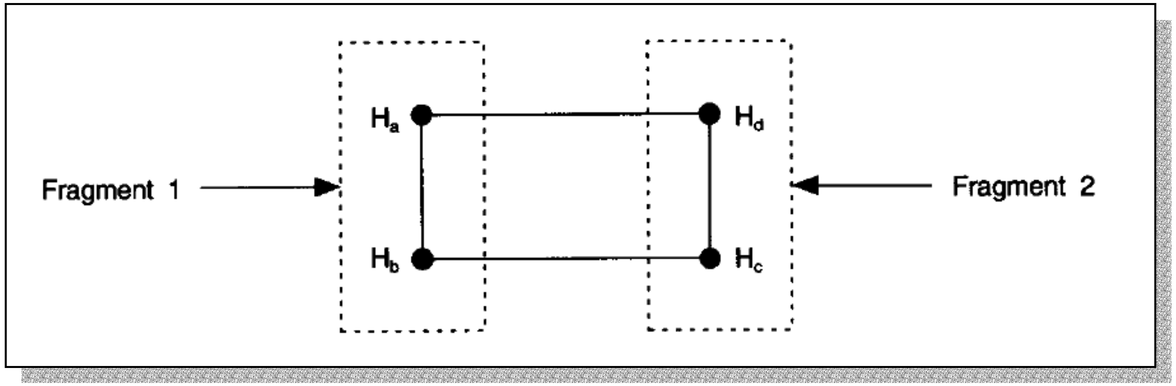
$$\phi_1 = N_1(1s_a + 1s_b + 1s_c + 1s_d)$$
$$\phi_2 = N_2(1s_a + 1s_b - 1s_c - 1s_d)$$
$$\phi_3 = N_3(1s_a - 1s_b - 1s_c + 1s_d)$$
$$\phi_4 = N_4(1s_a - 1s_b + 1s_c - 1s_d)$$

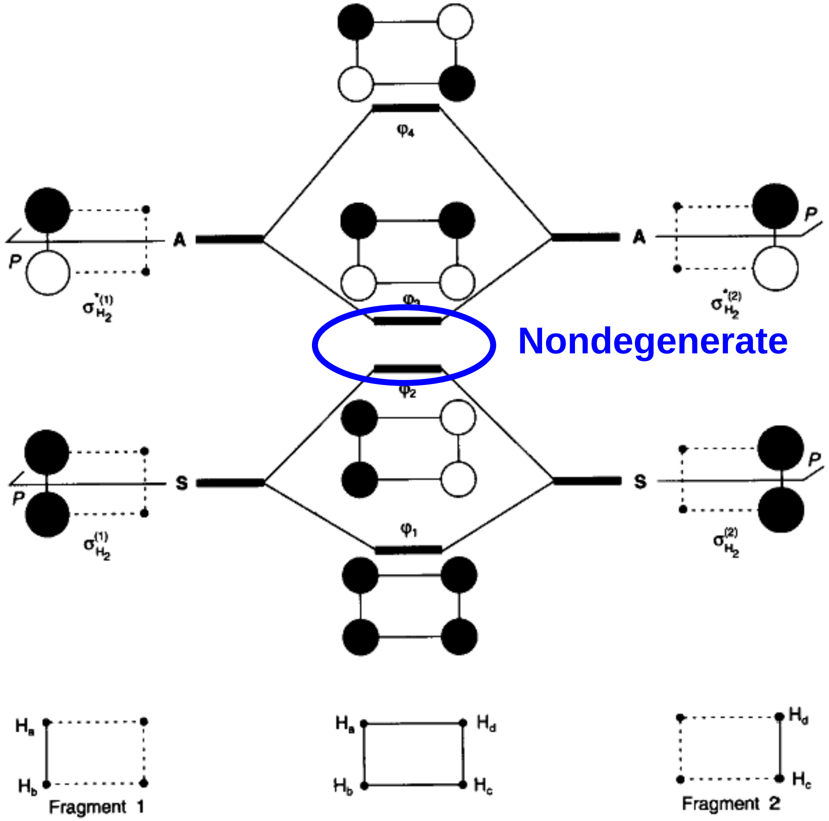
$$\langle 1s_a \mid 1s_b \rangle = \langle 1s_a \mid 1s_d \rangle = \langle 1s_b \mid 1s_c \rangle = \langle 1s_c \mid 1s_d \rangle = S$$
$$\langle 1s_a \mid 1s_c \rangle = \langle 1s_b \mid 1s_d \rangle = S'$$
$$\langle 1s_i \mid 1s_i \rangle = 1(i = \text{a, b, c, d})$$
$$\langle \phi_1 \mid \phi_1 \rangle = 1 = N_1^2(4 + 8S + 4S')$$

$$N_1 = \frac{1}{2(1 + 2S + S')^{1/2}} \qquad N_2 = N_3 = \frac{1}{2(1 - S')^{1/2}} \qquad N_4 = \frac{1}{2(1 - 2S + S')^{1/2}}$$

When the side of the square is 1 Å, $S = 0.469$, $S' = 0.263$
$N_1 = 0.337$, $N_2 = N_3 = 0.582$, $N_4 = 0.877$

Ex: H_4 (rectangular)

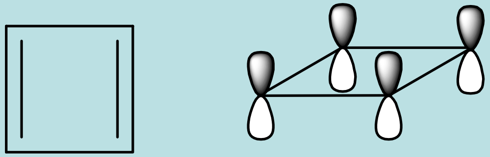




Nondegenerate

Figure 4.2. Construction of the MOs of rectangular H_4.

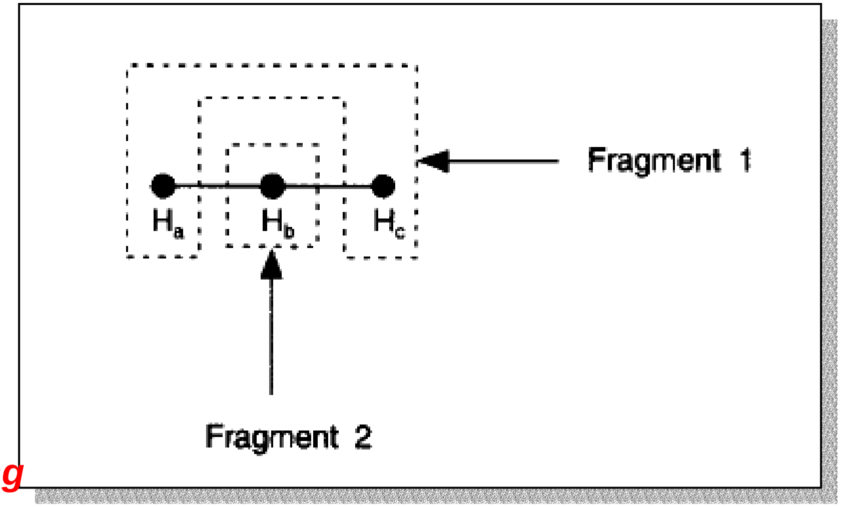
This explain why cyclobutadiene is a closed-shell molecule and is rectangular



cyclobutadiene

Jahn-Teller effect: geometry distort to destroy degeneracy and get closed-shell species with lower energy

Ex: H_3 (linear)



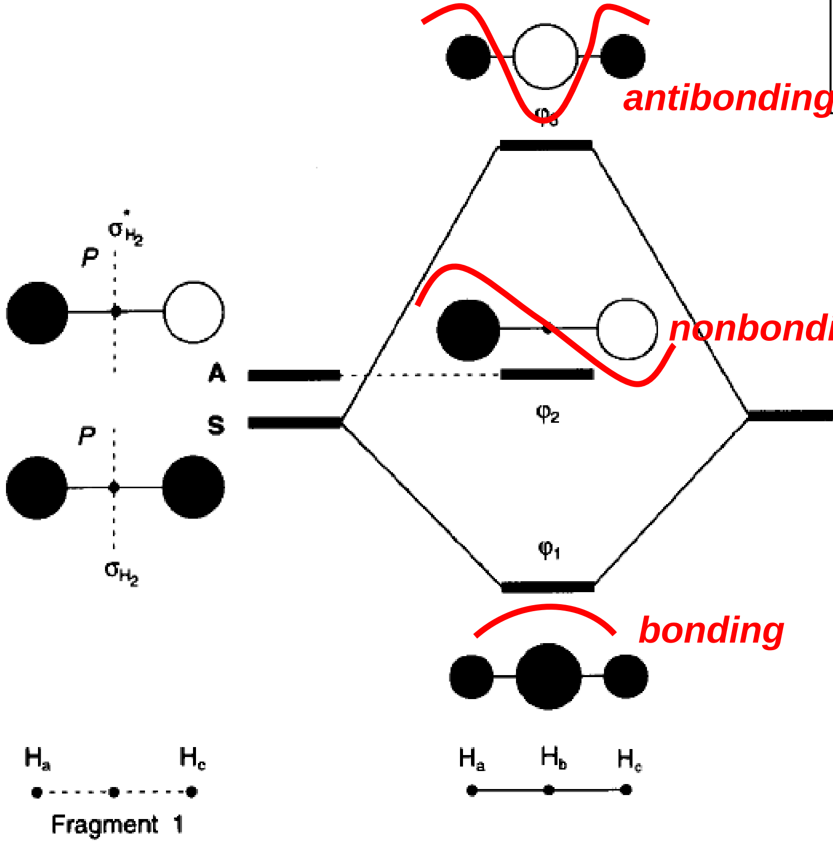
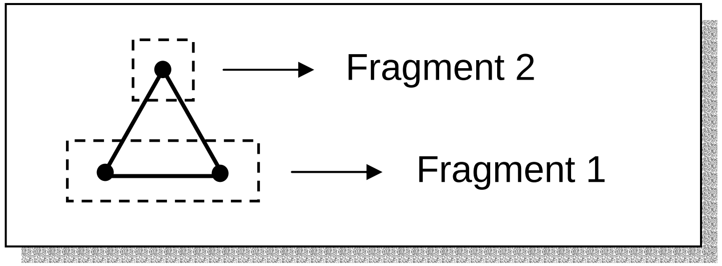


Figure 4.3. Construction of the MOs of linear H_3.

Notice the population Of H_b is large in φ_1 and φ_3?

Ex: H_3 (triangular)



Fragment 2

Fragment 1

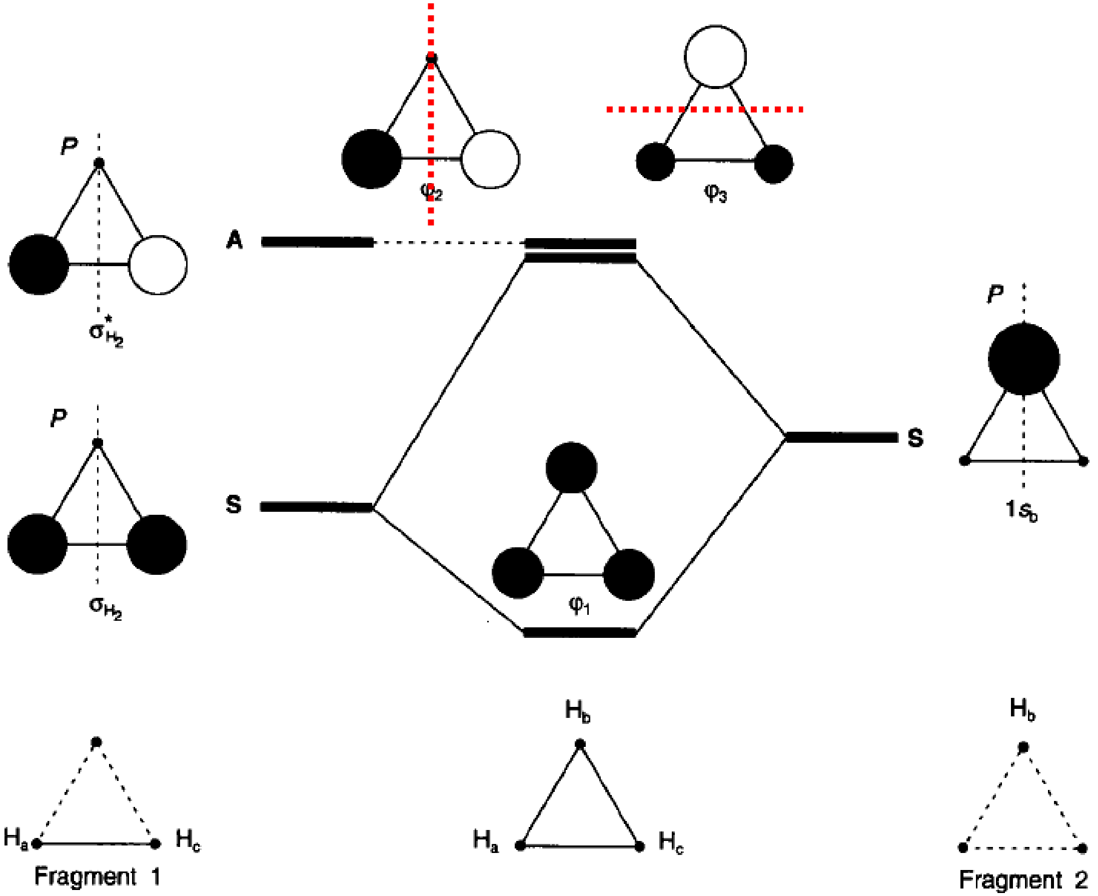


Figure 4.5. Construction of the MOs of triangular H_3.

➢ Geometry and orbital correlation diagram

Experimentally, H_3^+ is found to be triangular and H_3^- linear

- Orbital correlation diagram for bending H_3

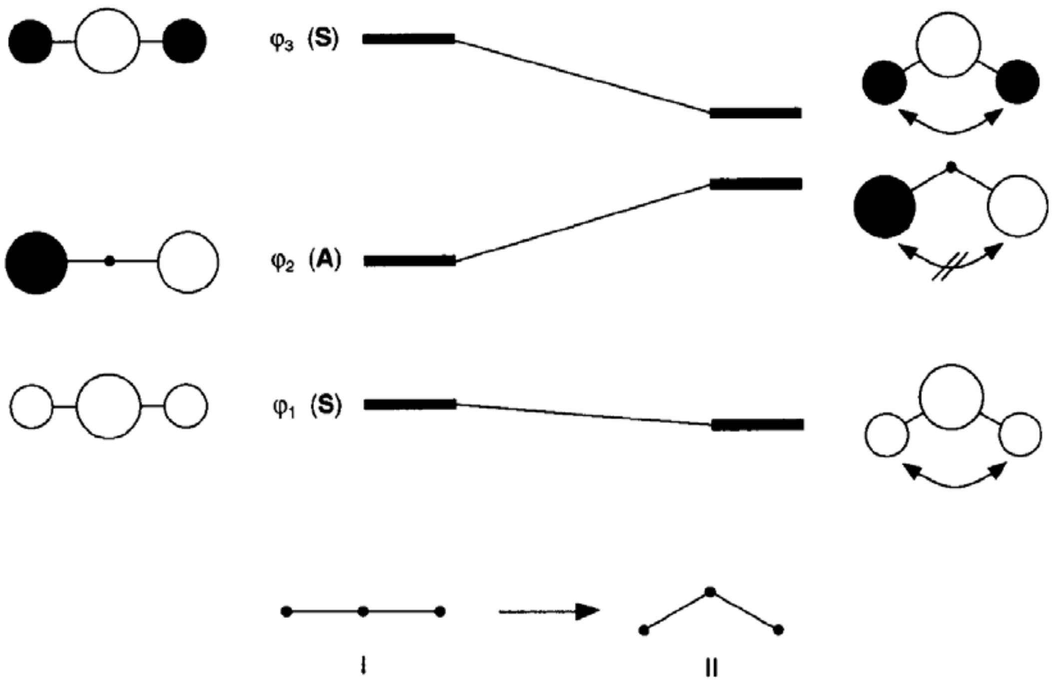


Figure 9.1. Energetic evolution of the MOs of an H_3 unit on bending.

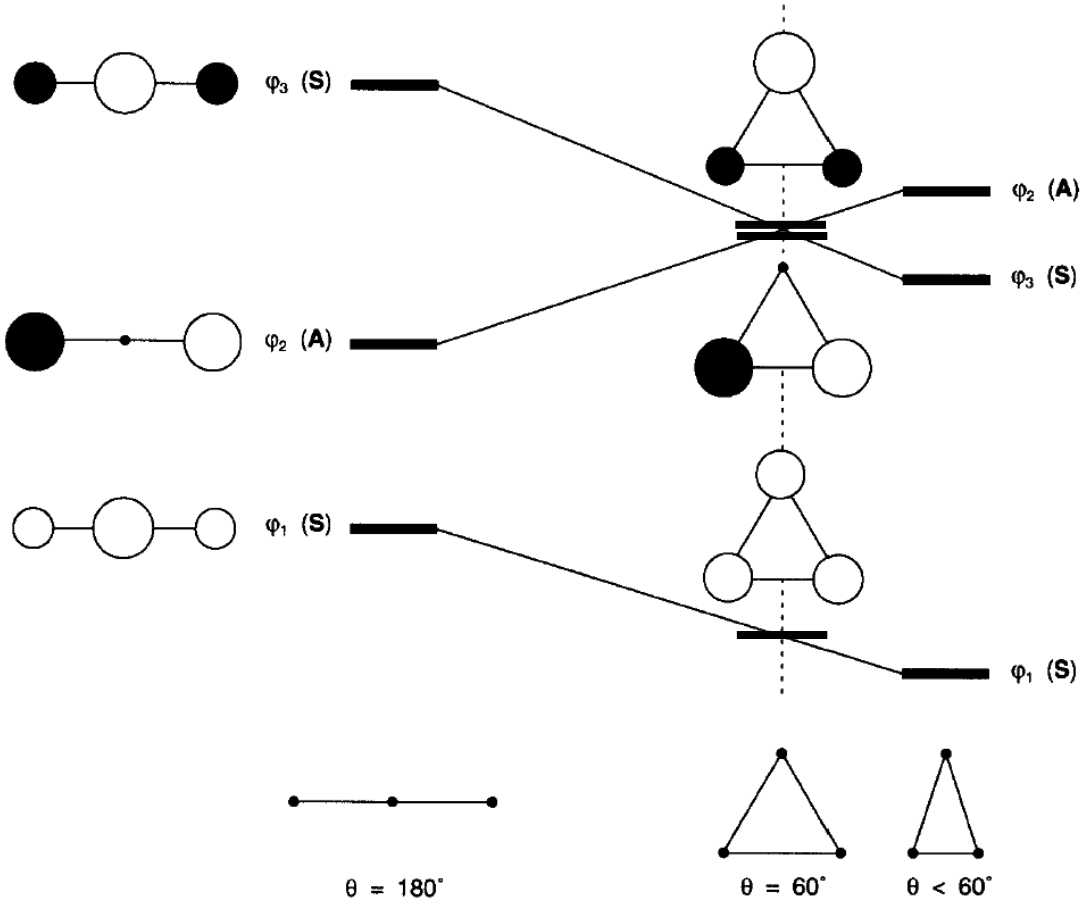
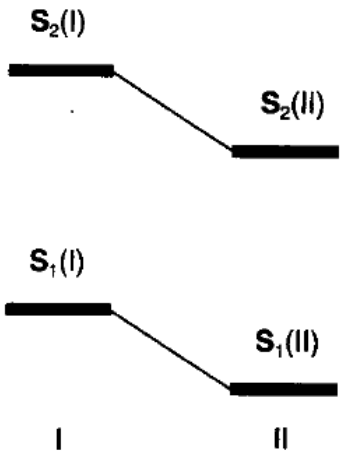


Figure 9.2. Orbital correlation diagram for the transformation H_3 (linear) to H_3 (triangular).

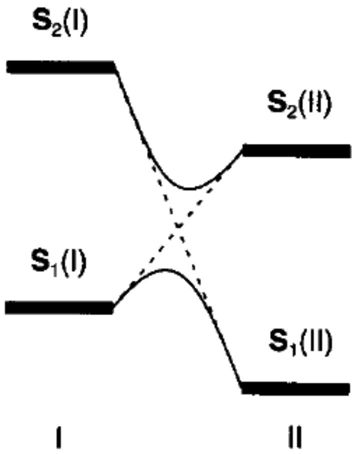
Now do you understand why H_3^+ is triangular and H_3^- is linear?
Note: nuclear repulsion disfavor $\theta < 60^\circ$

- Rules for orbital correlation diagram

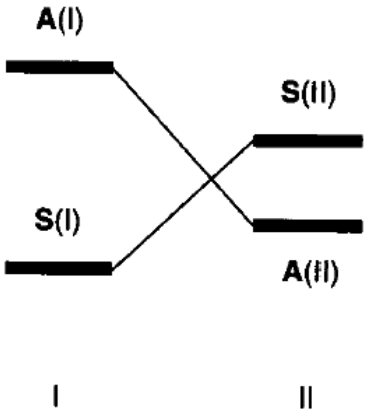
- Stabilization/destablization of the MOs
  - bonding ↑ antibonding ↓ => energy lowering
  - bonding ↓ antibonding ↑ => energy increasing
- Conservation of orbital symmetry
- The non-crossing rule for MOs of the same symmetry



9-2a



9-2b



9-2c

Ex: H_4 (linear)

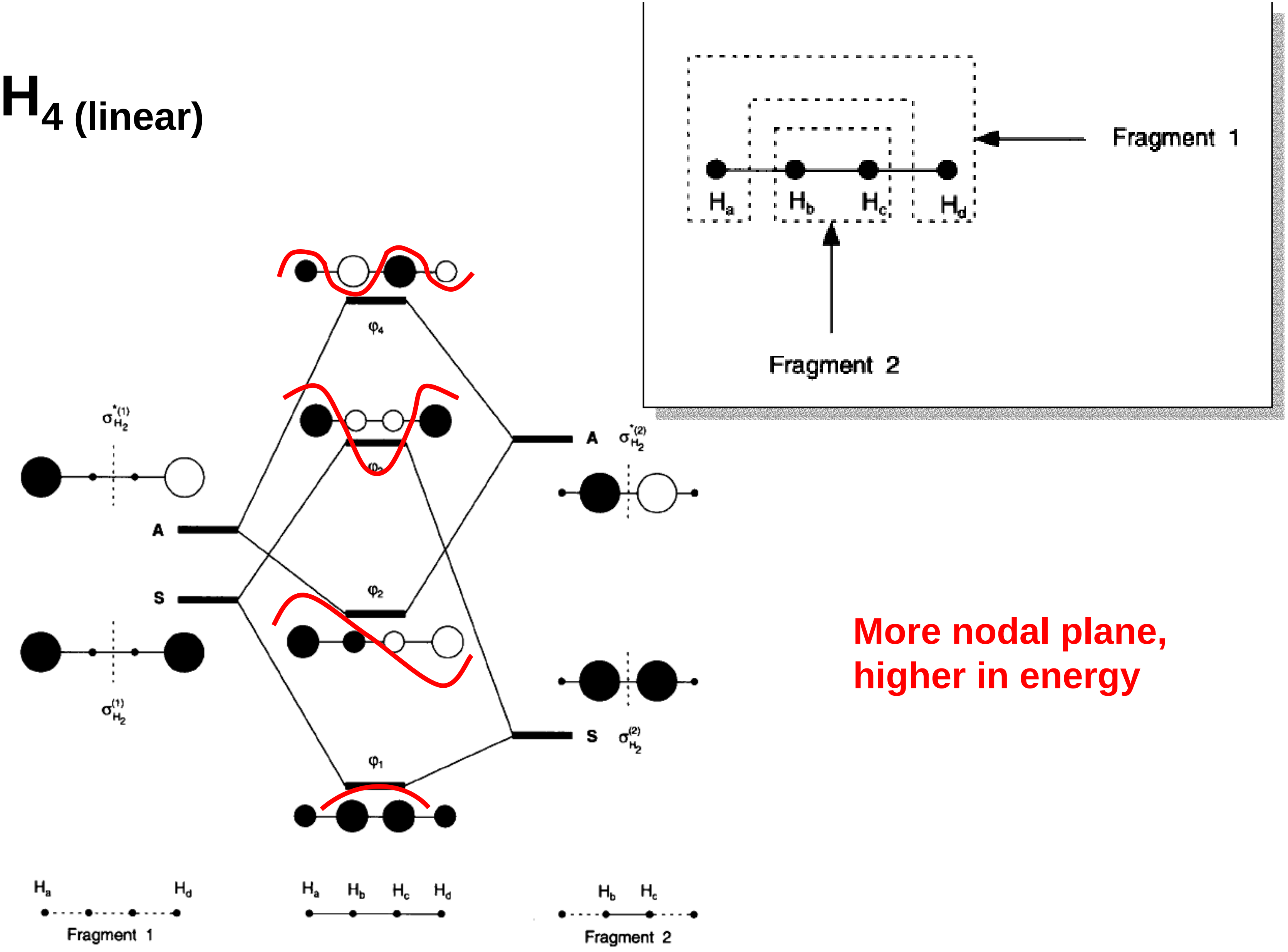
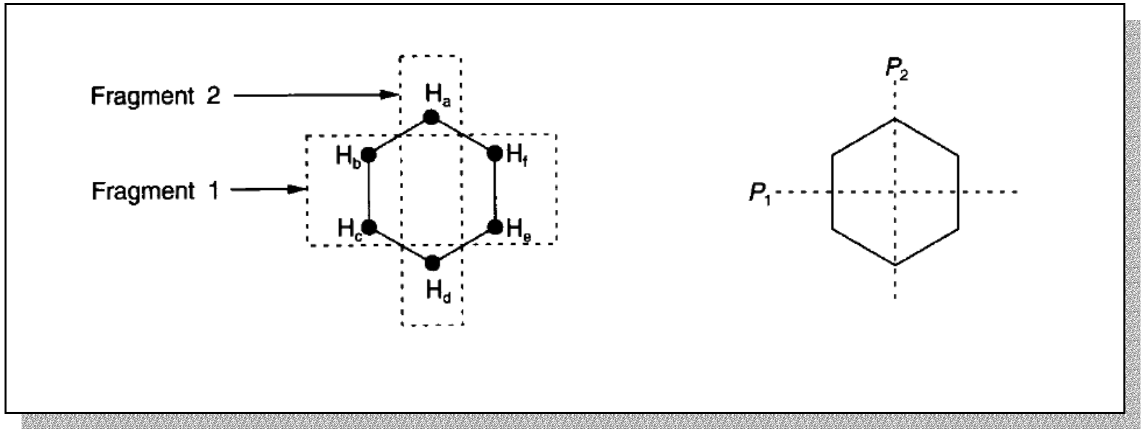


Figure 4.4. Construction of the MOs of linear H_4.

More nodal plane, higher in energy

Ex: H_6 (hexagonal)



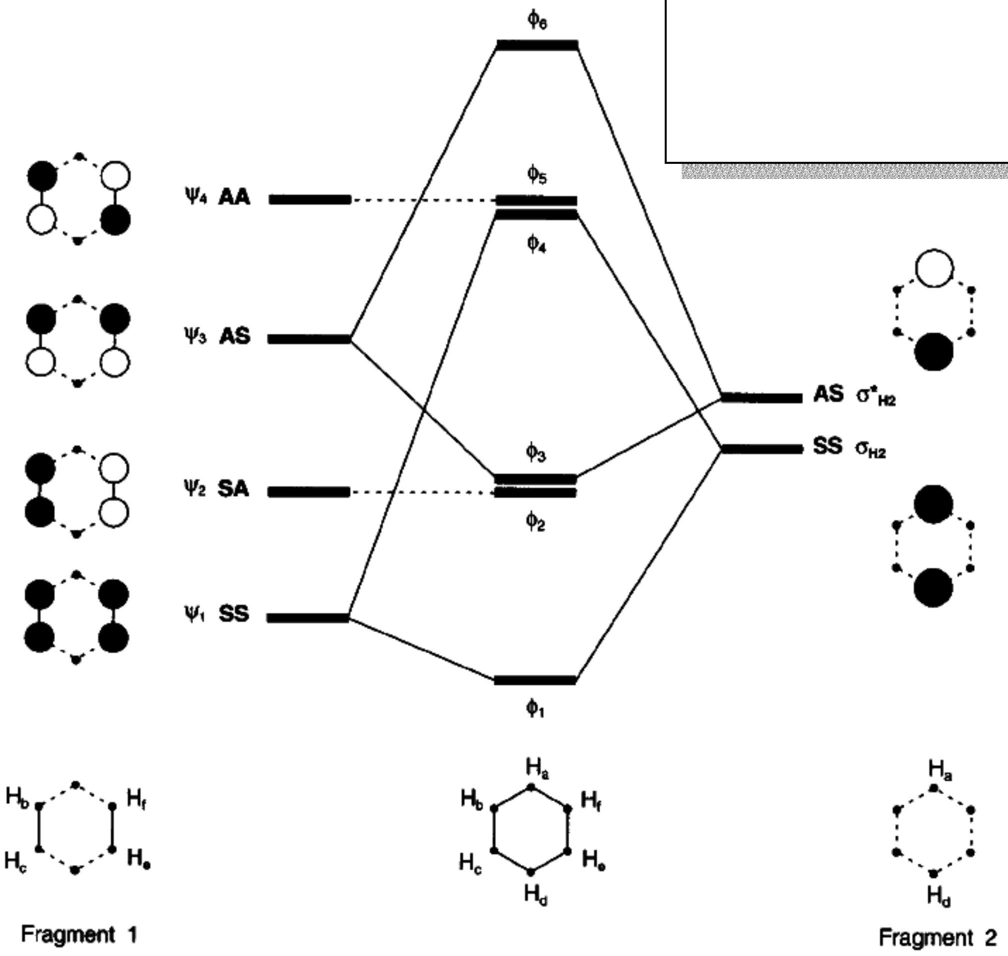
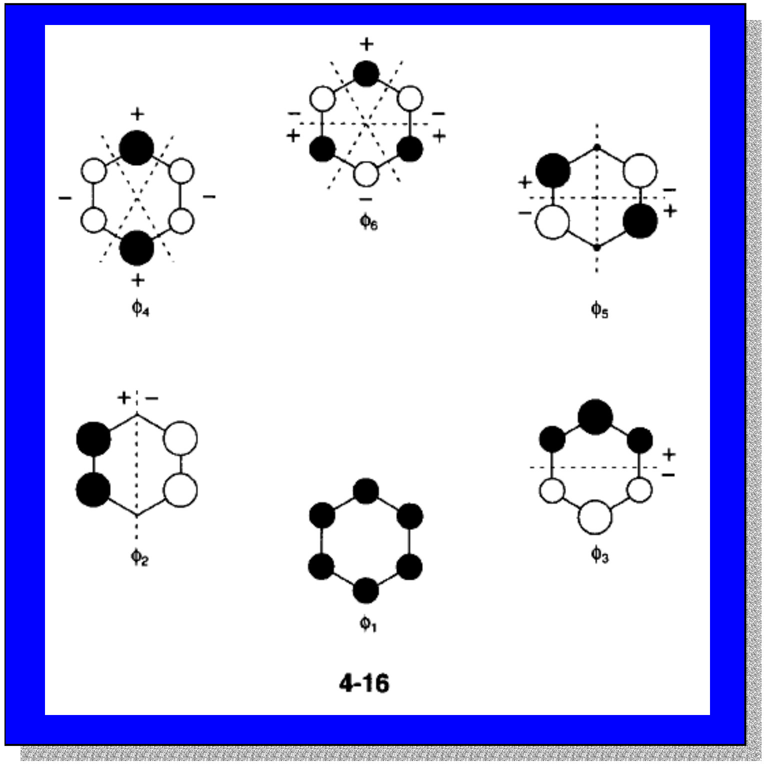


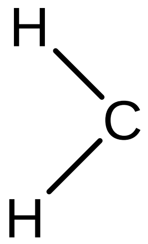
Figure 4.7. Construction of the MOs of hexagonal H_6.

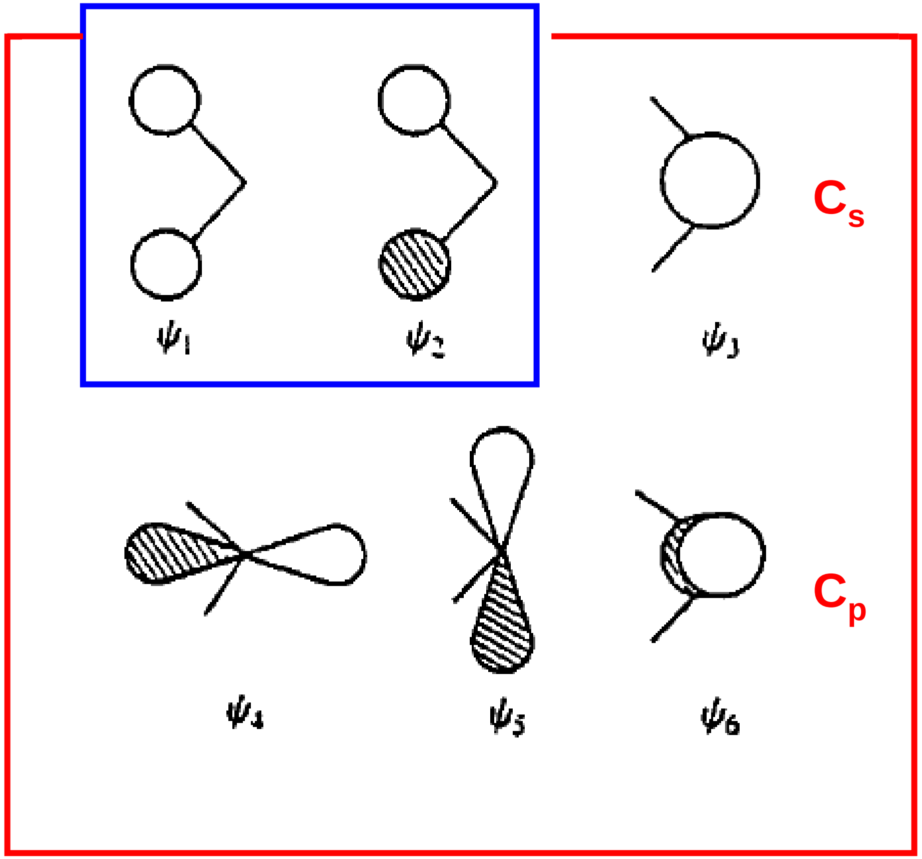


4-16

➢ Building up MOs of simple molecules

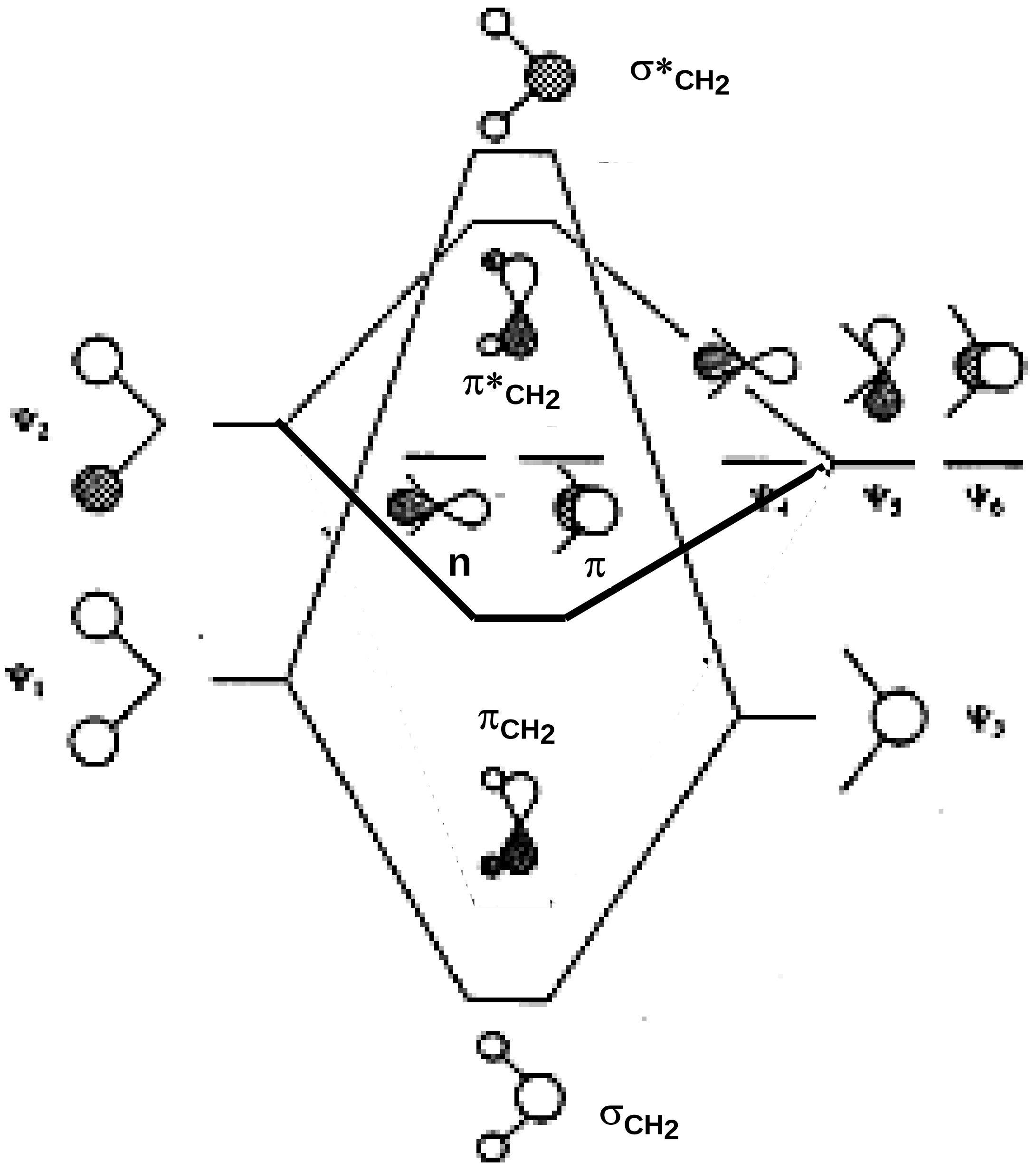
Ex: CH_2




Linear combination of H

C_s

C_p



-**Same symmetry**

Ψ1, Ψ3, Ψ4

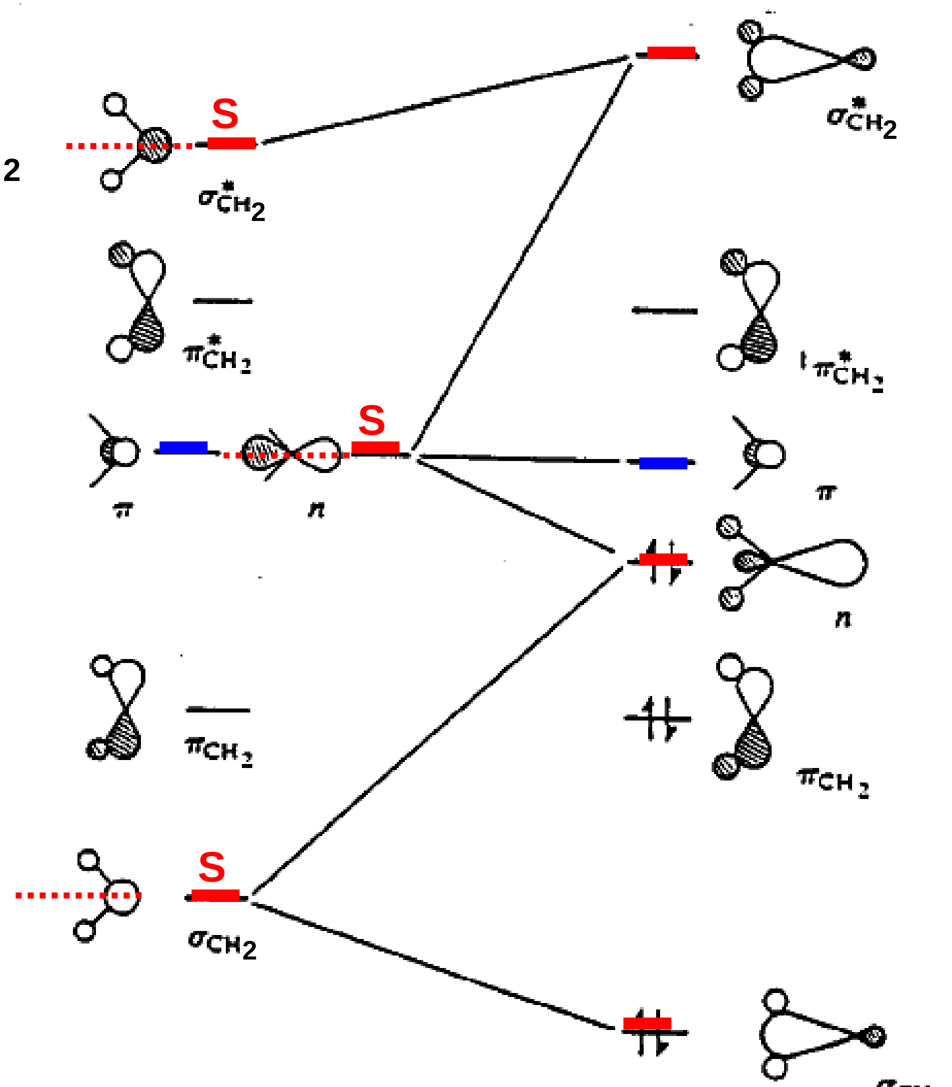
closer in energy

Ψ2, Ψ5

- **Energy difference between $\pi_{CH_2}-\pi^*_{CH_2}$ smaller than $\sigma_{CH_2}-\sigma^*_{CH_2}$ because of smaller overlap**

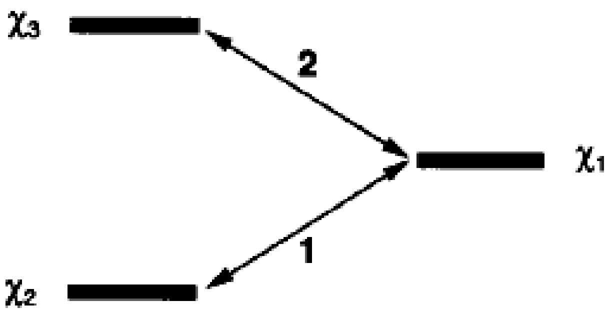
- # of electrons in CH_2
  4 + 1 + 1 = 6

Ψ4 (*n*) is also of the same symmetry, should also Interact with hydrogens



2nd order interaction

- **Three orbital interactions**

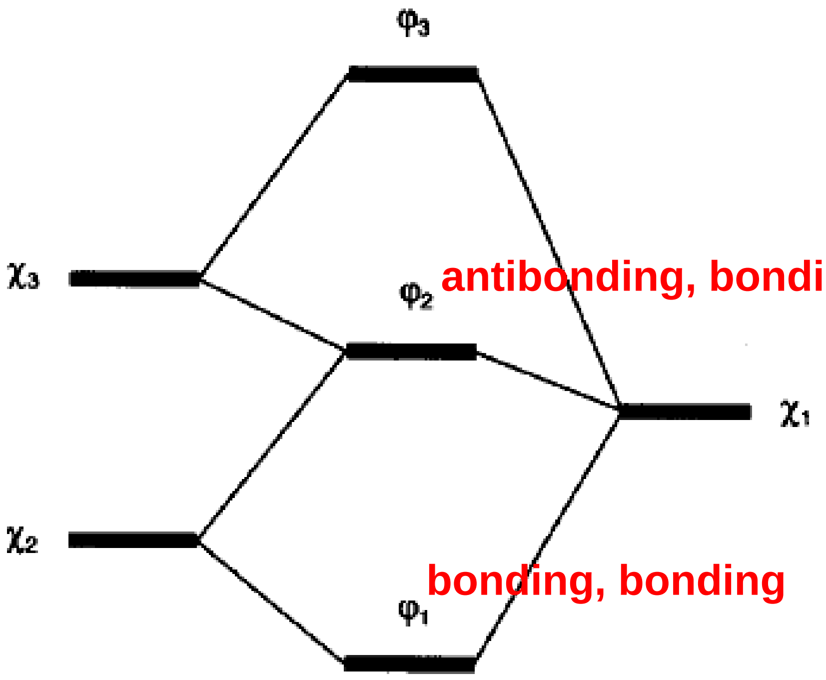


6-1

antibonding, antibonding

antibonding, bonding

bonding, bonding



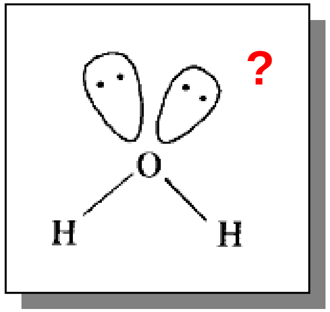
6-2

φ_1 = x1 + x2 + x3

φ_2 = x1 – x2 + x3

φ_3= – x1 – x2 + x3

- Nonequivalence of oxygen lone pairs in the water molecule



Photoelectron spectrum of water shows the lone pair orbitals are nonequivalent and are separated by 2.1 eV

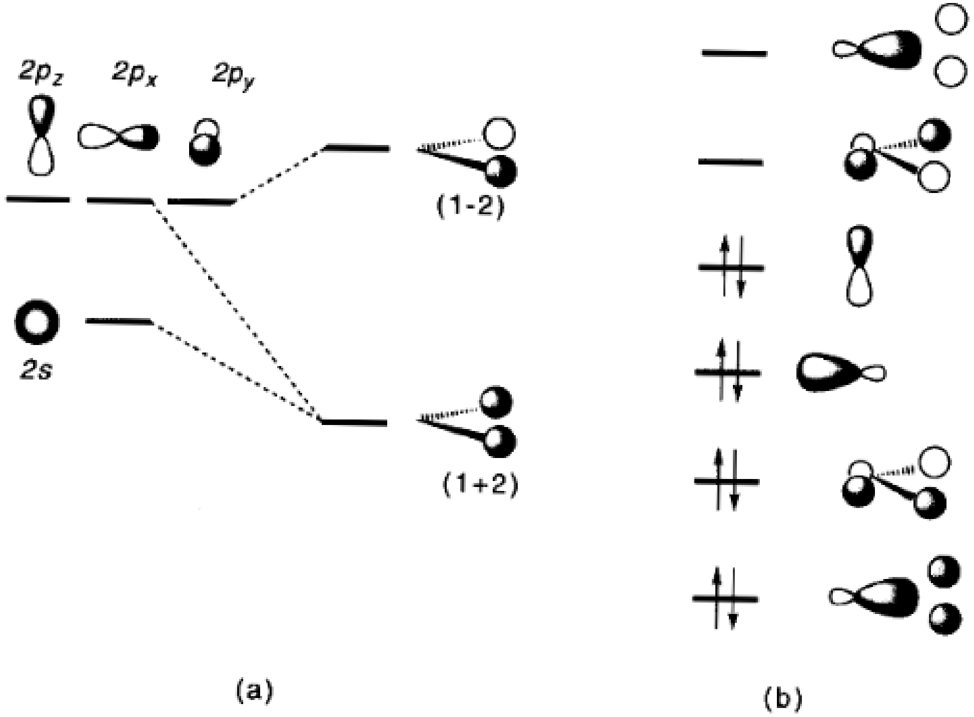


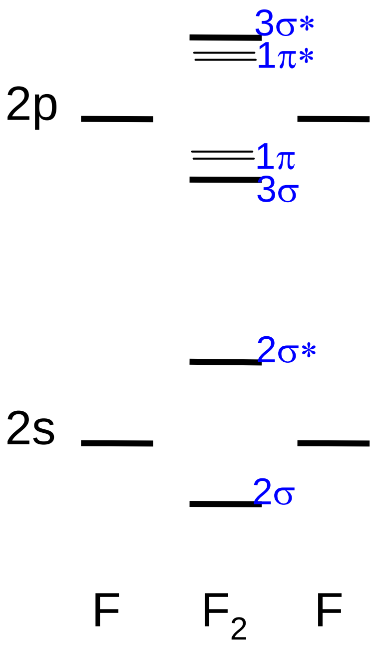
Fig. 2.24. Orbital diagram showing (a) the symmetry-allowed interactions between the set of O 2p orbitals and the two H_2 orbitals (1+2) and (1-2) in the H_2O molecule. (b) The set of MOs in the H_2O molecule obtained from the interaction of the orbitals in (a). Note that the two lone-pair orbitals in H_2O are not degenerate.

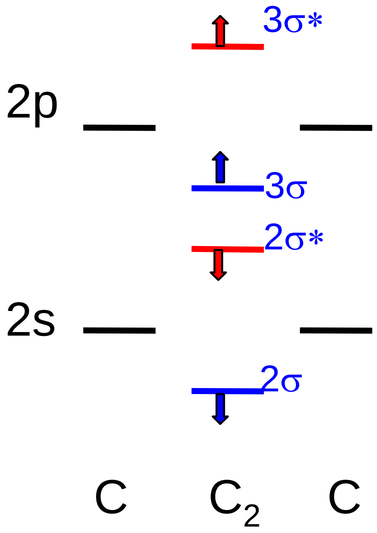
- Another example of 2nd order interaction differences in electronic structure of F_2 and C_2

F_2: $(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(1\pi^*)^4$

C_2: $(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi_u)^4$ *why 3σ is not populated first?*

=> *energy raised because of mixing of 2σ and 3σ (∵ same symmetry)*

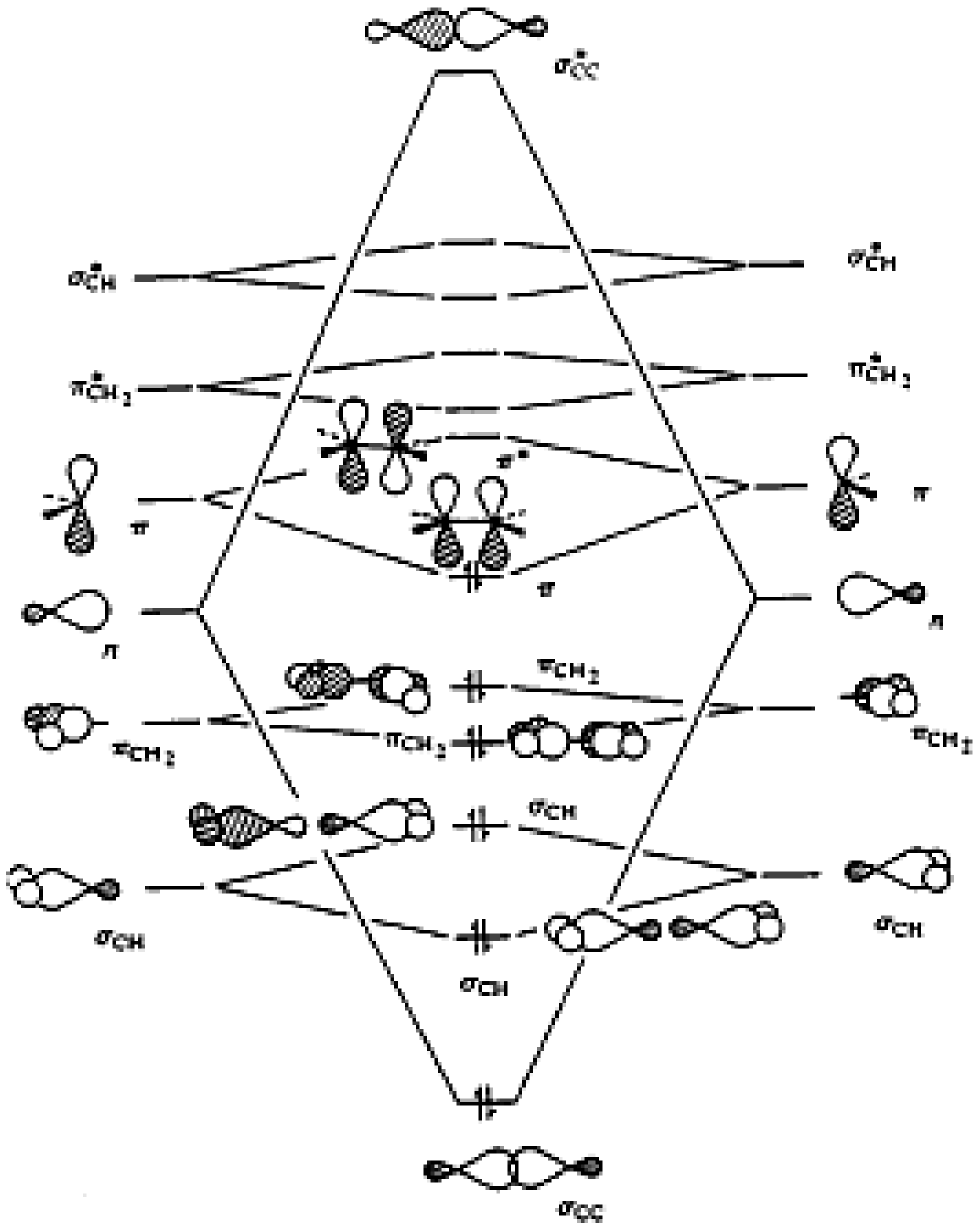




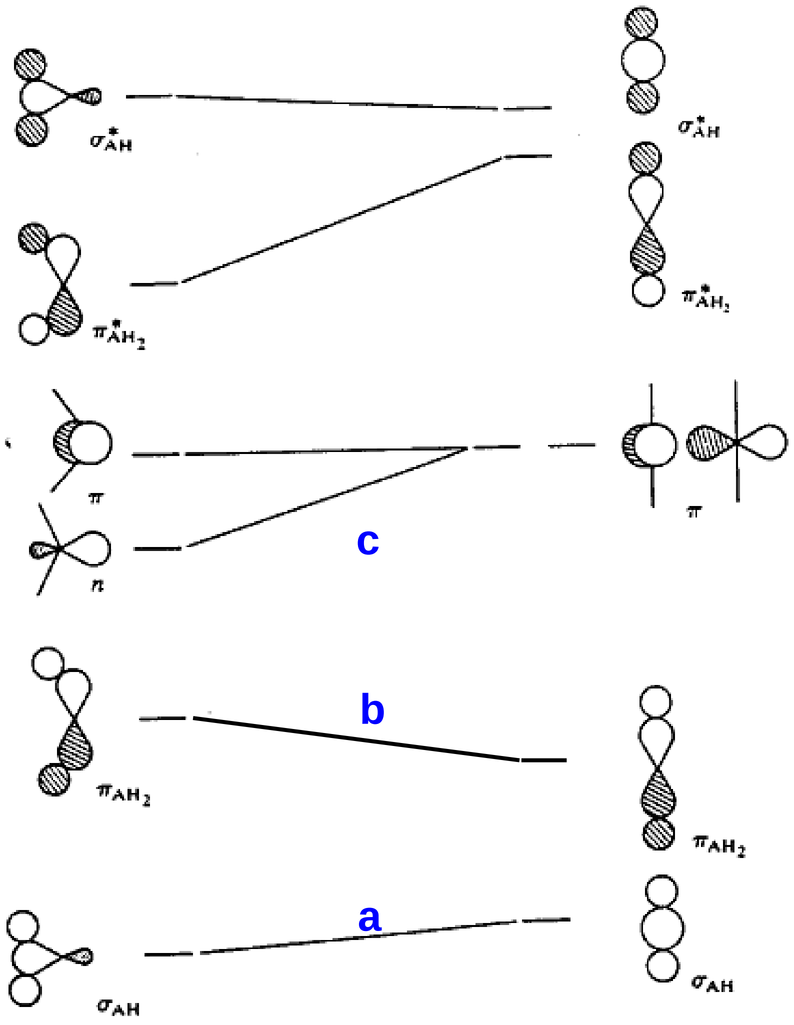
- Combine CH_2 and CH_2 to get $CH_2{=}CH_2$

The lone pairs (n) form a σ bond and the π orbitals form a π bond

Net bonding with 12 electrons:
1 σ bond
1 π bond



- Walsh diagram for correlating linear and bent AH_2



a. i) weak bonding between H…H lost
   ii) stabilization from p orbital lost

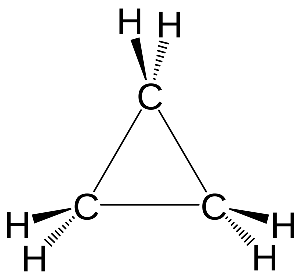
b. i) H moves to maximum overlap
   ii) out of phase H…H become further apart

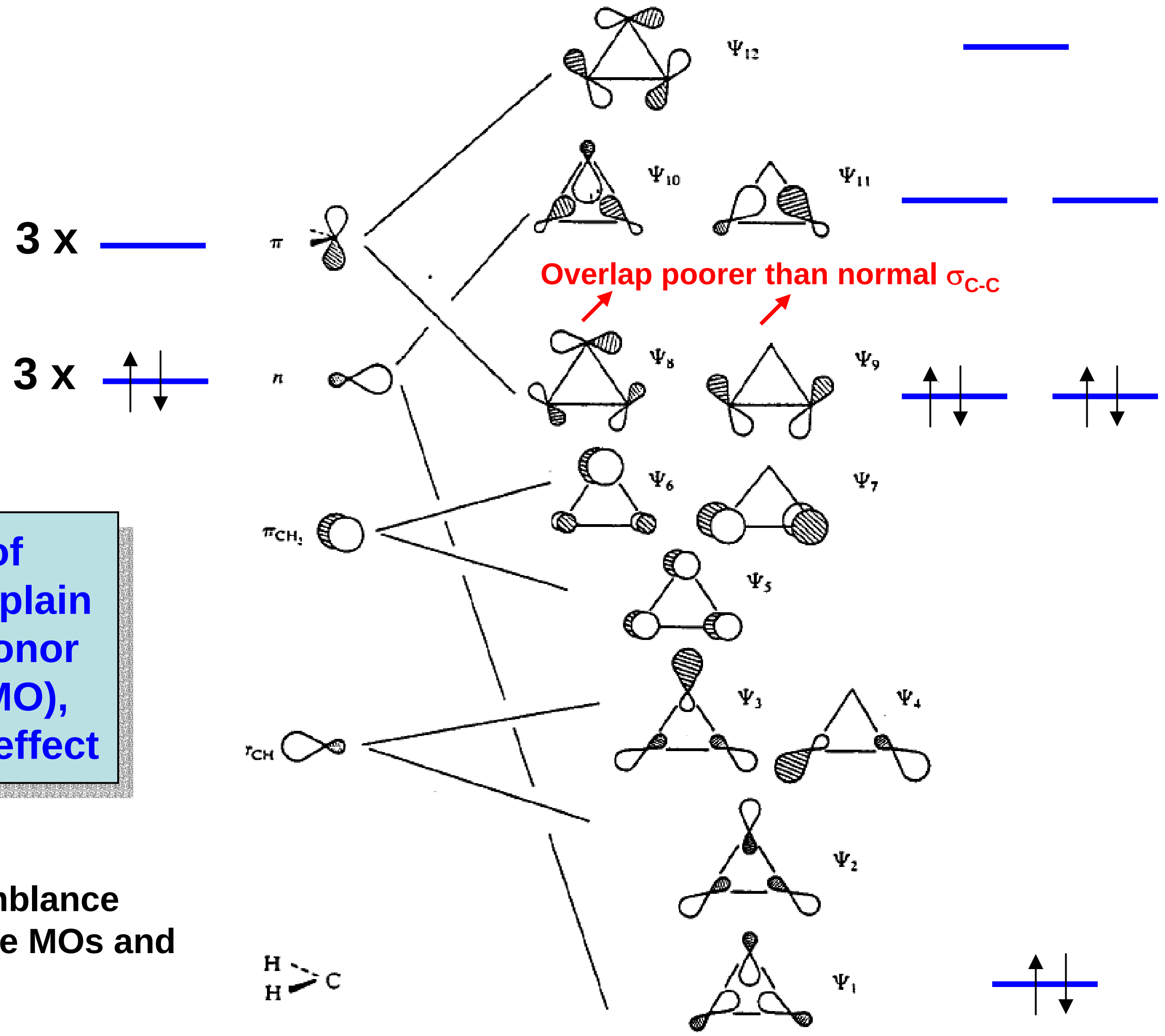
c. loses s character

Walsh diagram provides rationales for

- ➢Linear BeH_2, BH_2^+ (4 e^-)
- ➢Bent CH_2 (6 e^-)
- ➢Bent H_2O (8 e^-)

Ex: cyclopropane



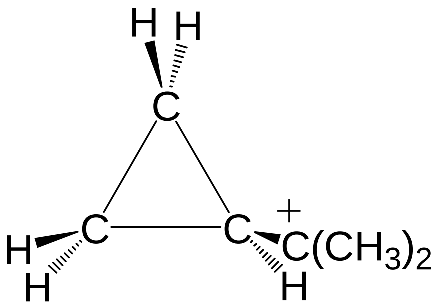


Overlap poorer than normal $\sigma_{C\text{-}C}$

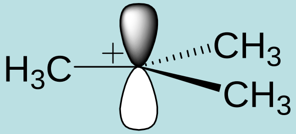
Poor alignment of p orbitals can explain strain, good e^- donor ability (high HOMO), and substituent effect

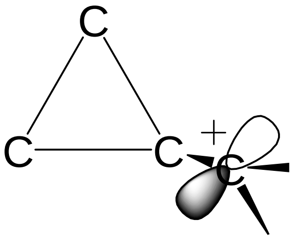
Do you find the resemblance between cyclopropane MOs and H_3 MOs?

Preferred structure of

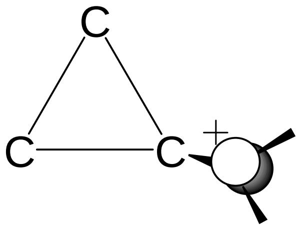


It is known that the cation part is planar





or

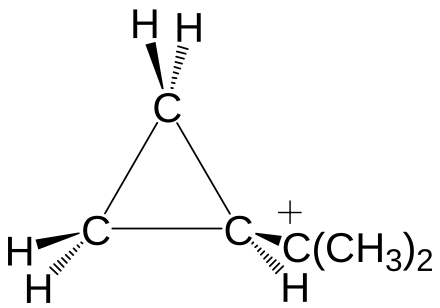


?

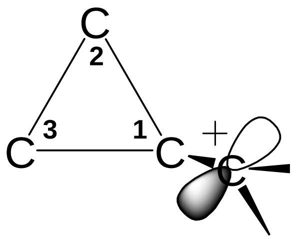
favored

not favored

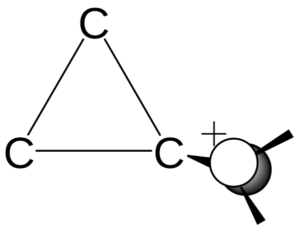
Structure of



C_1-C_2 longer than w/o the cation part
C_2-C_3 shorter



favored



disfavored

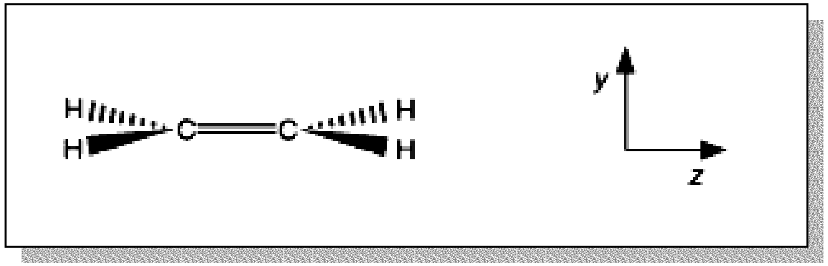
How do you rationalize?

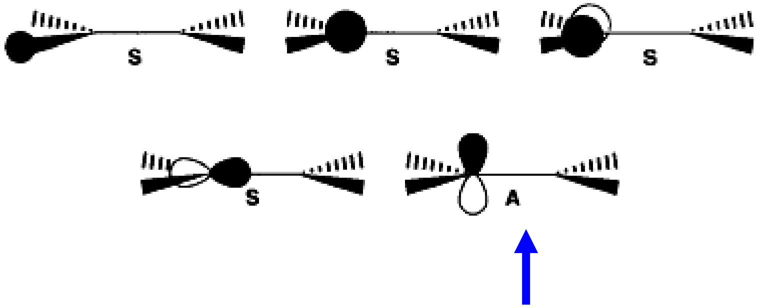
Hint: empty orbital interact with filled orbital
Hint: electron flows out of bonding orbital => lengthen bonds
electron flows out of antibonding => shorten bonds

➢ π systems and conjugation

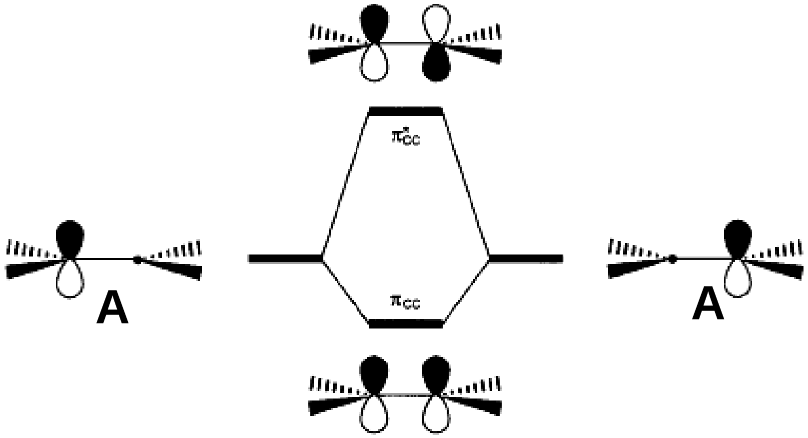
π Electrons are less tightly held than the σ electrons, often responsible for the electrical and optoelectrical properties of a material

Ex: $CH_2{=}CH_2$

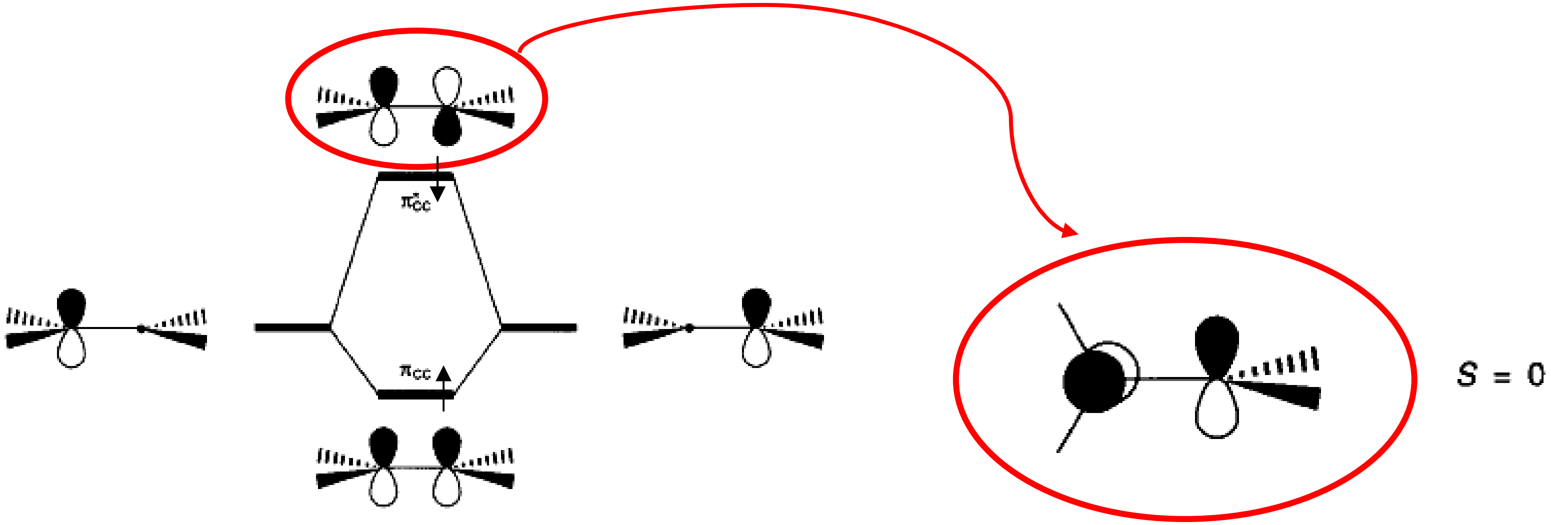




Antisymmetrical with respect to molecular plane



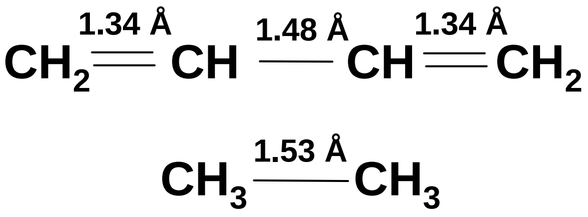
- In the excited state, the geometry may relax to different conformation



No energy destablization caused by orbital interaction

- Conjugation (C=C-C=C-…….)

- $CH_3\text{-}CH_2\text{-}CH{=}CH_2 + H_2 \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ $\Delta H = -30.2$ kcal/mol
- $CH_2{=}CH\text{-}CH_2\text{-}CH{=}CH_2 + 2\ H_2 \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ $\Delta H = -60.4$ kcal/mol
  (unconjugated diene)
- $CH{=}CH\text{-}CH{=}CH_2 + 2\ H_2 \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$ $\Delta H = -56.5$ kcal/mol
  (conjugated diene)



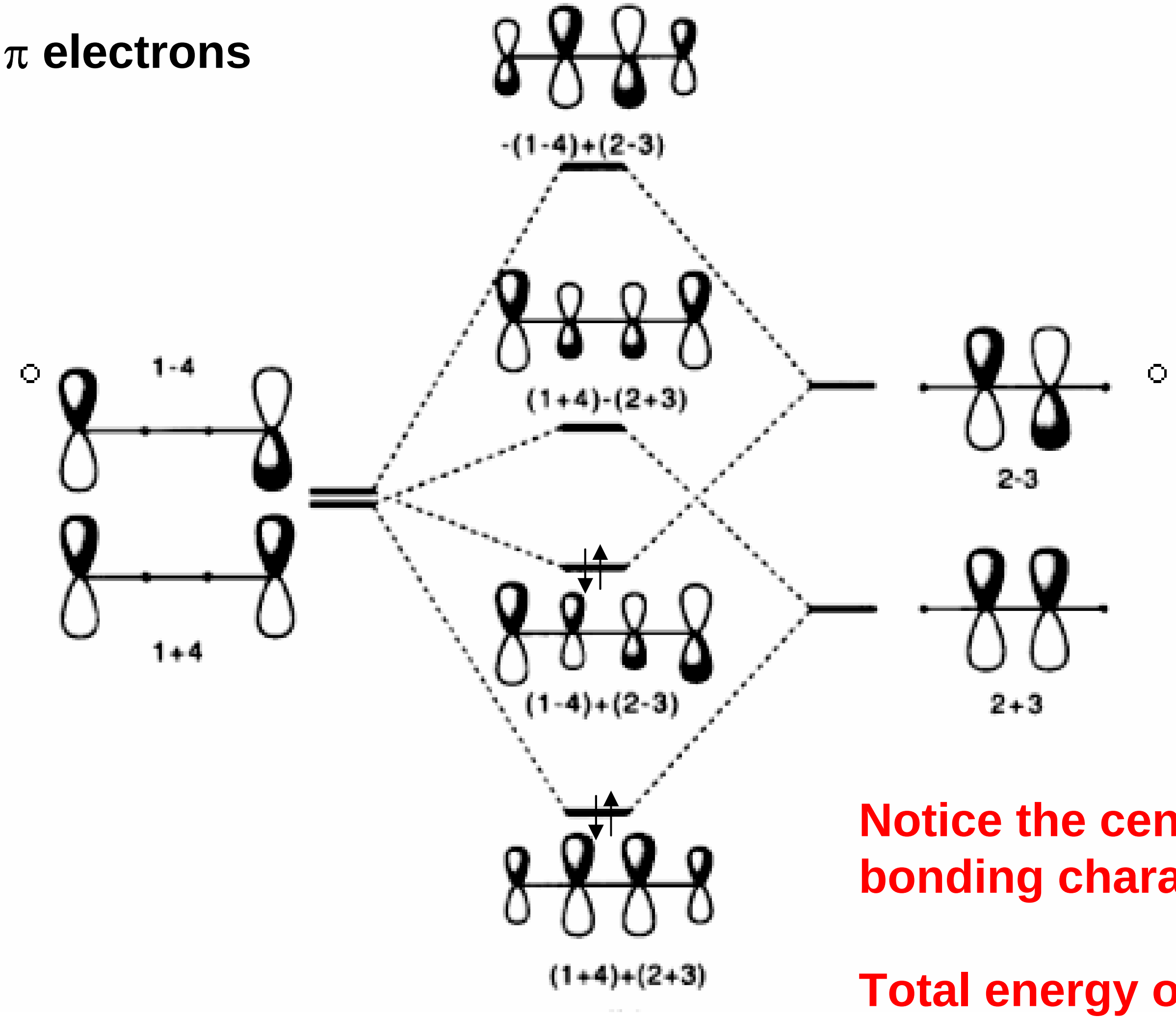
$$CH_2 \overset{1.34\ \text{Å}}{=\!=} CH \overset{1.48\ \text{Å}}{-\!-} CH \overset{1.34\ \text{Å}}{=\!=} CH_2$$

$$CH_3 \overset{1.53\ \text{Å}}{-\!-} CH_3$$

Why conjugated diene more stable than unconjugated diene?

Why C-C bond shorter in conjugated diene?

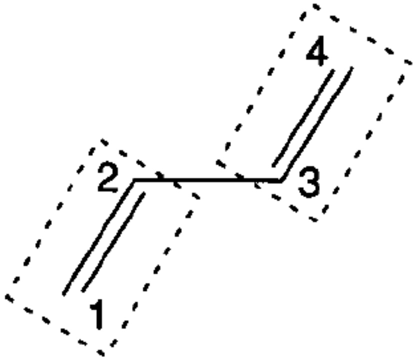
4 π electrons



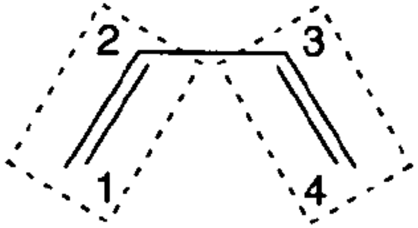
Notice the center bond has net bonding character

Total energy of butadiene is lower than 2 isolated system (ex: 2+3)

Butadiene in reality: not linear



Trans



Cis

Trans **is more stable than** ***cis*****.**

Hint: Use orbital correlation diagram to rationalize it.
Or, think about steric effect

➢ Lewis structure and bond localization

Molecular orbital (delocalized in nature) is useful, but sometimes it is easier to think in terms of localized orbitals!

Localized orbitals can represent electron density in a conceptually useful way and give concise picture of orbital interactions for the local structure of interest. However, keep in mind that localized orbitals are not eigenfunctions, not orthogonal to each other, and cannot be used in correlations with physical observables such as photoelectron spectra.