Molecular Orbital Theory (MO)

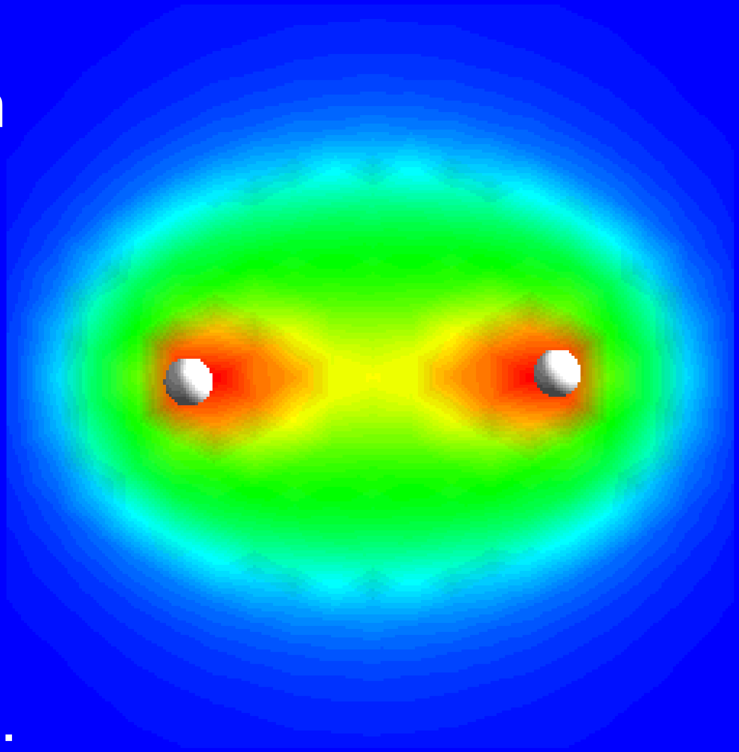
Combination of **atomic** orbitals on **all atoms** in a molecule

- Suitable symmetry
- Similar energy

n AOs forms *n* MOs

Diatomic molecules: H_2, F_2, CO,....

Polyatomic molecules: BF_3, CH_4,....

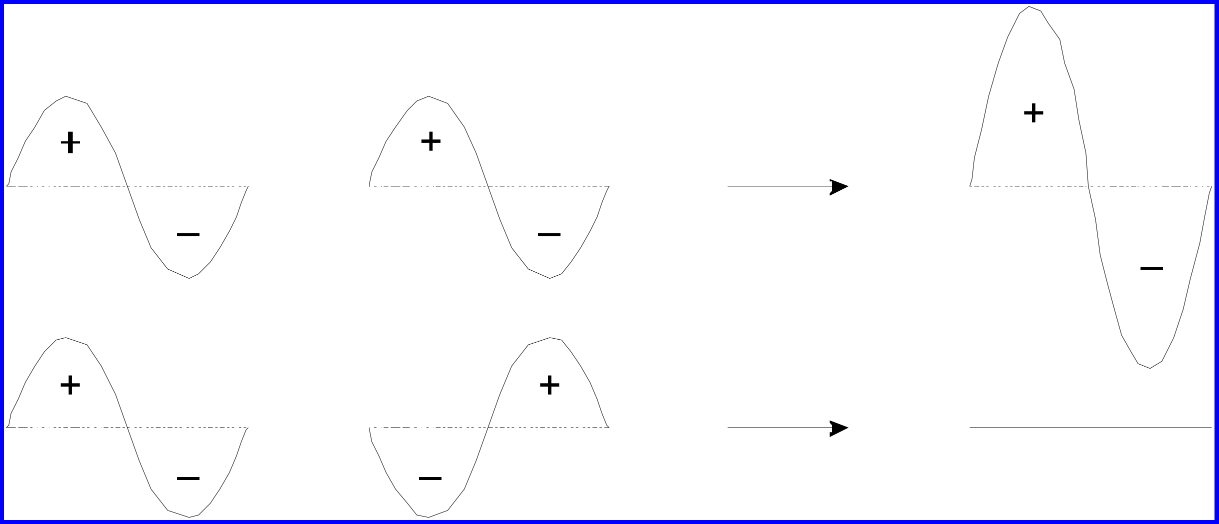


Bonding MO in an H_2 molecule

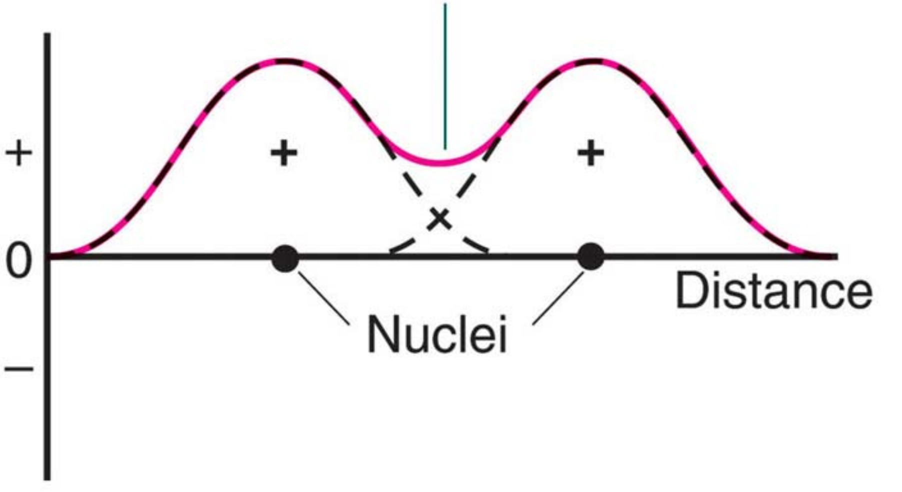
Wave Interference

Constructive

Destructive

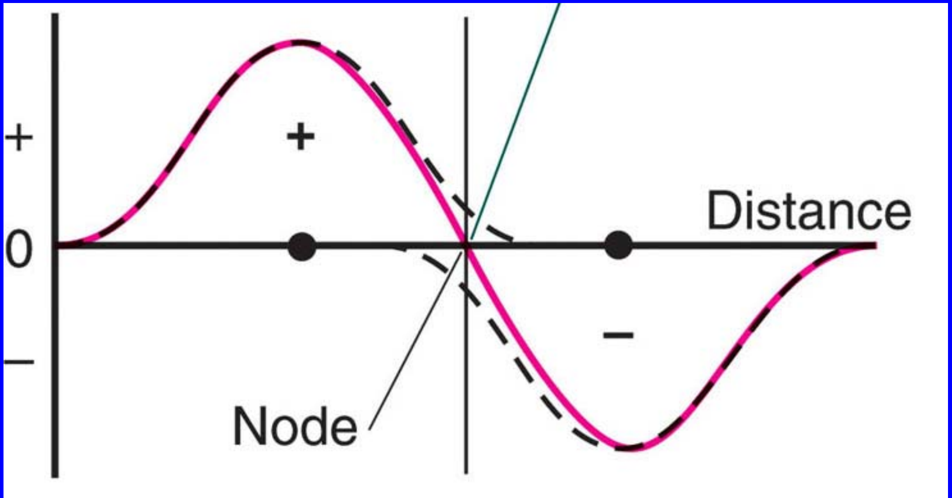


LCAO = Linear Combination of Atomic Orbitals



Combination of 2 wave functions (orbitals) with the SAME sign

$$\Psi = c_1\,\Psi_A + c_2\,\Psi_B$$
$$\Psi^* = c_3\,\Psi_A - c_4\,\Psi_B$$



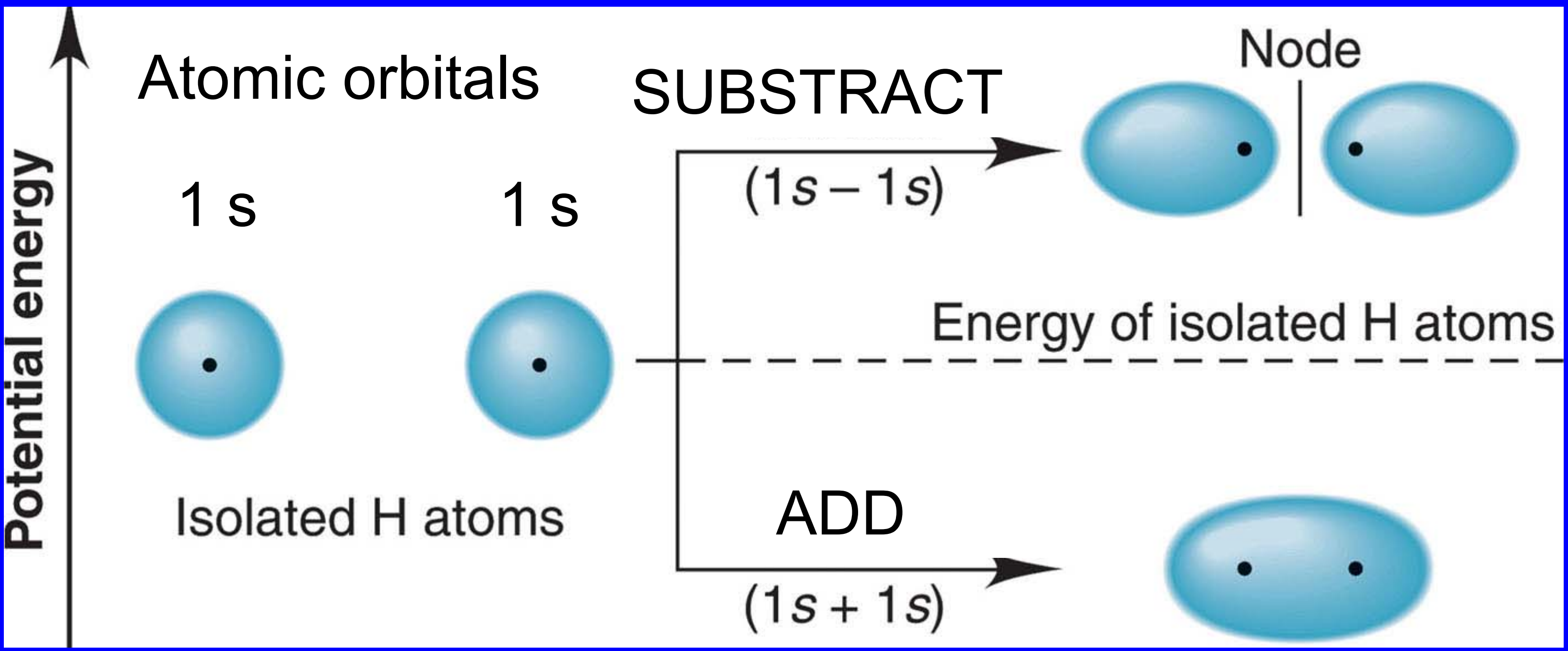
Combination of 2 wave functions (orbitals) with OPPOSITE sign

LCAO = Linear Combination of Atomic Orbitals

$\Psi = c_1 \Psi_A + c_2 \Psi_B$

$\Psi^* = c_3 \Psi_A - c_4 \Psi_B$

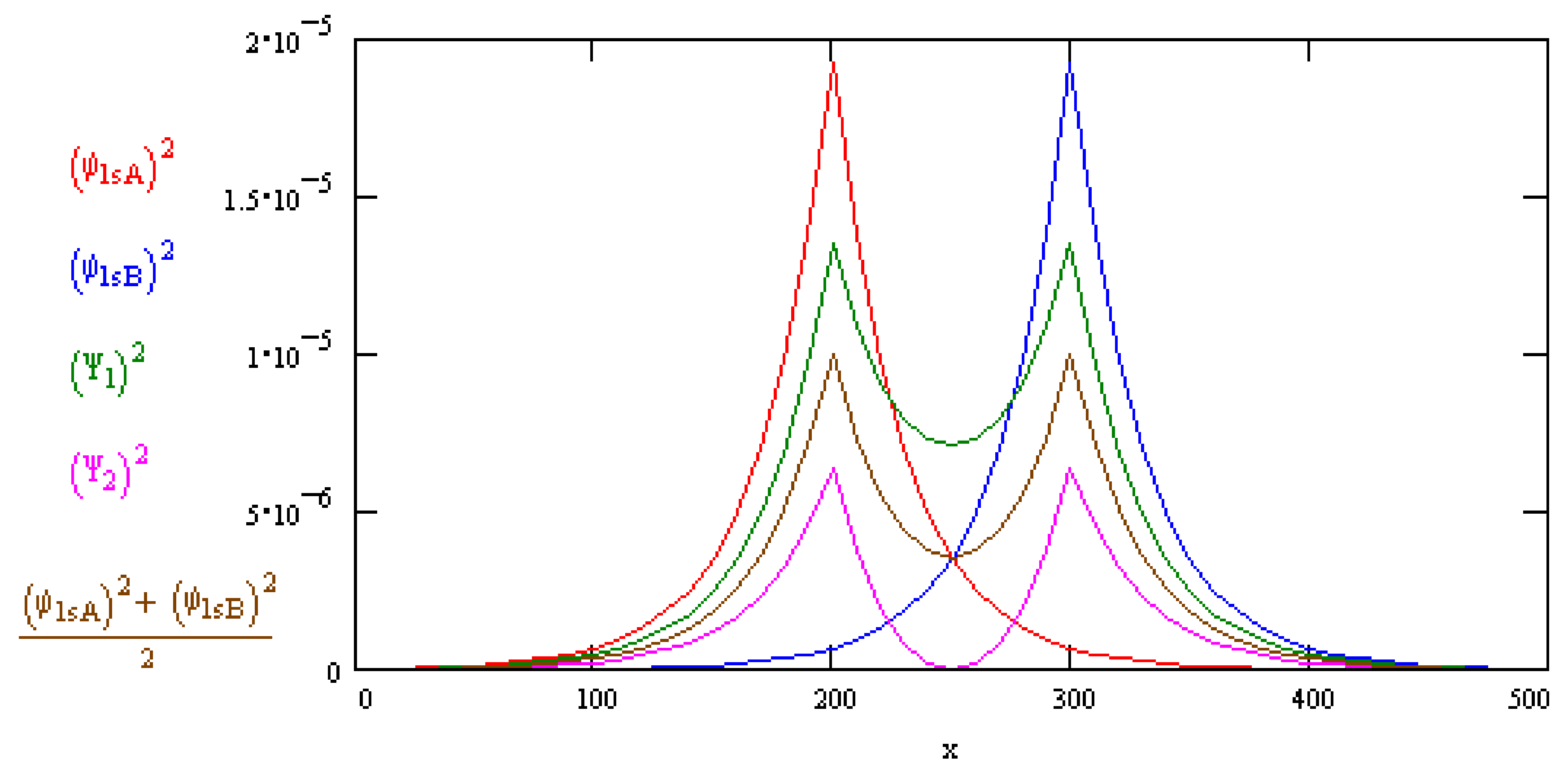
Ψ^* Antibonding MO



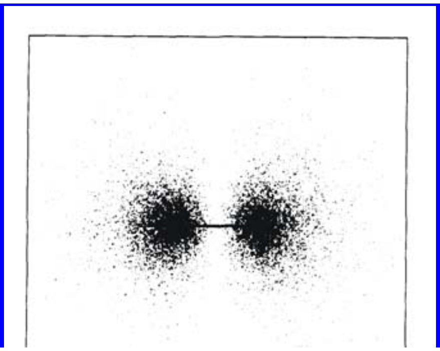
Ψ Bonding MO

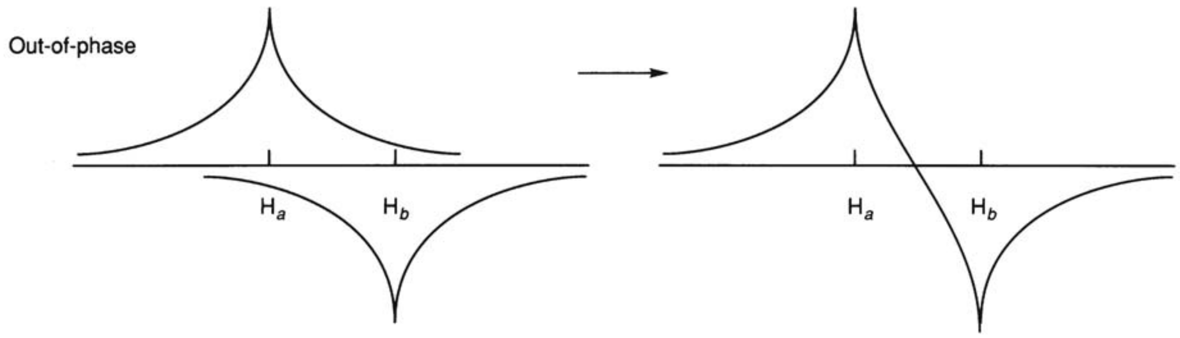
Number of MO = Number of AO

LCAO = Linear Combination of Atomic Orbitals



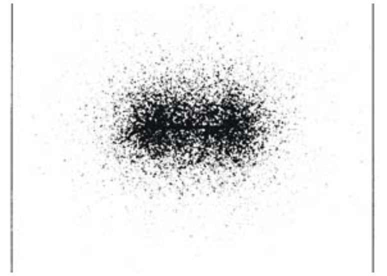
Ψ* Antibonding MO

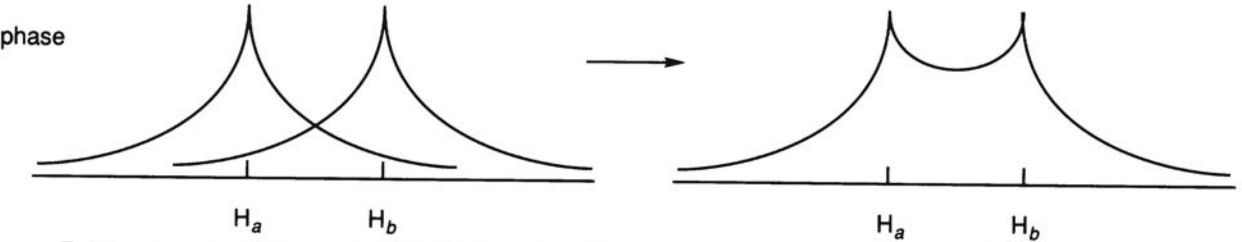




Destructive interference of the waves from two hydrogen 1*s* orbitals on adjacent atoms (the 'out-of-phase' combination).

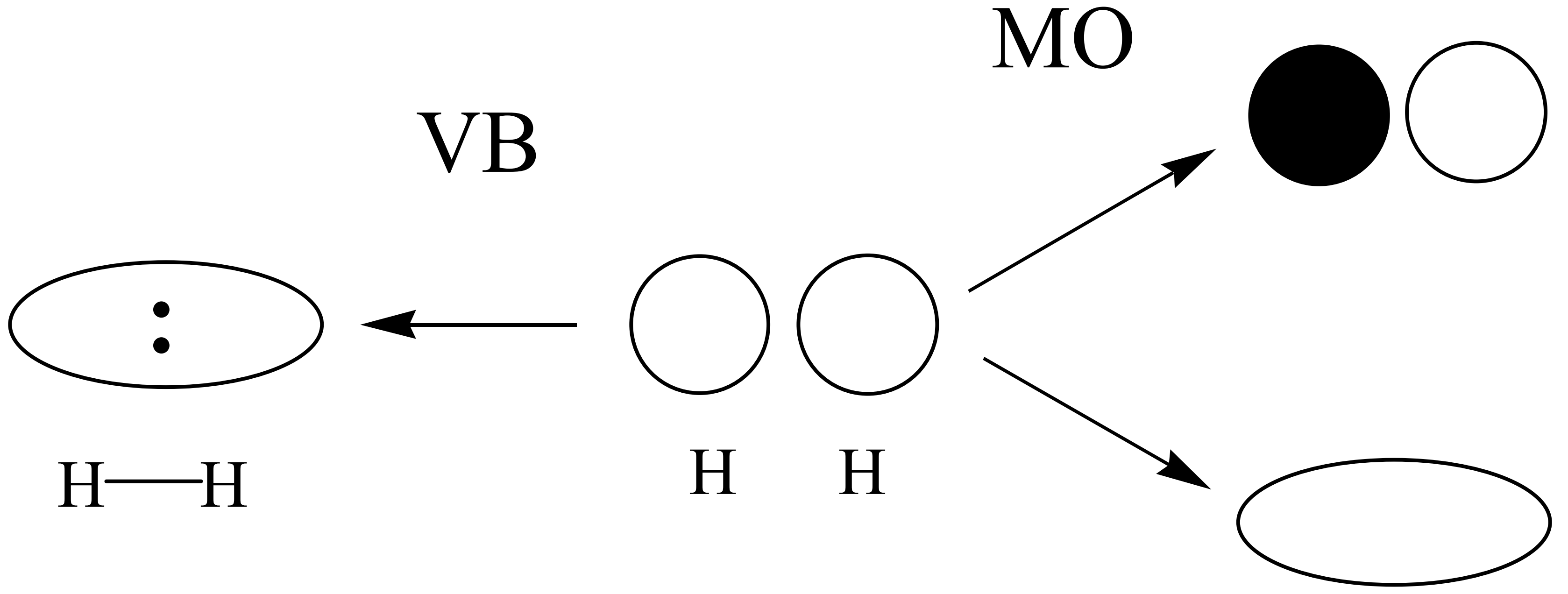
Ψ Bonding MO





Reinforcement of the waves from two hydrogen 1*s* orbitals on adjacent atoms (the 'in-phase' combination).

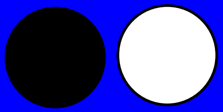
Differences between VB and MO

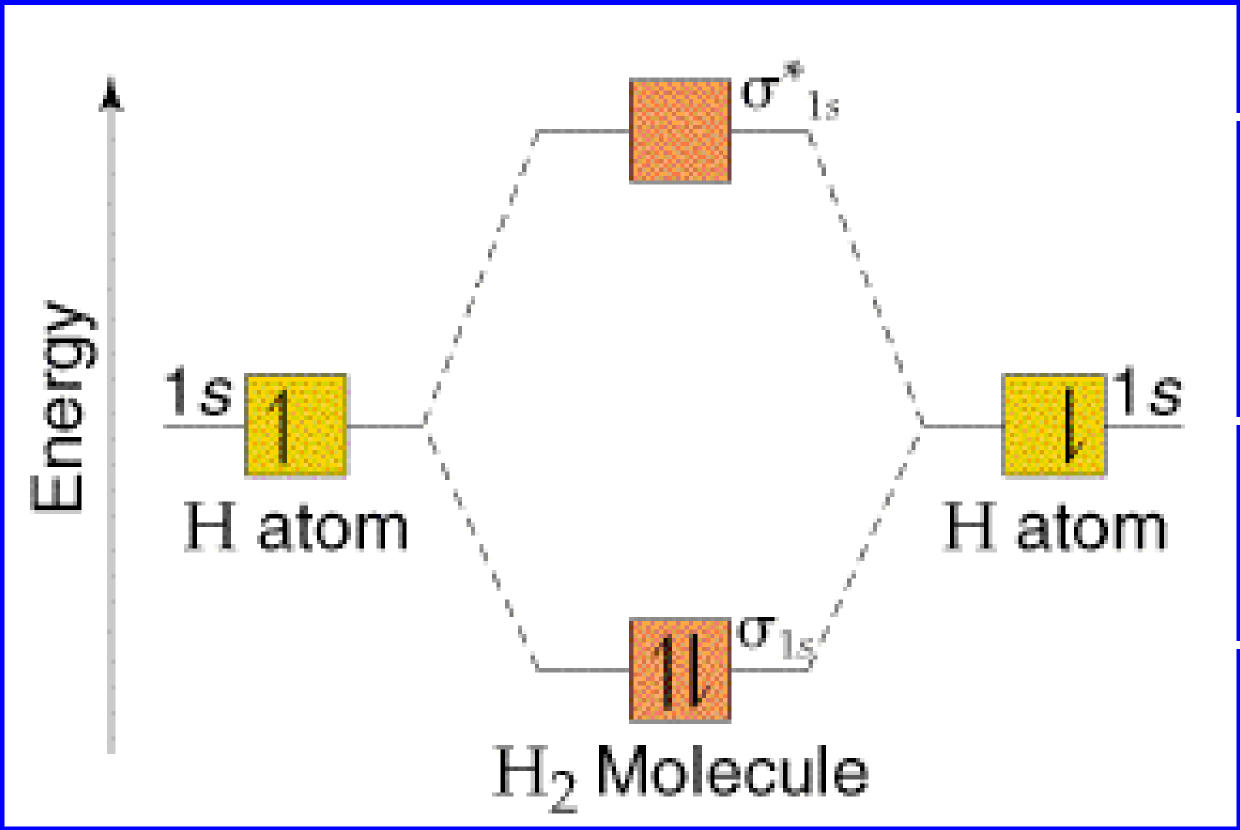


Localized bonds

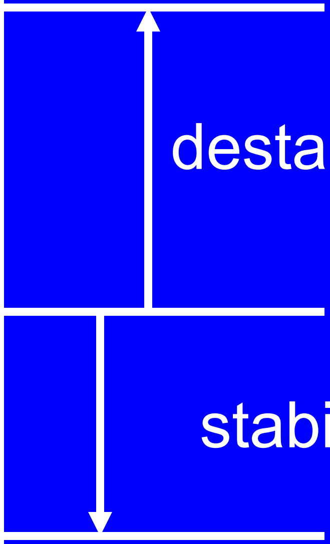
Delocalized bonds

Y* Antibonding MO





Energetic

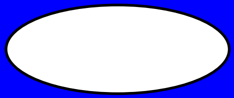


destabilization

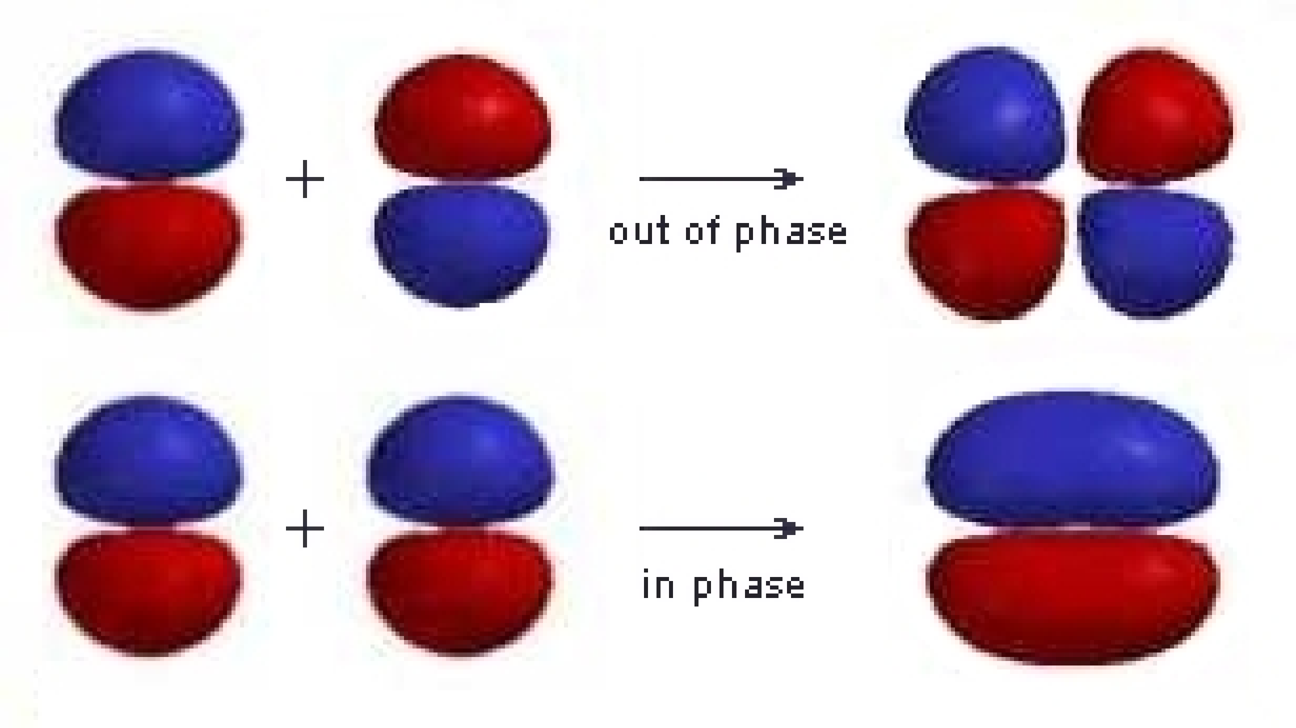
stabilization

In comparison
with free atoms

Y Bonding MO



π MO by Combination of p AO

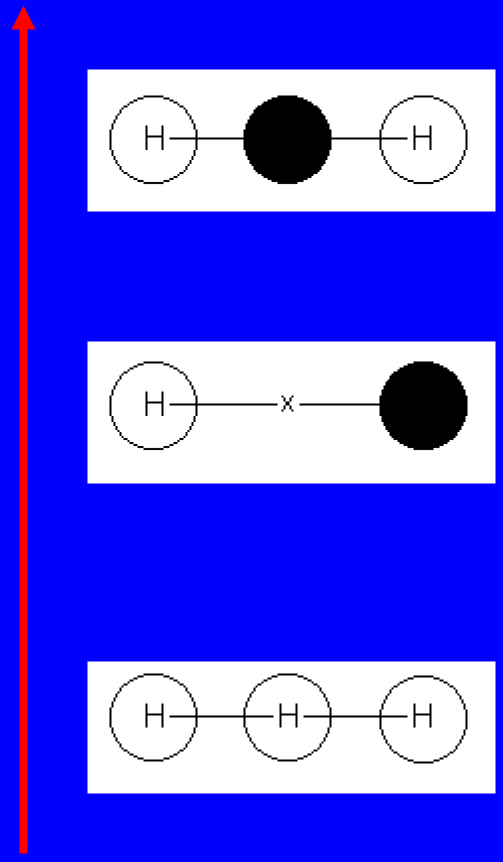


Antibonding π MO

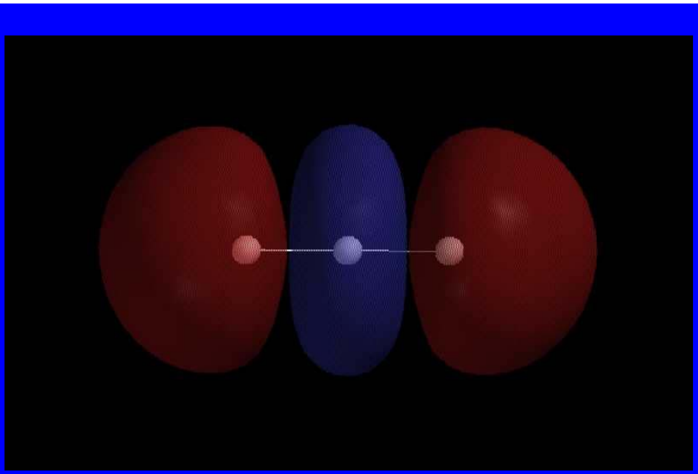
Bonding π MO

H$_3^+$

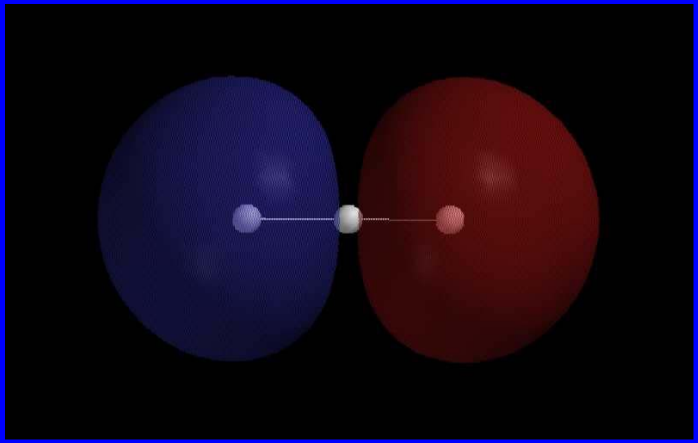
Energy incr. stability decr.



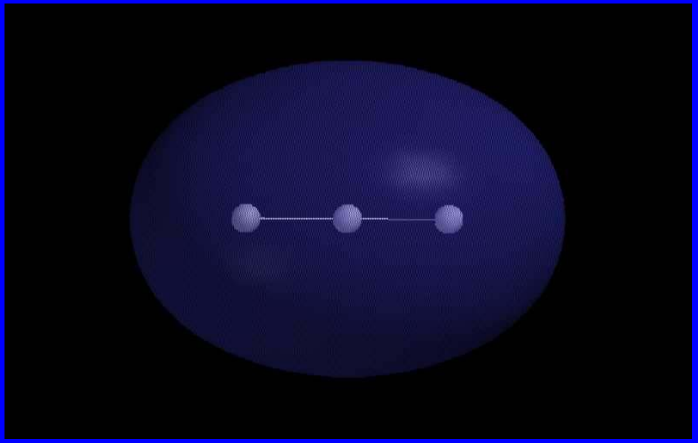
Antibonding MO



Nonbonding MO



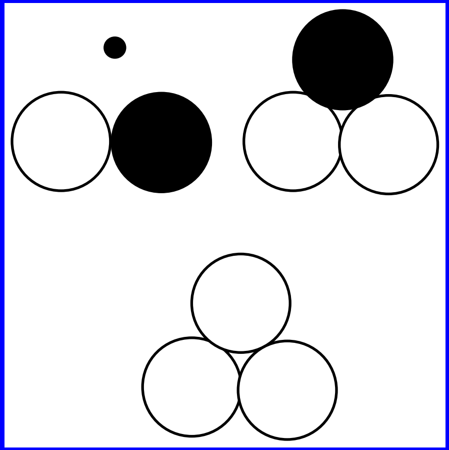
Bonding MO



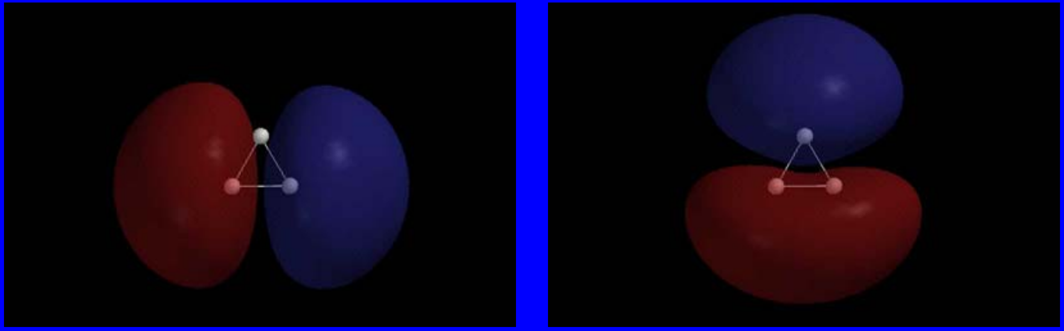
Number of nodal planes incr.

H_3^+

Energy incr.
stability decr.



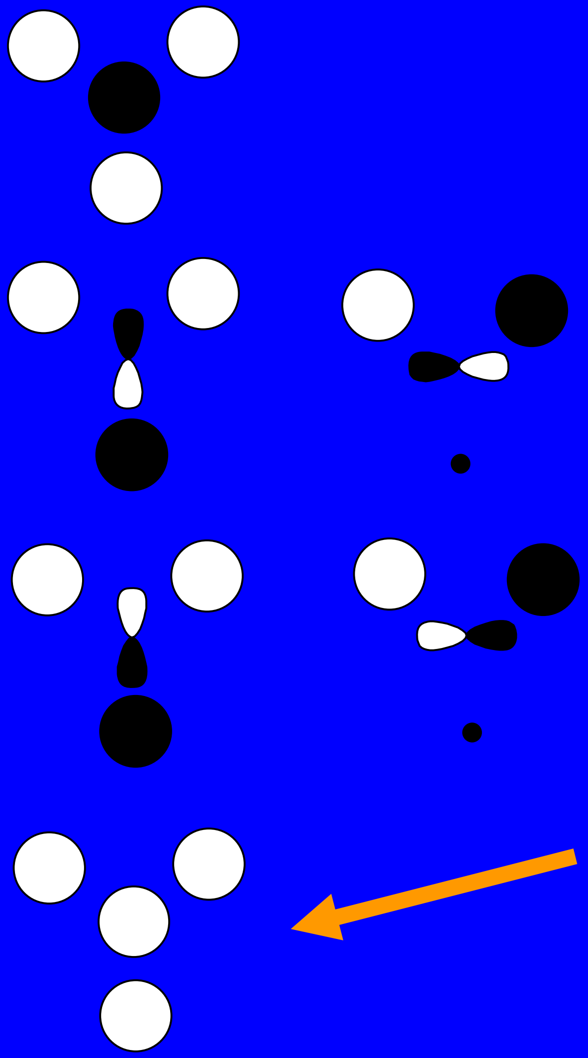
Antibonding MO



Bonding MO

Number of nodal planes incr.

LCAO = Linear Combination of AO



LCAO
n atoms with m orbitals

$$\Psi_i = c_1 \Psi_1 + c_2 \Psi_2 + c_3 \Psi_3 + \ldots + c_n \Psi_n$$

6 AOs (s+2p+3s) will form 6 MOs

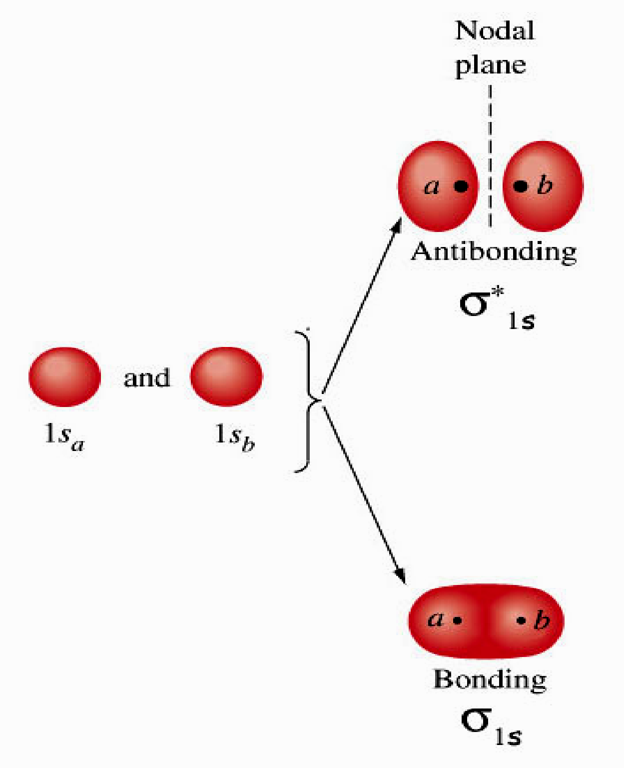
- •MO with the lowest energy
- •no nodal plane
- •the most bonding
- •combination of one AO on each atom
- •all AOs with the same sign

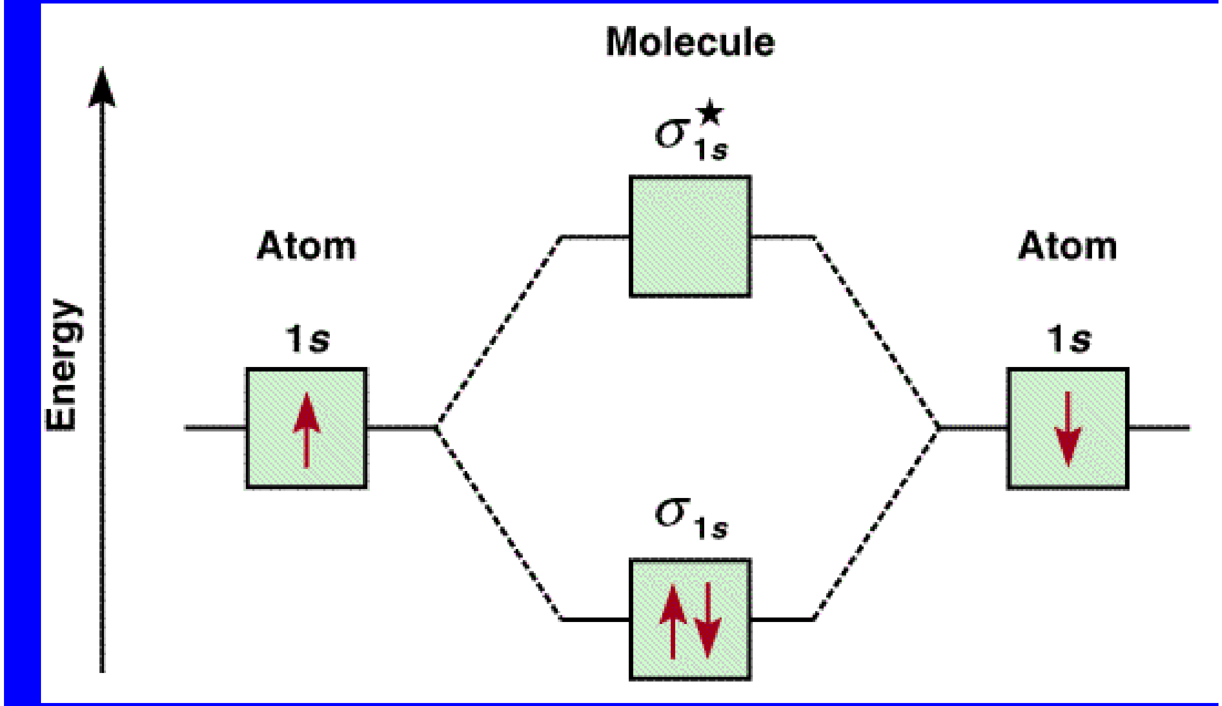
Filling Electrons to MOs

Aufbau
Hund
Pauli

Rules for filling electrons to MOs

Antibonding MO

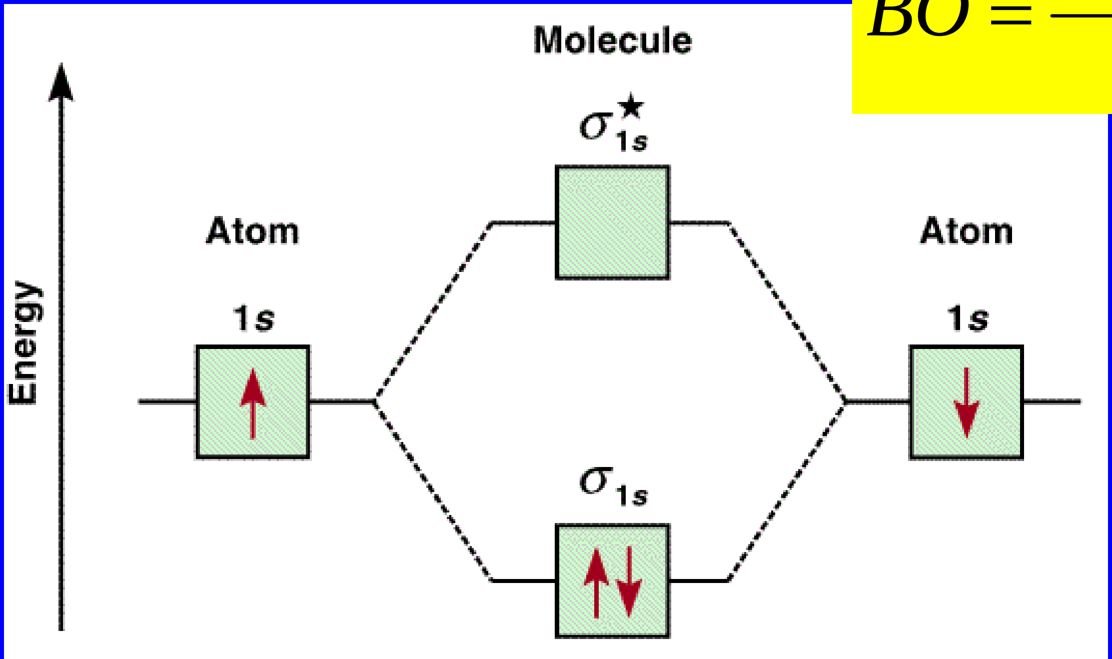




Bonding MO

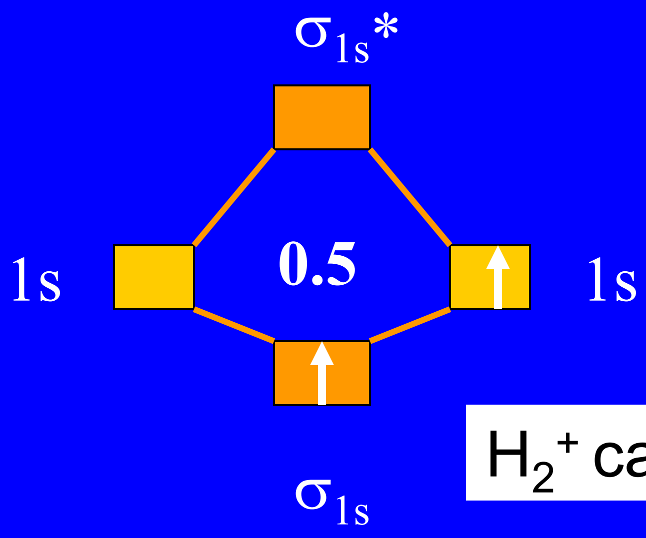
Bond Order

$$BO = \frac{eMO - eMO^{*}}{2}$$

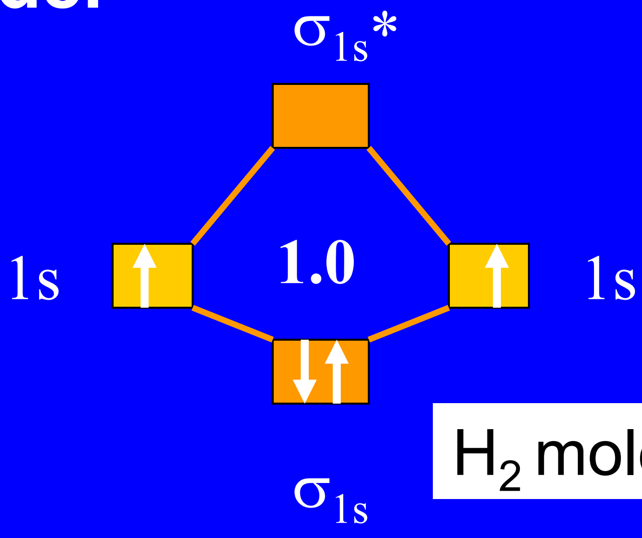


Bond Order = ½ (number of e in bonding MOs
– number of e in antibonding MOs)

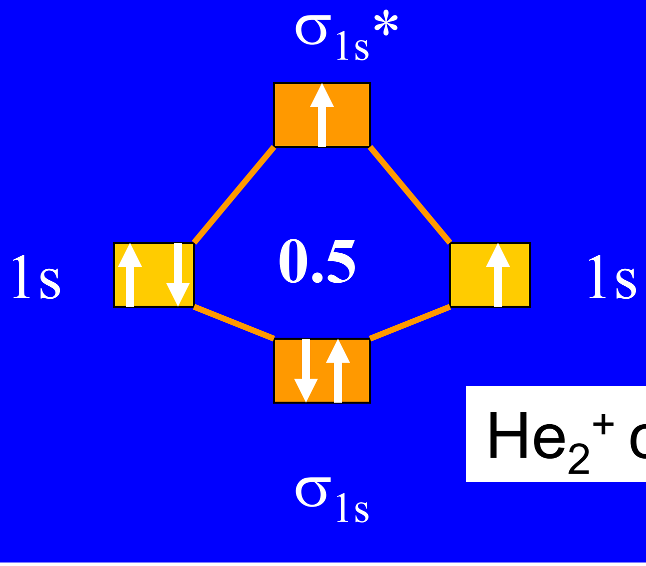
Bond Order



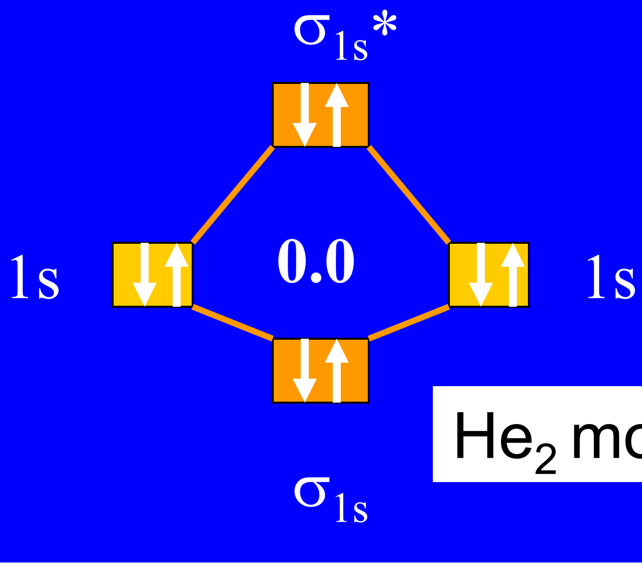
H_2^+ cation



H_2 molecule



He_2^+ cation

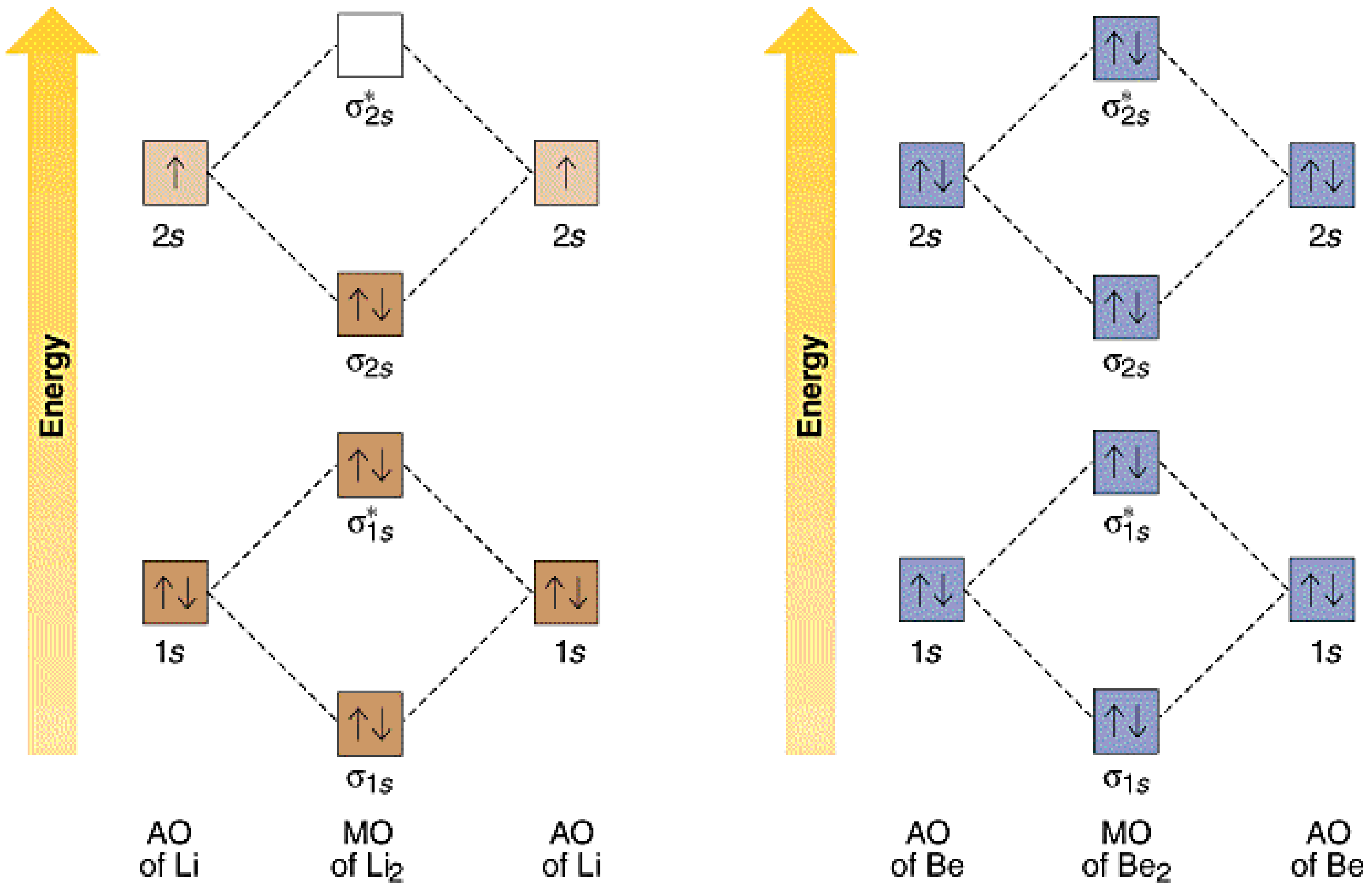


He_2 molecule

Bond Order

Molecule	Bond. electrons	Antibond. electrons	Bond Order	Bond length, Å	Bond energy, kJ mol^{-1}
H_2^+	1	0	0.5	1.06	255
H_2	2	0	1	0.74	432
He_2^+	2	1	0.5	1.08	230
He_2	2	2	0	---	0

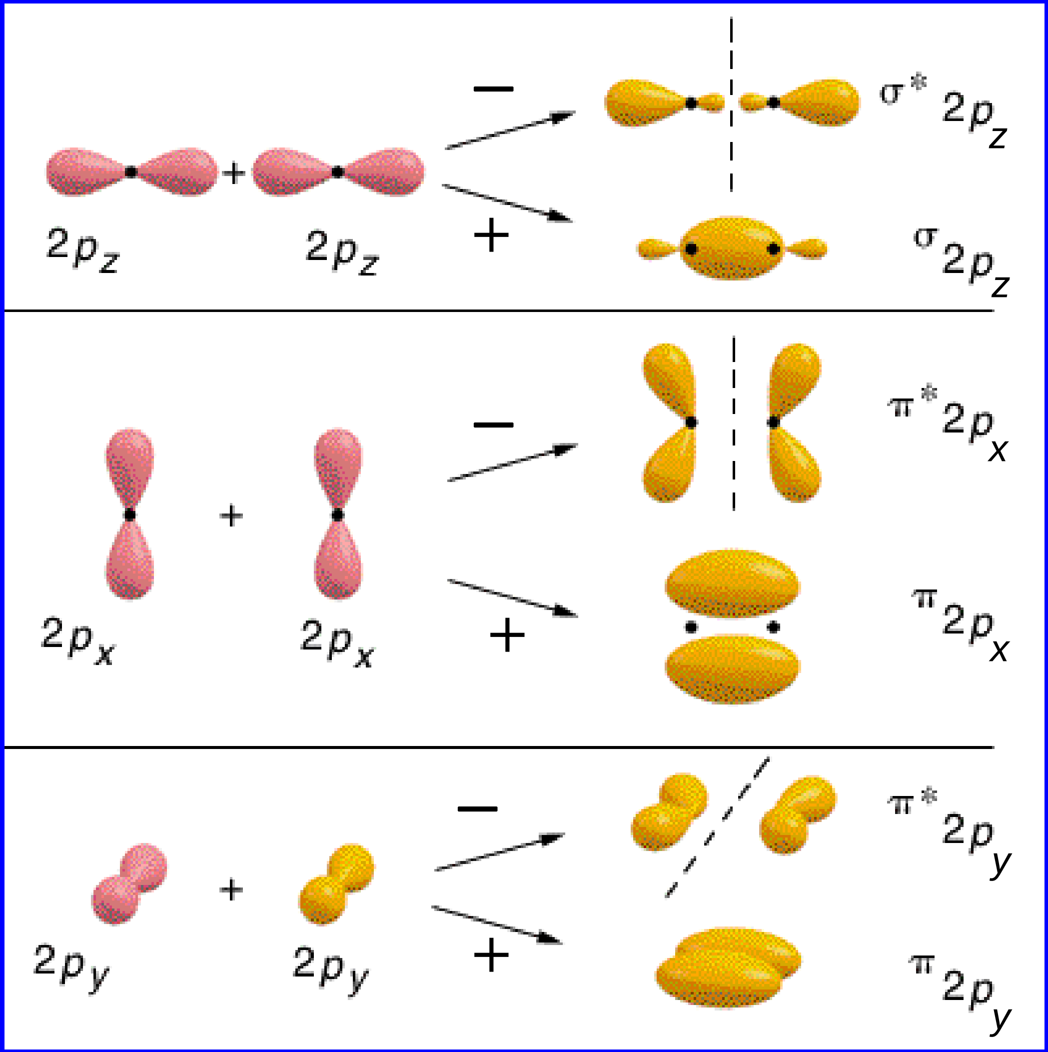
One-electron bond: 1 bonding electron forms a stronger bond than 2 bonding and 1 antibonding electrons



A Li_2 bond order = 1

B Be_2 bond order = 0

MOs by Combination of p AOs



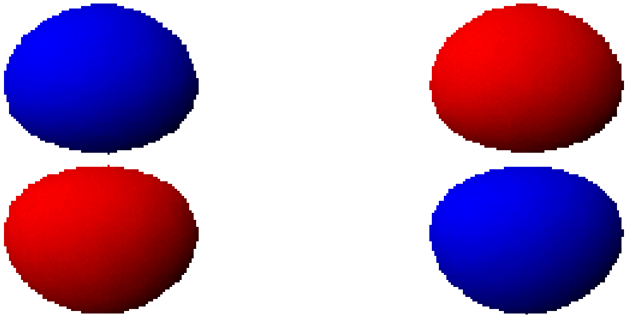
MOs by Combination of p AOs

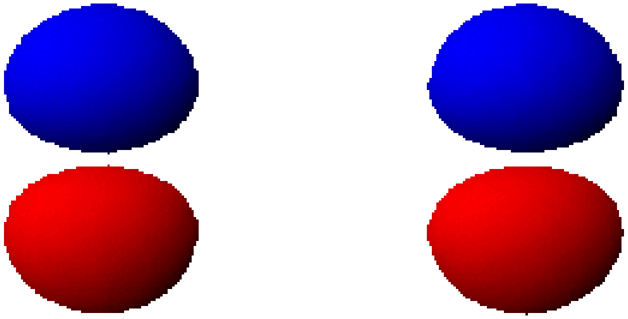
Antibonding MO $\sigma_{2pz}{}^*$

Bonding MO σ_{2pz}

MOs by Combination of p AOs

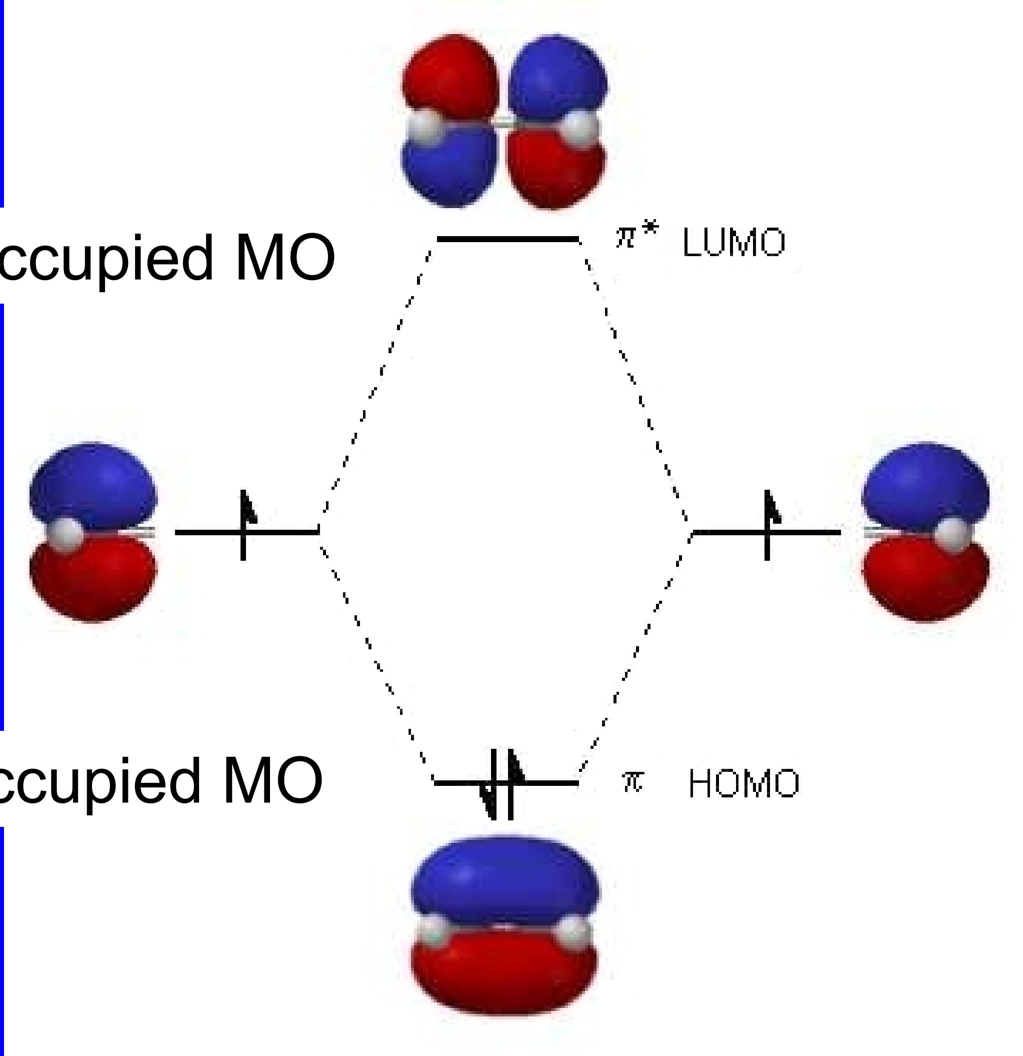
Antibonding MO π_{2px}^*





Bonding MO π_{2px}

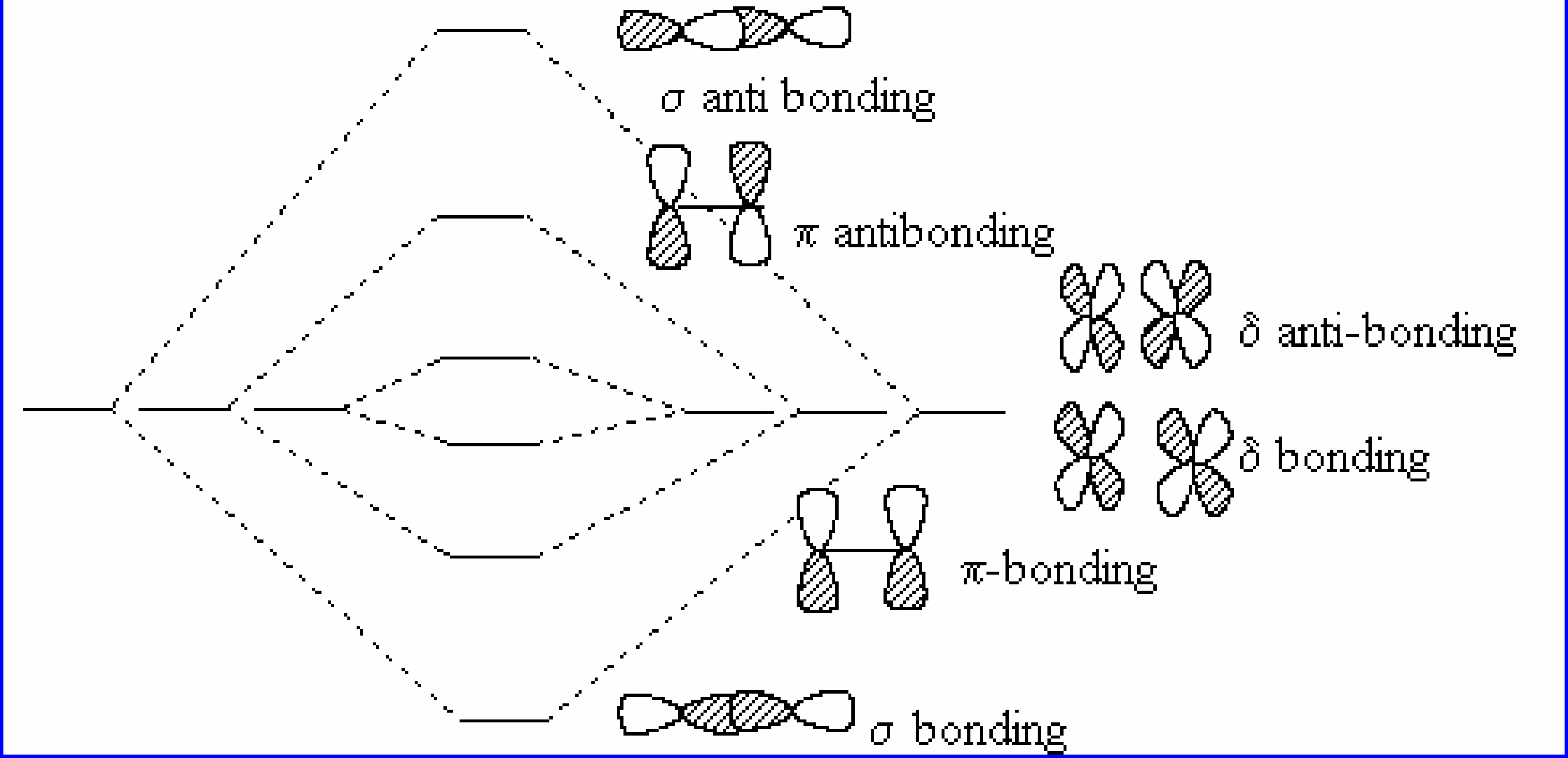
Pi Bond in Ethene



LUMO = lowest unoccupied MO

HOMO = highest occupied MO

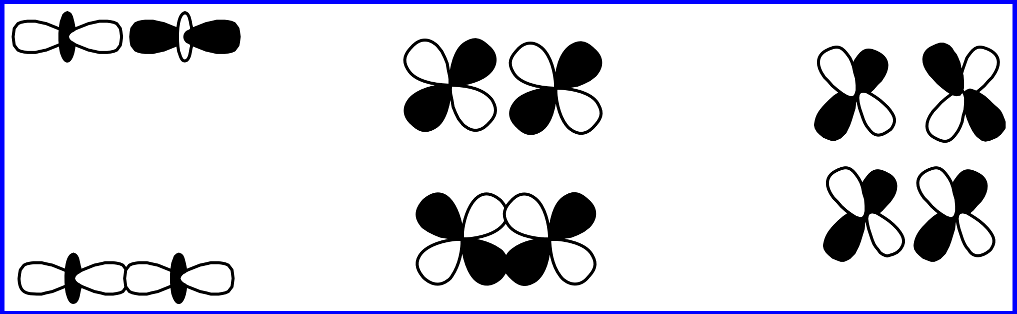
Types of MO

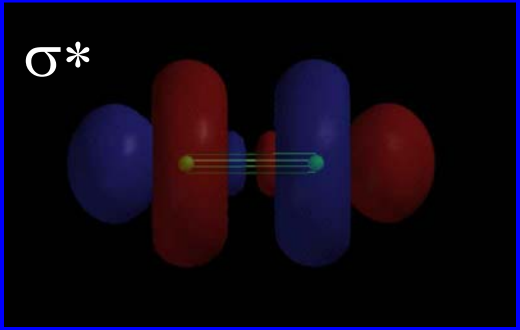


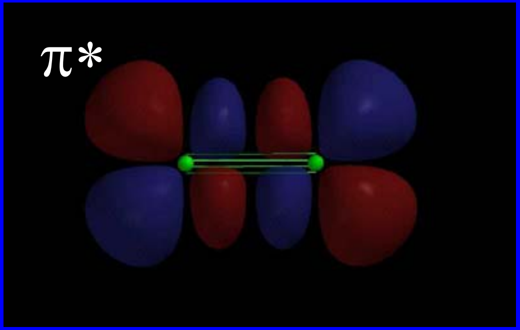
Better overlap decreases energy of bonding MO and increses energy of antibonding MO:

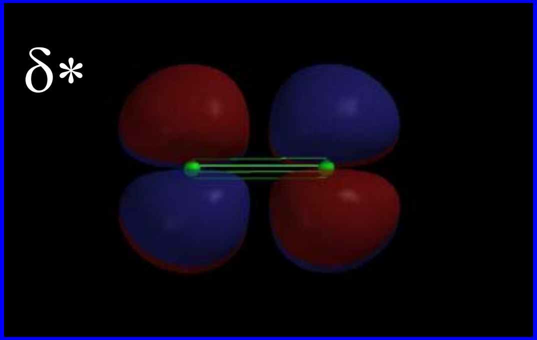
$\sigma > \pi > \delta$

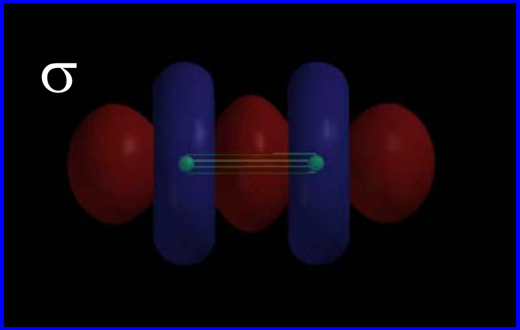
MO from d orbitals

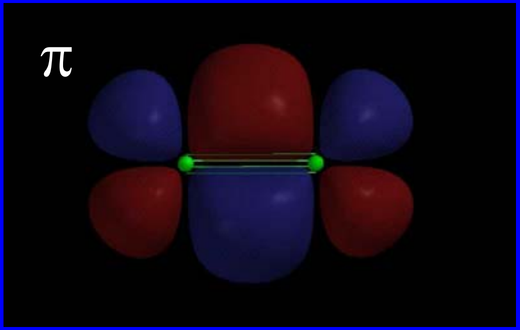


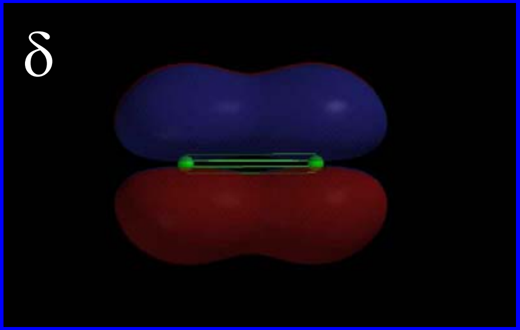












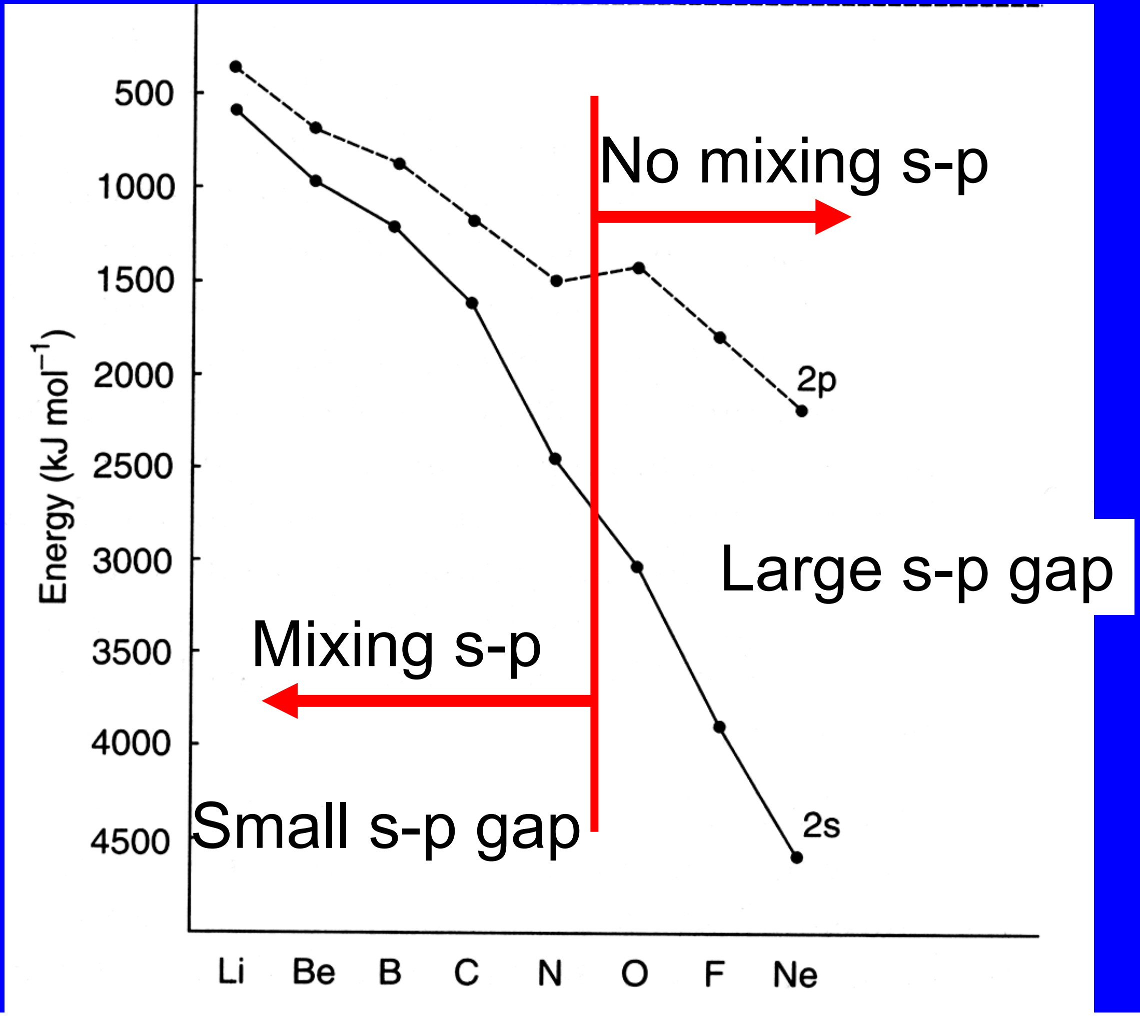
d(z^2) d(z^2)

d(xz) d(xz)
d(yz) d(yz)

d(x^2-y^2) d(x^2-y^2)
d(xy) d(xy)

Mixing of s-p orbitals

Energetically similar orbitals on the same atom can mix



No mixing s-p

Large s-p gap

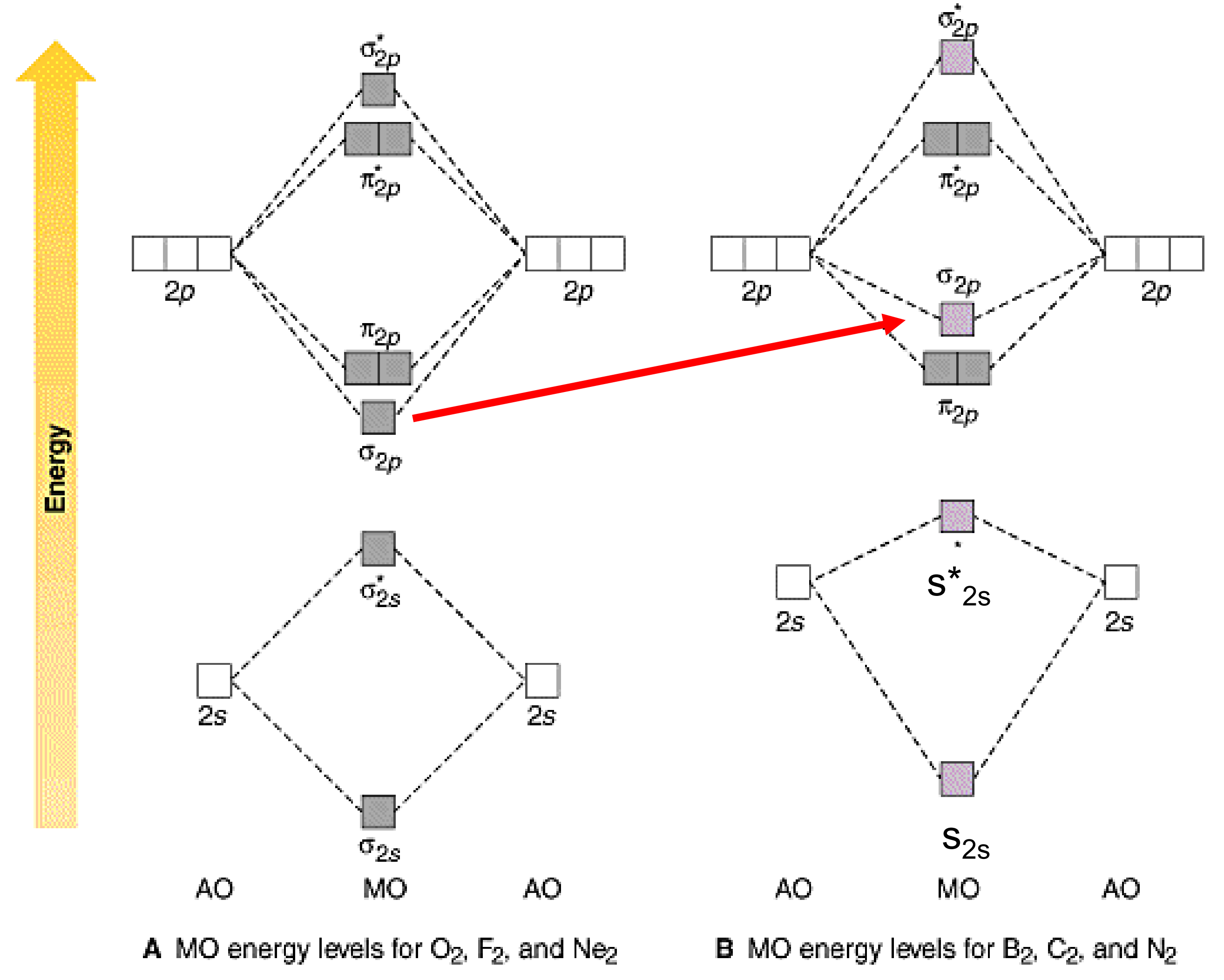
Mixing s-p

Small s-p gap

Energy

No mixing s-p

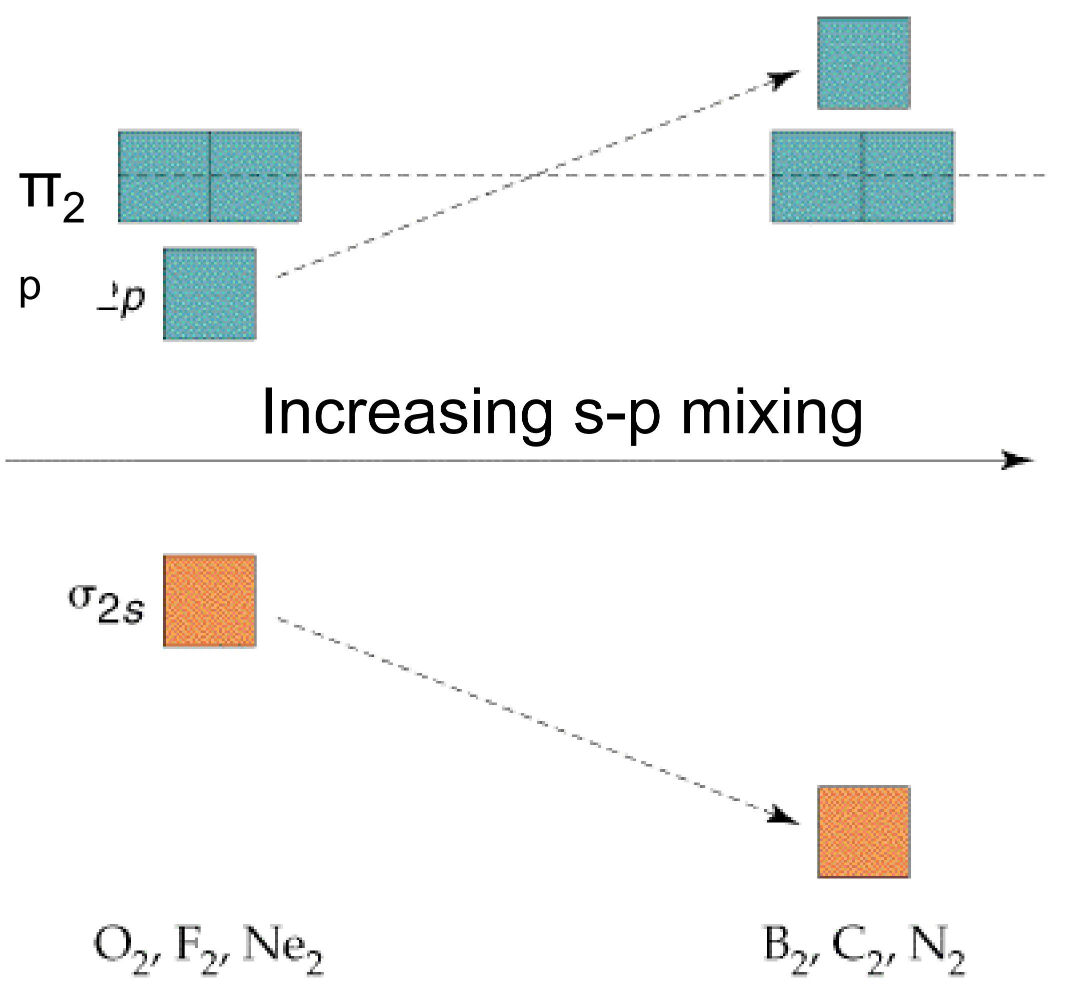
Mixing s-p



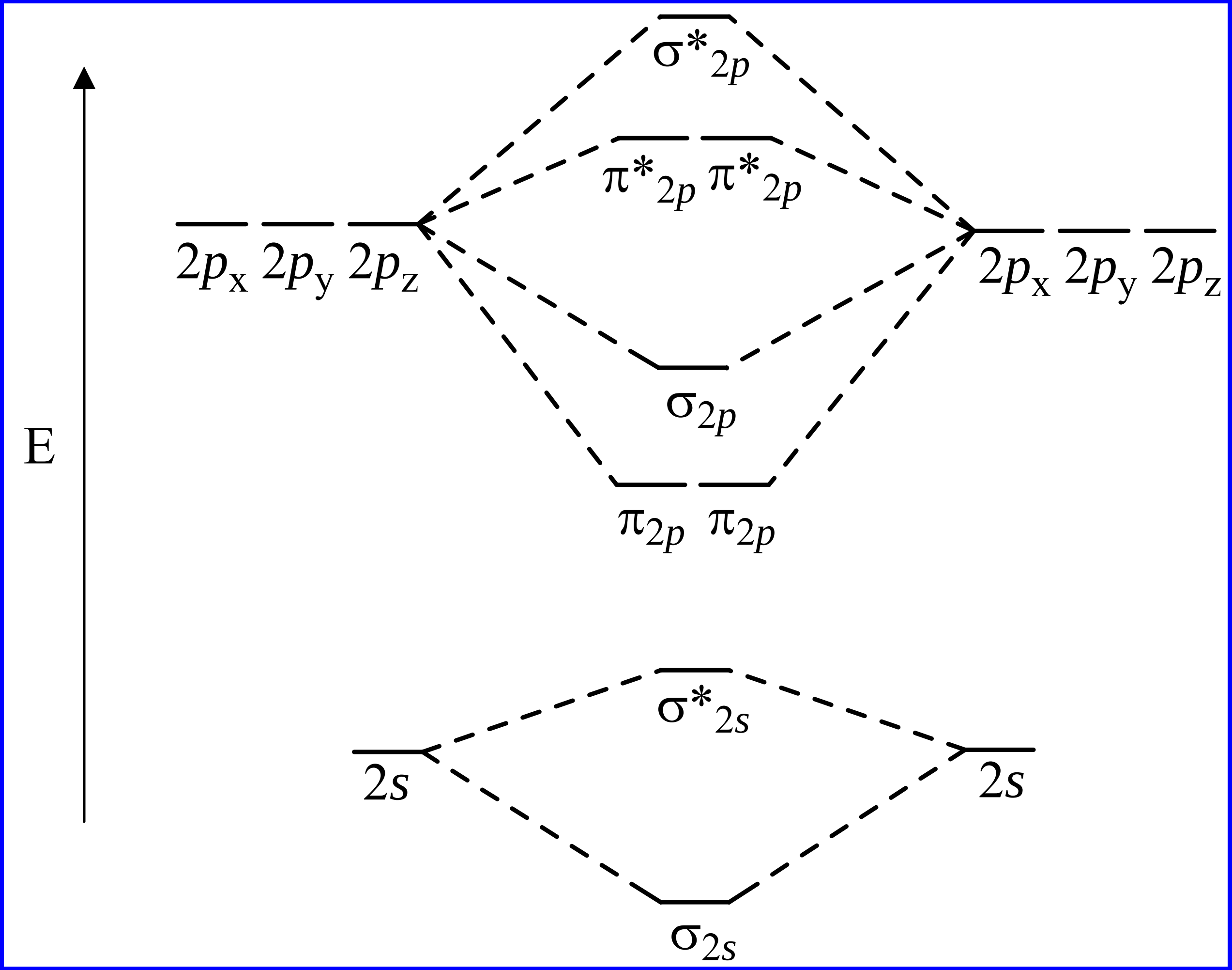
from O_2 to Ne_2

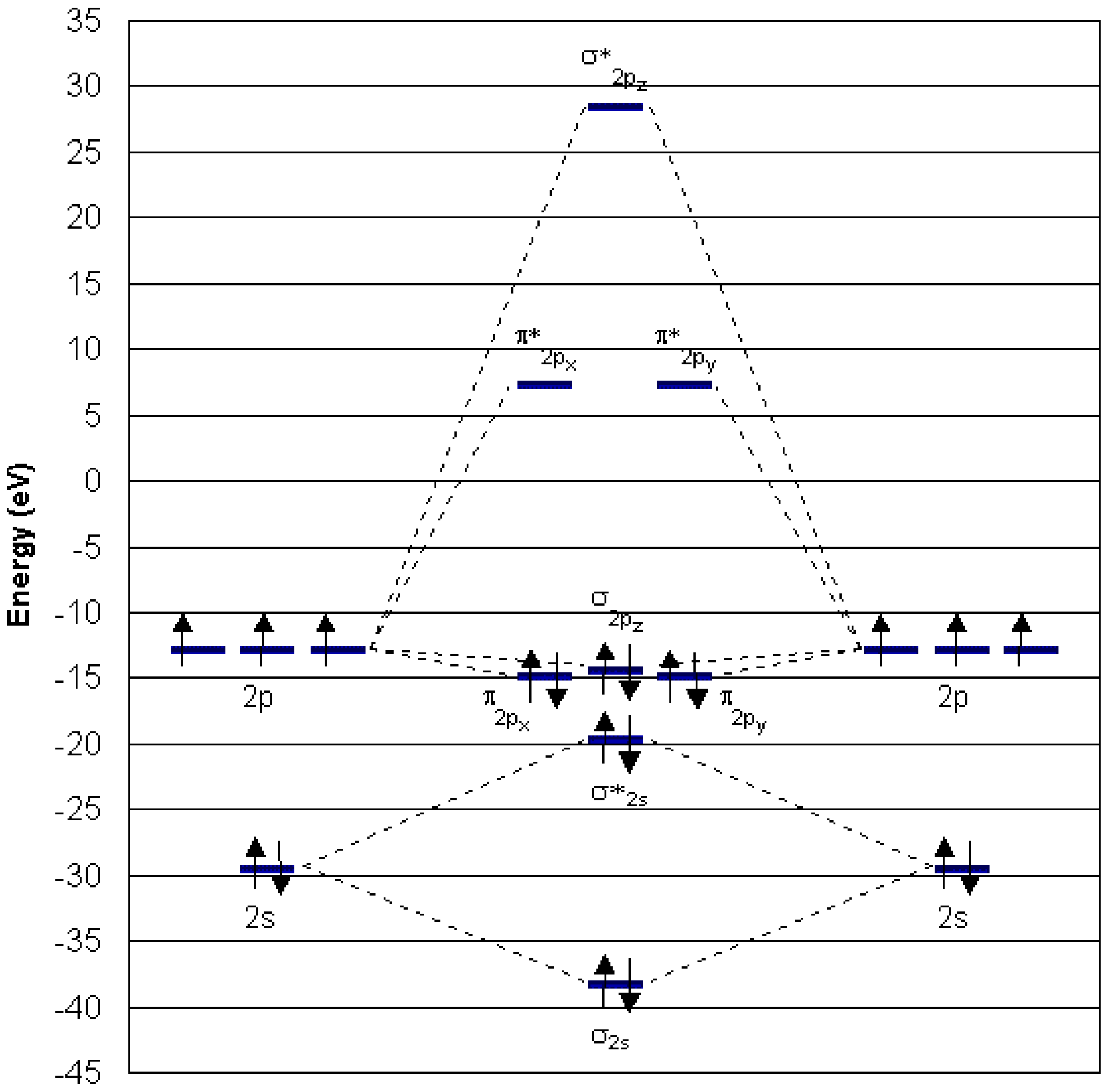
from H_2 to N_2

Diatomic Molecules

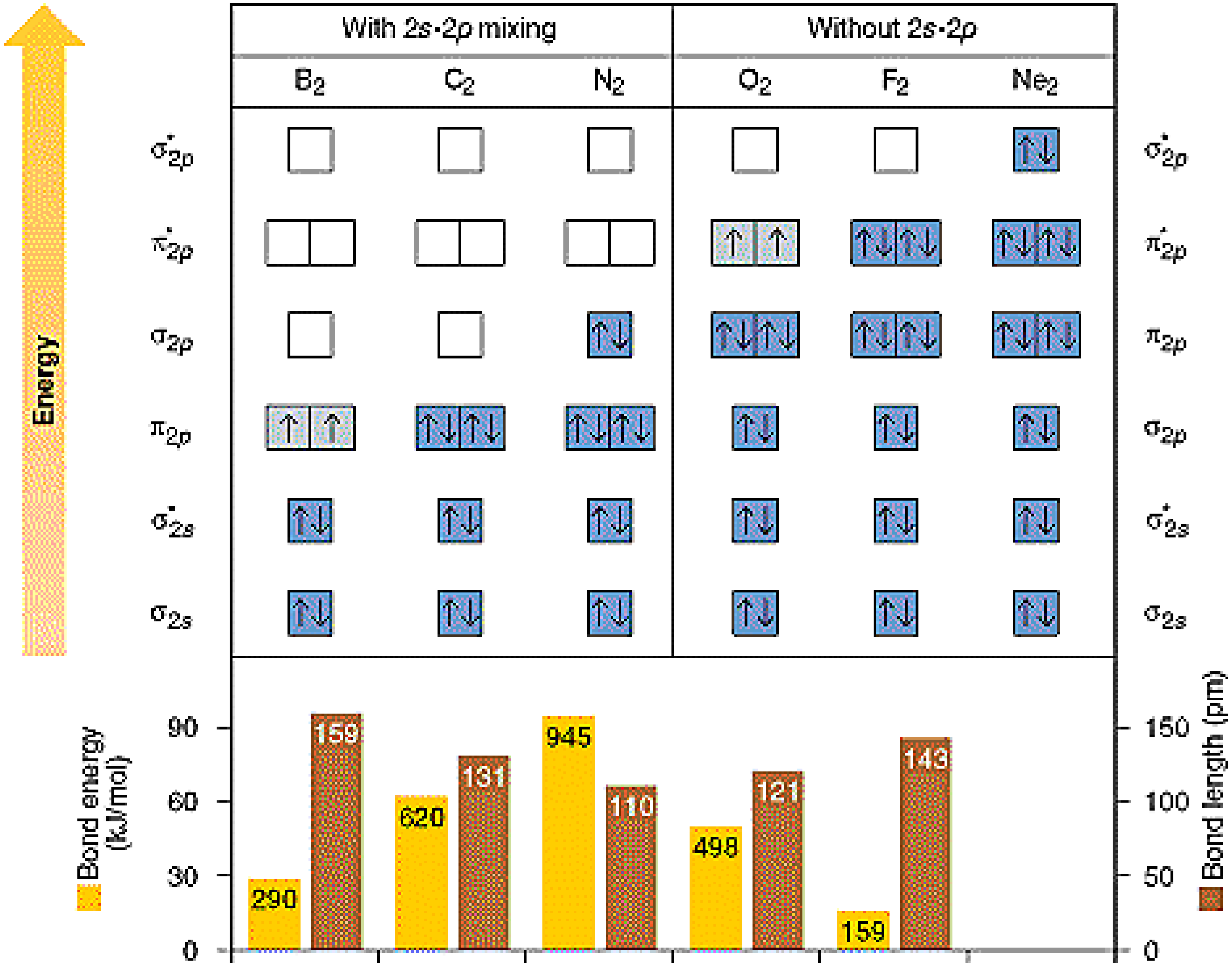


Interaction Diagram for Li_2 to N_2



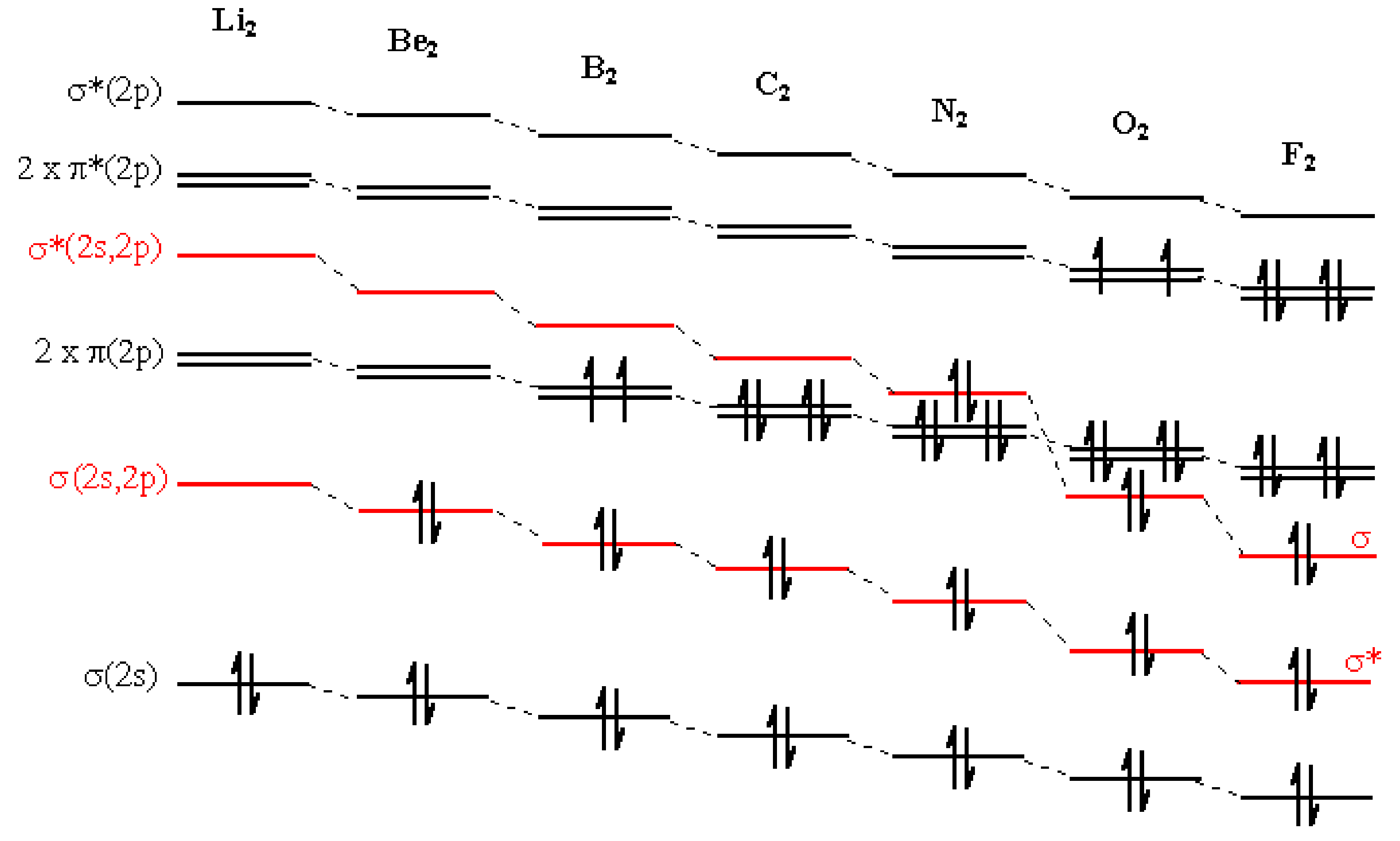


Energy (eV)
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
σ* 2pz
π* 2px
π* 2py
σ 2pz
π 2px
π 2py
2p
2p
σ*2s
2s
2s
σ2s



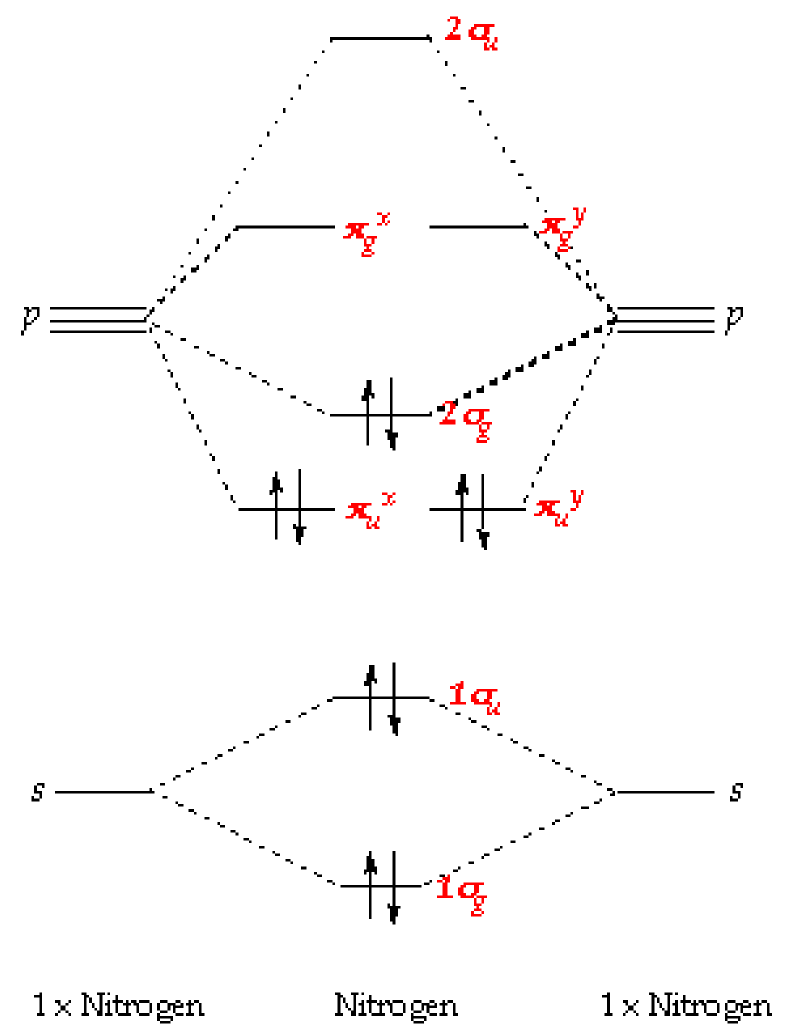
Bond order	1	2	3	2	1	0
Magnetic properties	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—
Valence electron configurations	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^4$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^4(\sigma_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^4$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^4(\sigma^*_{2p})^2$

Diatomic Molecules

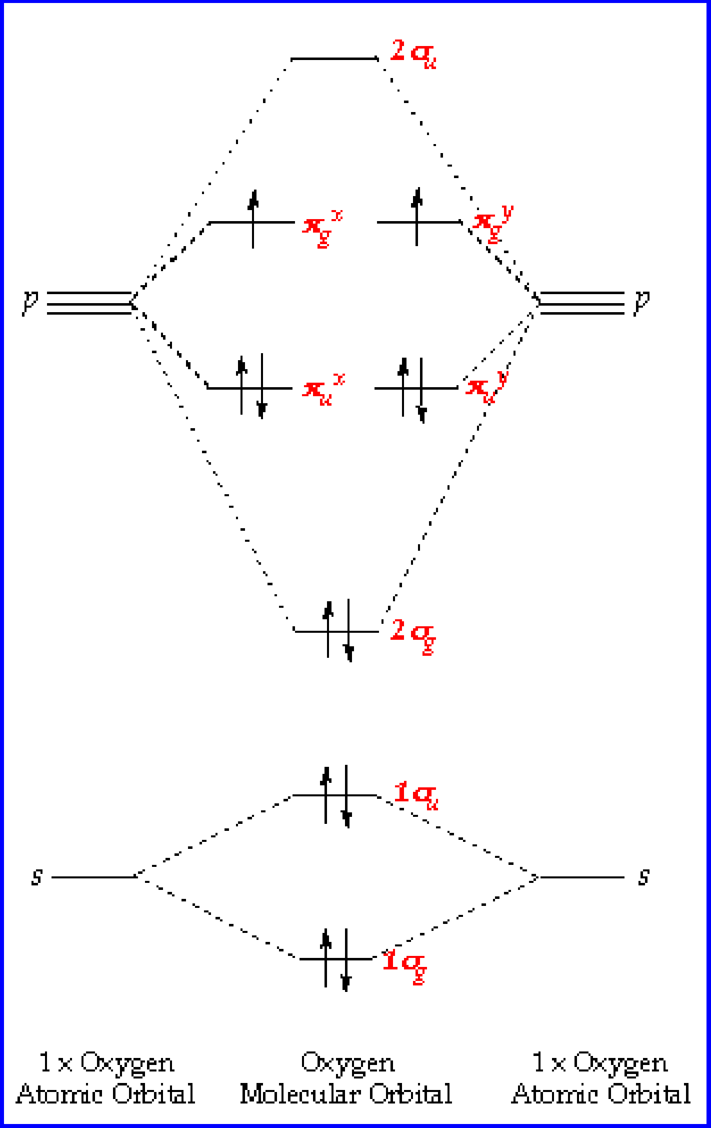


Diatomic Molecules in the Gas Phase

		Bond length (pm)	**E_{bond}(kJ mol^{-1})**
Li-Li	σ_{2s}^{2}	267	110
Be...Be	$\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}$	?	?
B-B	$\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \pi_{2p}^{2}$	159	290
C=C	$\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \pi_{2p}^{4}$	124	602
N≡N	$\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \pi_{2p}^{4}\ \sigma_{2p}^{2}$	110	942
O=O	$\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \sigma_{2p}^{2}\ \pi_{2p}^{4}\ \pi^{*}_{2p}{}^{2}$	121	494
F-F	$\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \sigma_{2p}^{2}\ \pi_{2p}^{4}\ \pi^{*}_{2p}{}^{4}$	142	155



N_2 Triple bond



O_2 paramagnetic molecule

Oxygen and its Molecular Ions

	O_2^+		O_2		O_2^-		O_2^{2-}	
Number of valence electrons	11		12		13		14	
Occupation of HOMO $\pi_x{}^*$ a $\pi_y{}^*$	↑		↑	↑	↑↓	↑	↑↓	↑↓
Bond order	2.5		2.0		1.5		1.0	
Bond length, pm	112		121		126		149	

Multiplicity

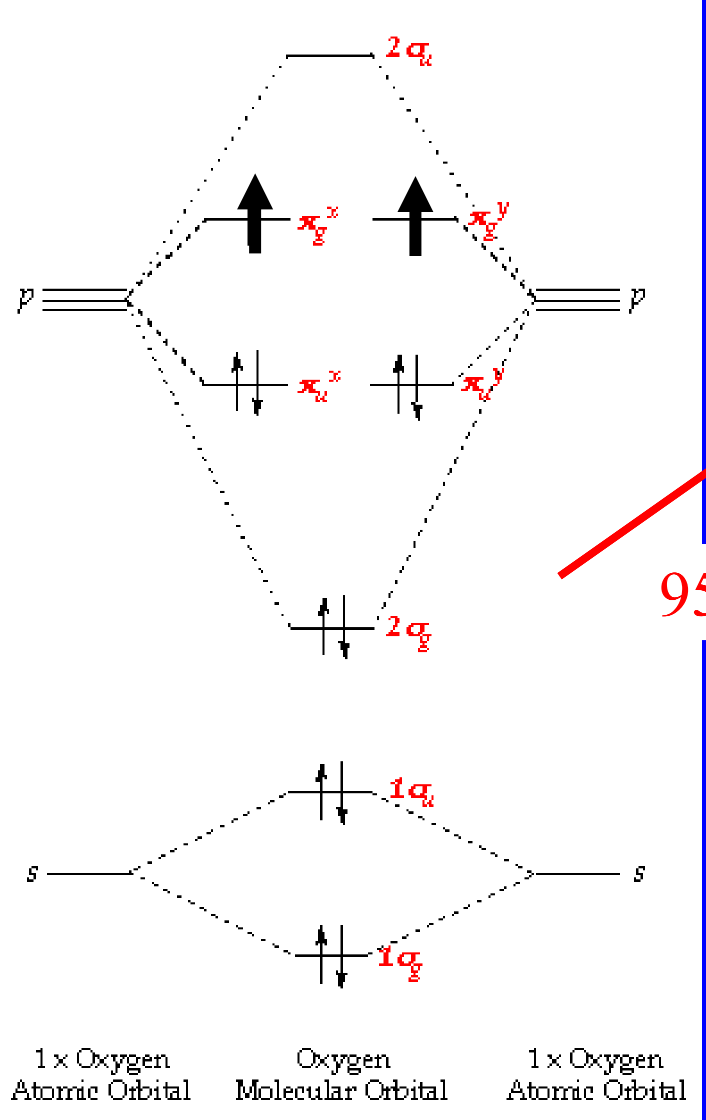
M = 2 **S** + 1

S = sum of unpaired spins (½) in an atom or a molecule

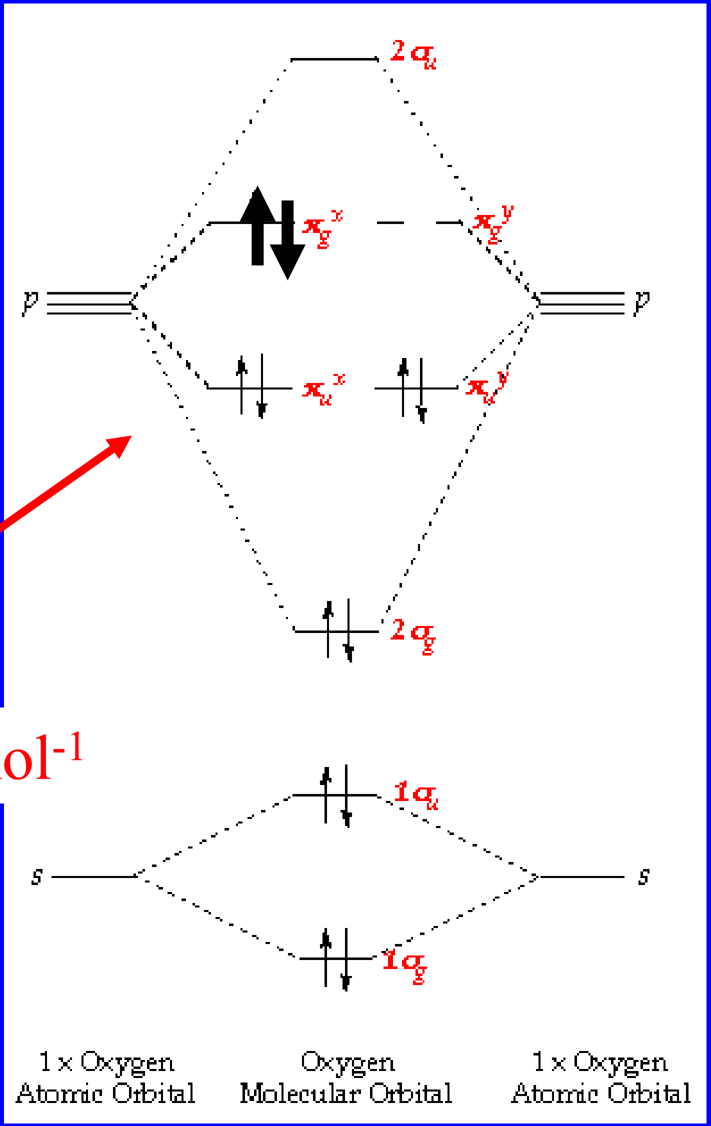
M		**S**	
1	singlet	0	↑↓
2	dublet	½	↑
3	triplet	1	↑↑
4	quartet	1½	↑↑↑
5	quintet	2	↑↑↑↑
6	sextet	2½	↑↑↑↑↑

Singlet Oxygen $^1\Delta$

Triplet Oxygen $^3\Sigma$



95 kJ mol^{-1}

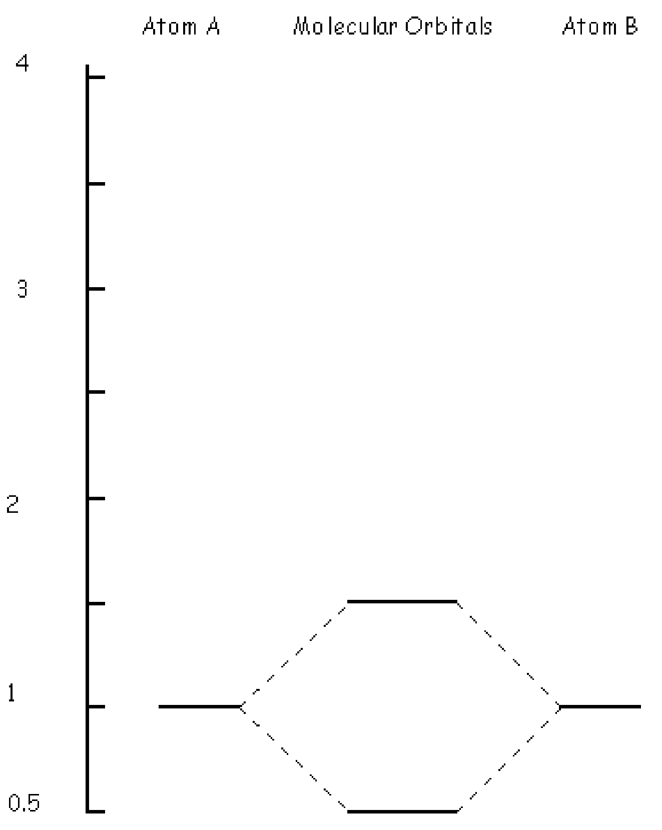


Isoelectronic Molecules

Number of valence electrs	Diatomic Species
9	BO, CN, CP, CO^+
10	N_2, CO, CN^-, BF, NO^+, TiO, SiO
11	O_2^+, ·NO, SO^+
12	O_2, SO
13	O_2^-, Cl_2^+, ·ClO
14	F_2, O_2^{2-}, ClO^-

MO in Polar Molecules

$\Psi^* = c_3\,\Psi_A - c_4\,\Psi_B$



$\Psi = c_1\,\Psi_A + c_2\,\Psi_B$

$\chi(A) \ll \chi(B)$ ionic bond

$c_1 \rightarrow 0$ bonding MO $= \Psi_B$

$c_4 \rightarrow 0$ antibonding MO $= \Psi_A$

$\chi(A) < \chi(B)$ a polar bond

$c_1 < c_2$ bonding MO has higher contribution from B

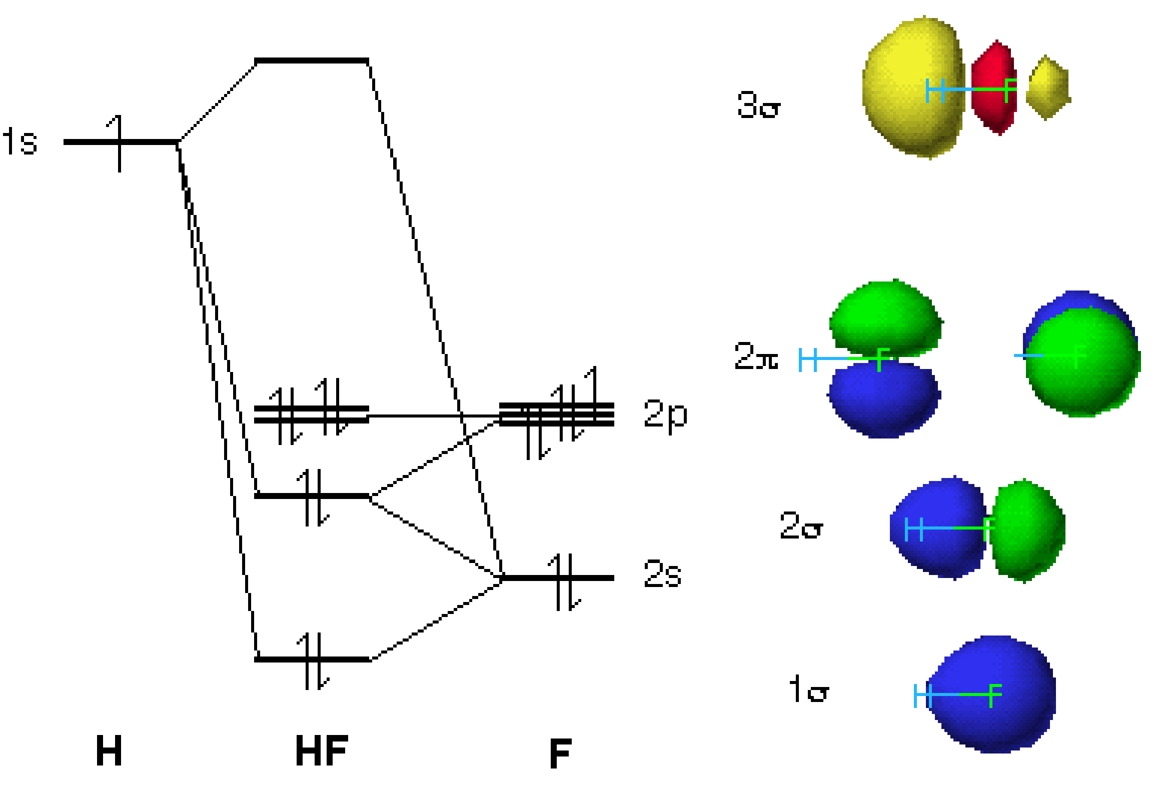
$c_3 > c_4$ antibonding MO has higher contribution from A

$\chi(A) = \chi(B)$ a nonpolar bond

$c_1 = c_2$ $c_3 = c_4$

Same contribution from A and B

MO in Polar Molecules - HF



antibonding MO

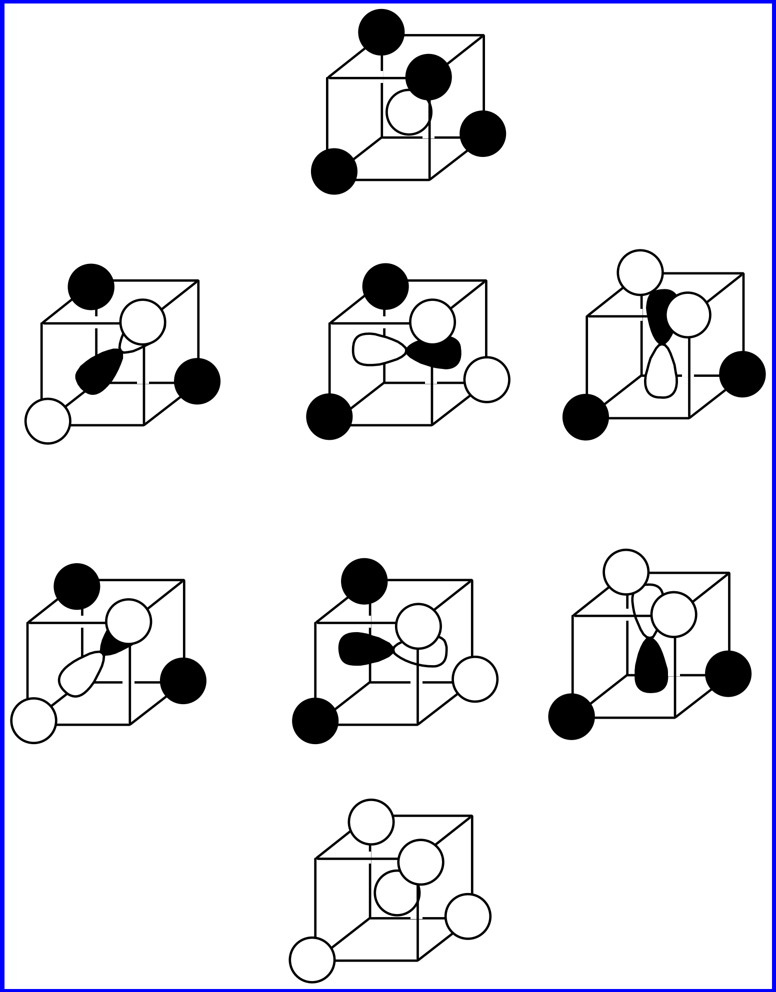
nonbonding MO

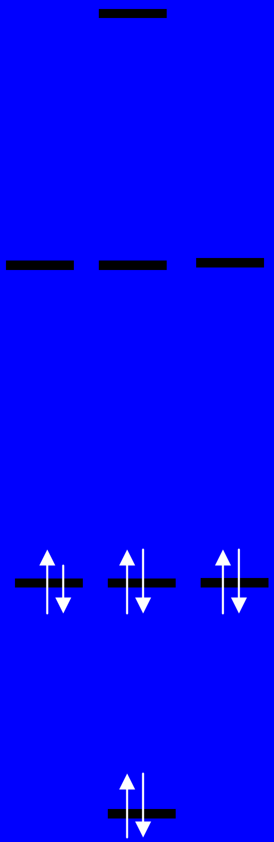
weakly bonding MO

bonding MO

Bonding MO concentrated on an atom with high electronegativity - F
Antibonding MO concentrated on an atom with low electronegativity - H

Molecular Orbitals in CH_4



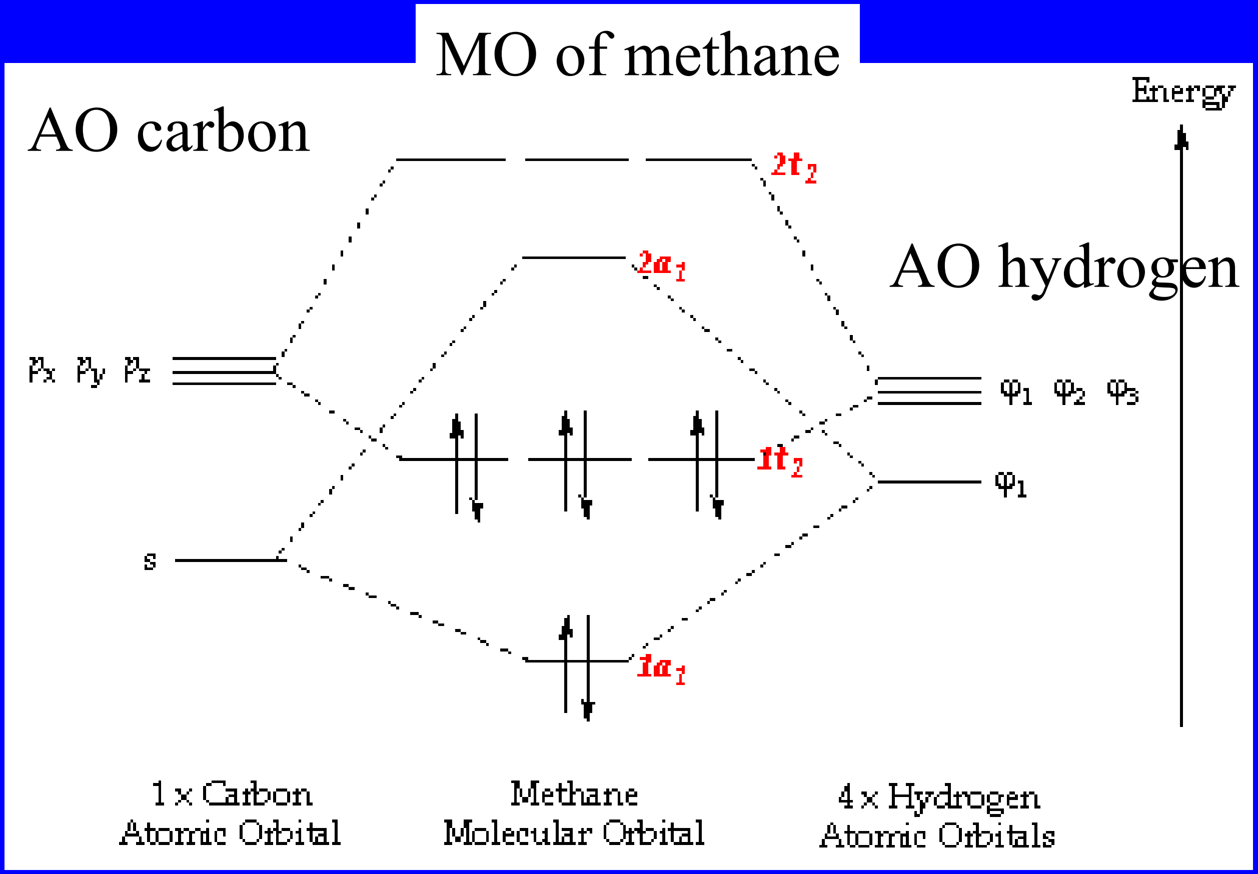


Atomic orbitals used

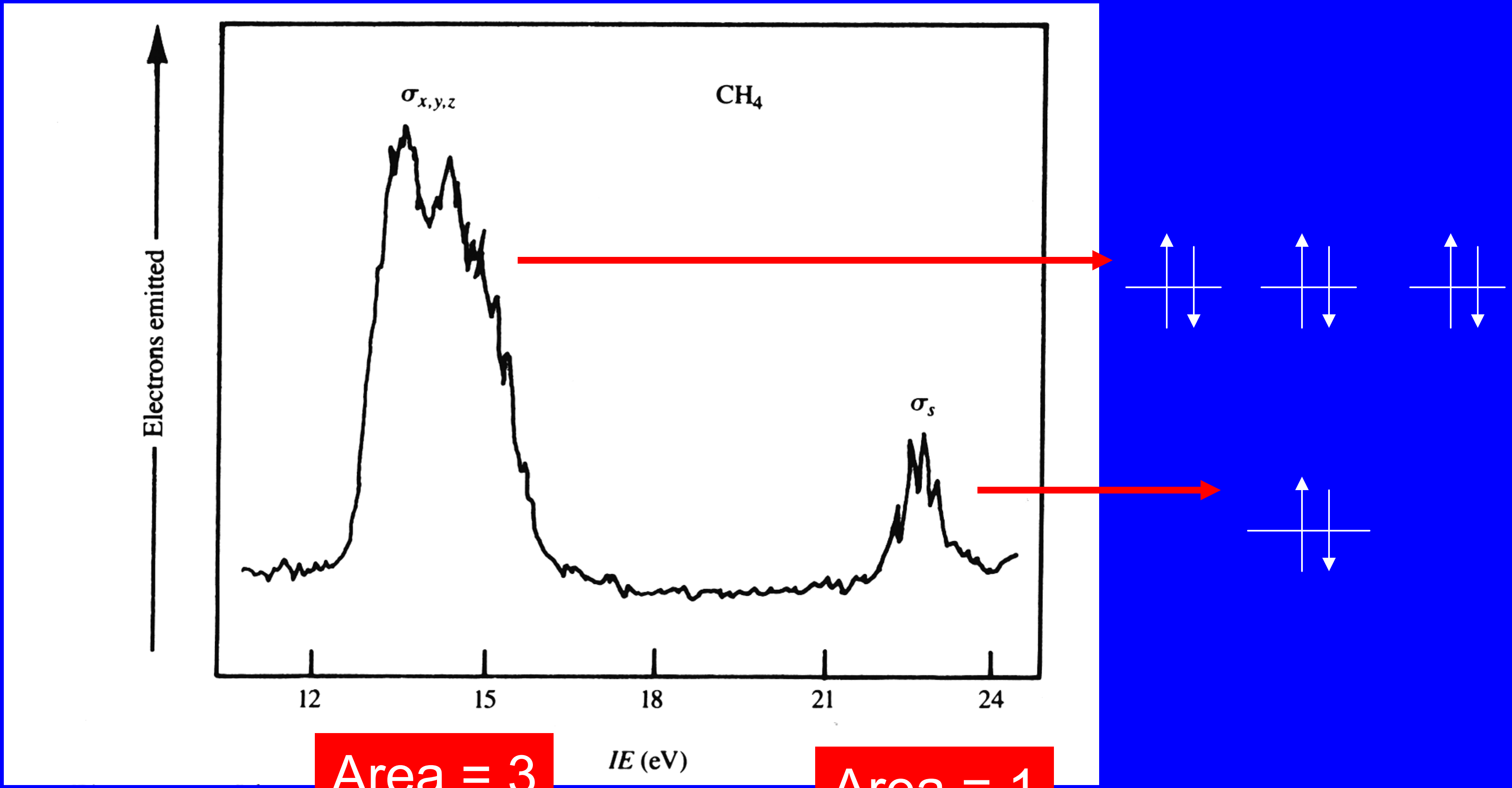
C s + 3×p
4H 4×s

C + 4H
8 electrons

Molecular Orbitals in CH_4

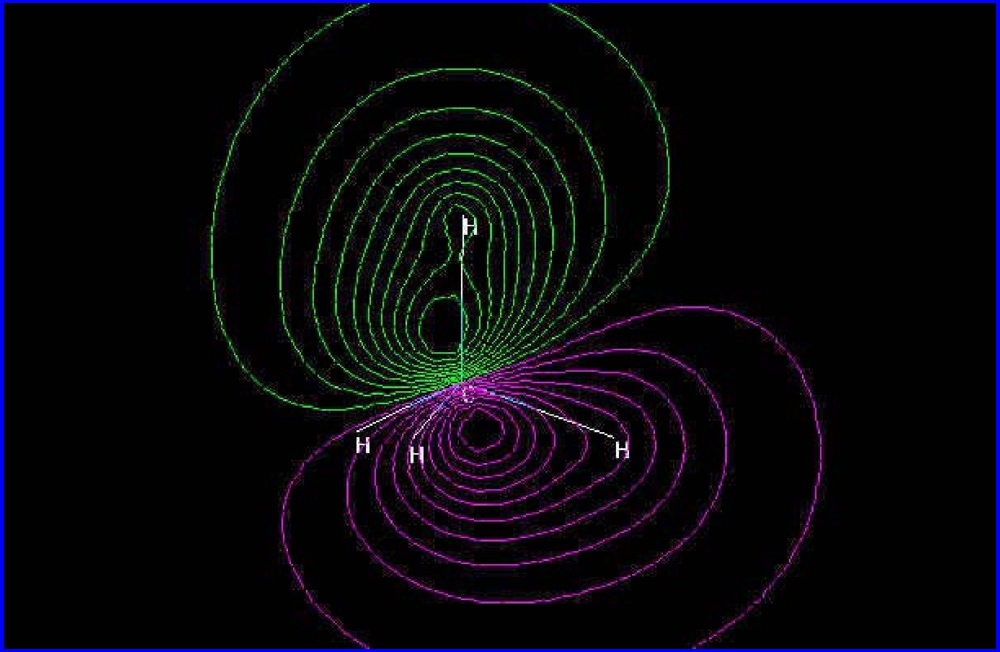


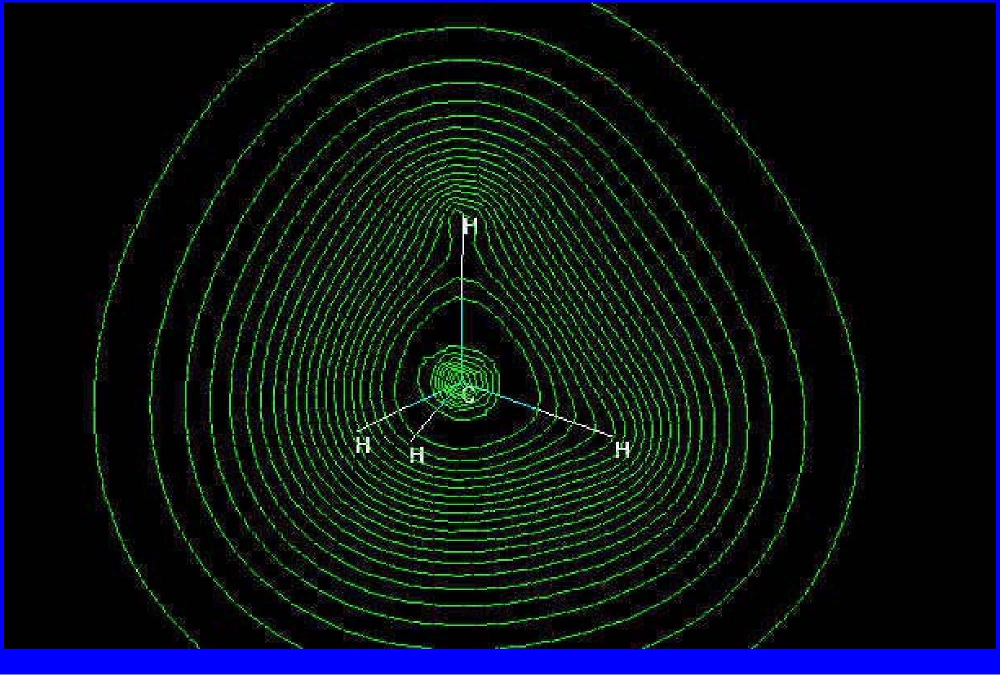
PES in Agreement with the MO Model



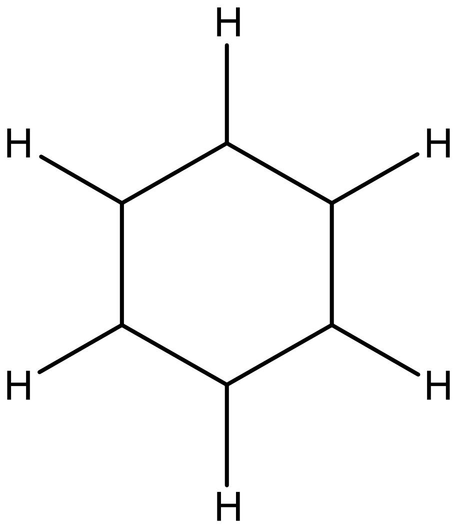
Area = 3

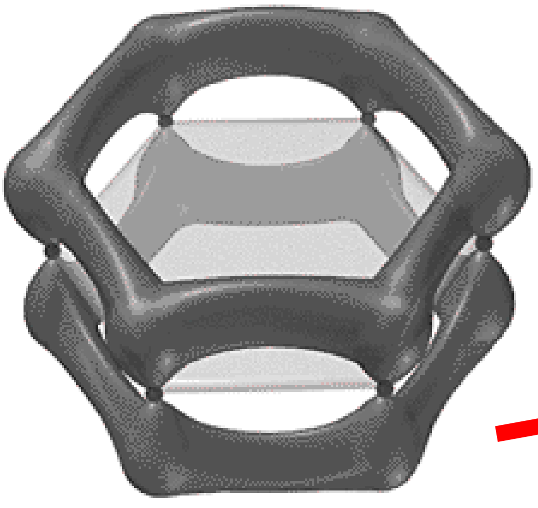
Area = 1

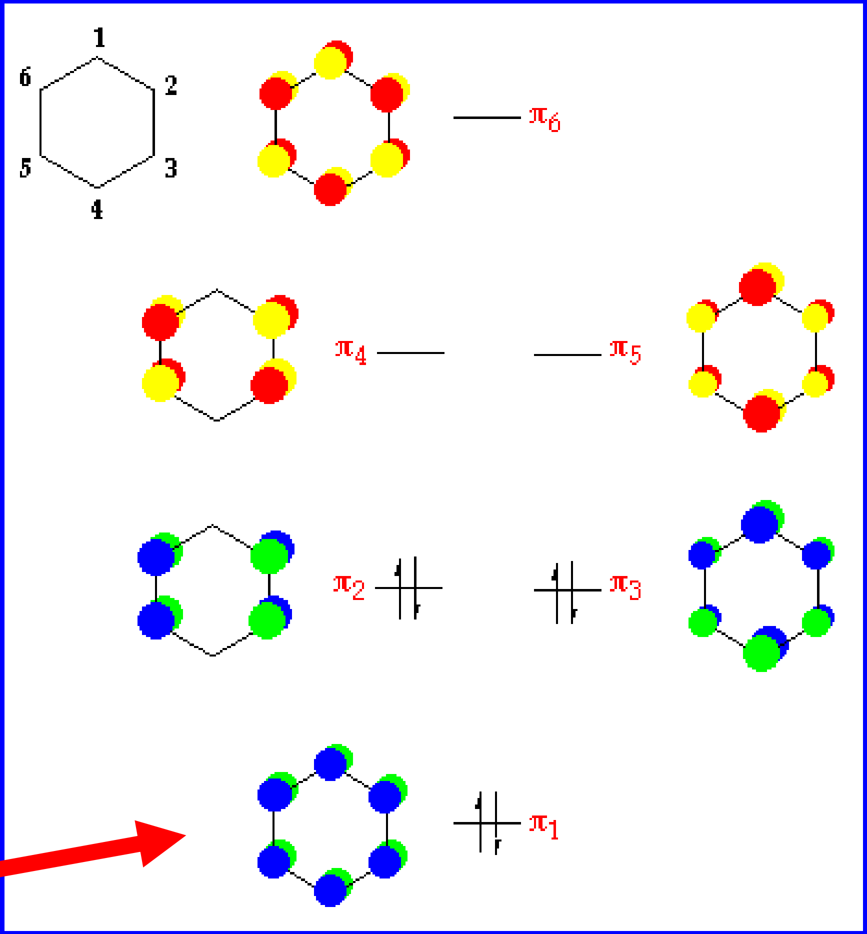

H
C
H
H
H


H
C
H
H
H

Benzene

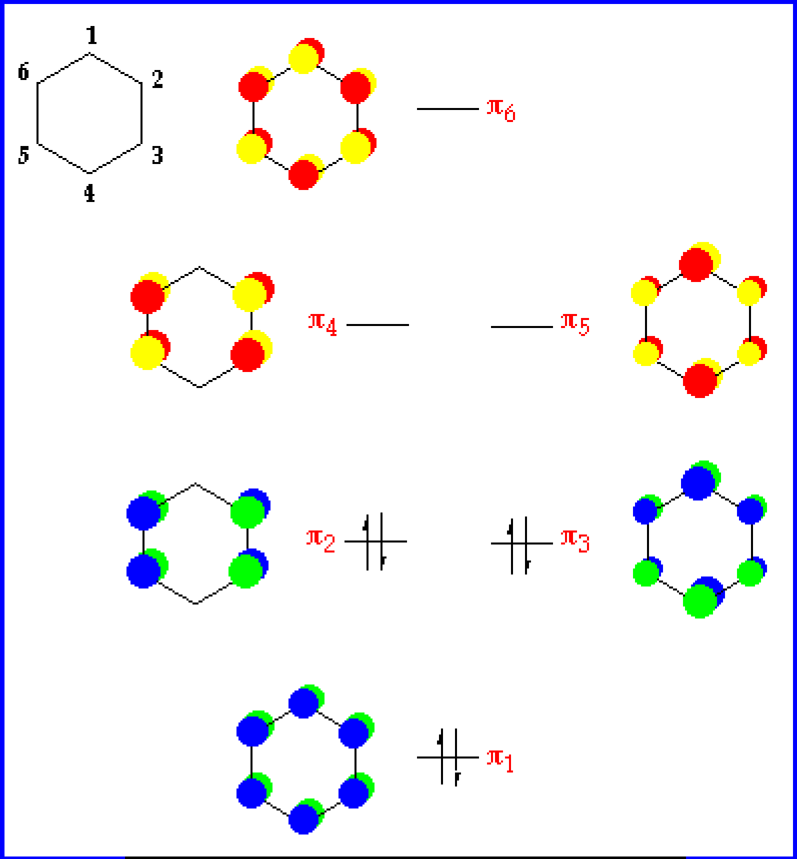


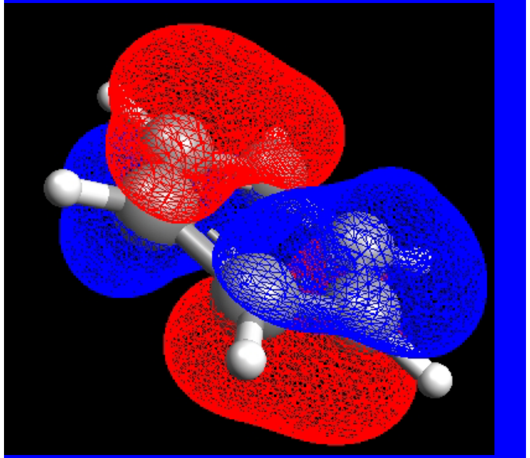

A Benzene, C_6H_6

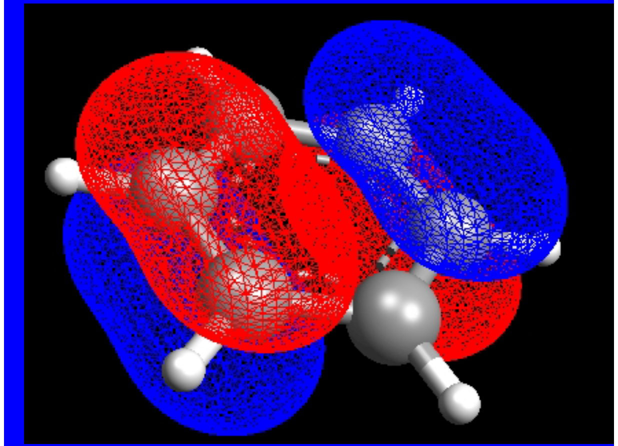


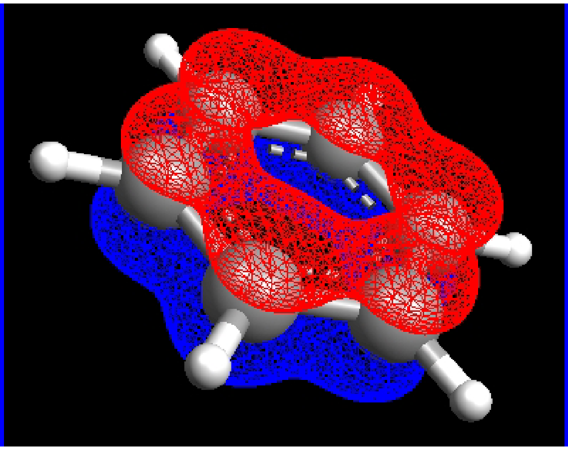
Separate sigma and pi system

Bonding MOs in Benzene

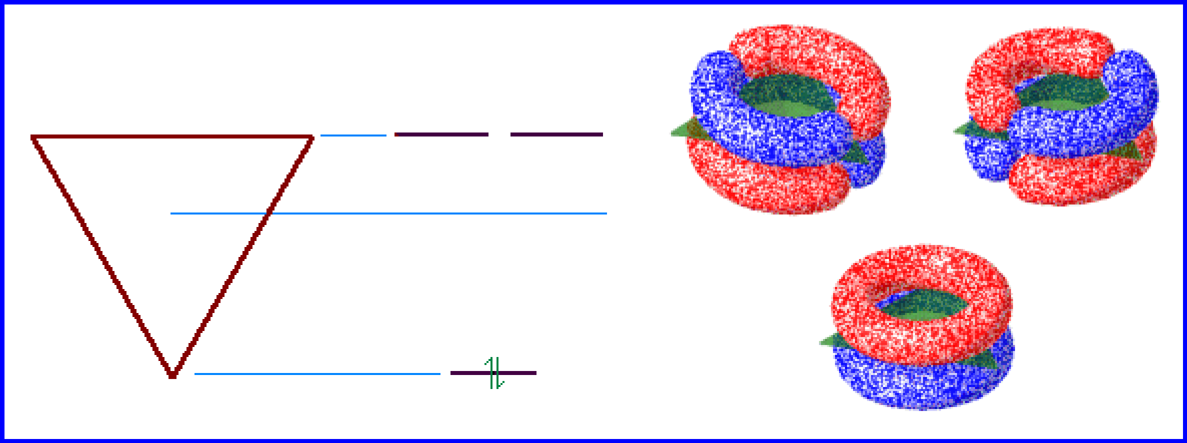




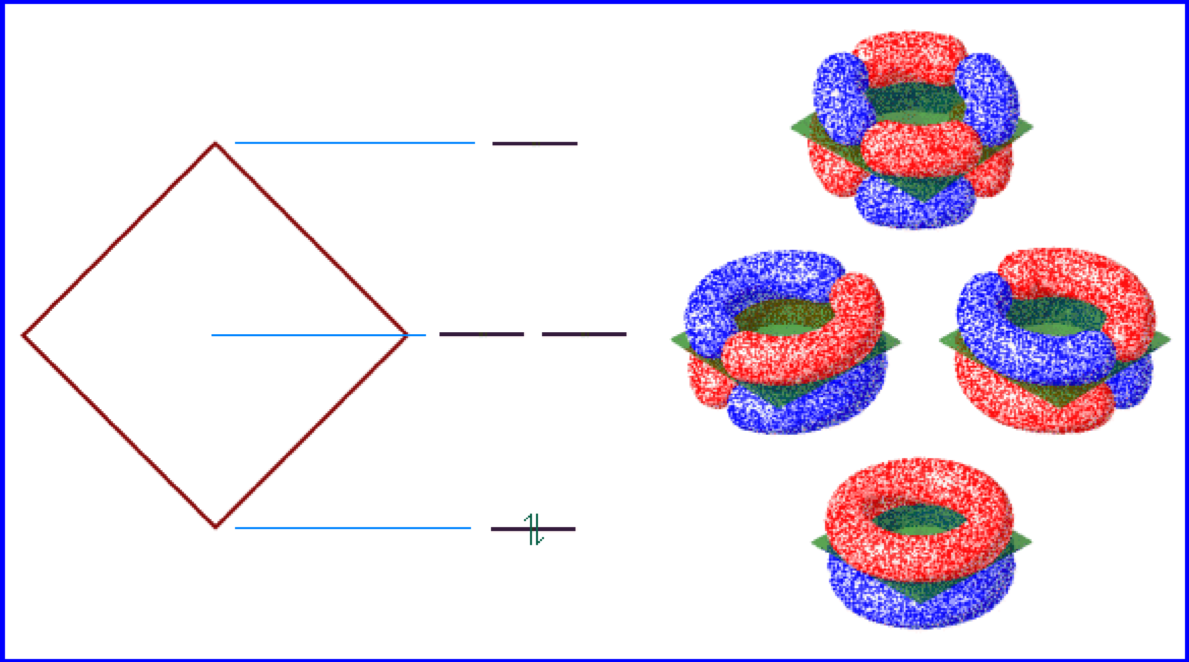




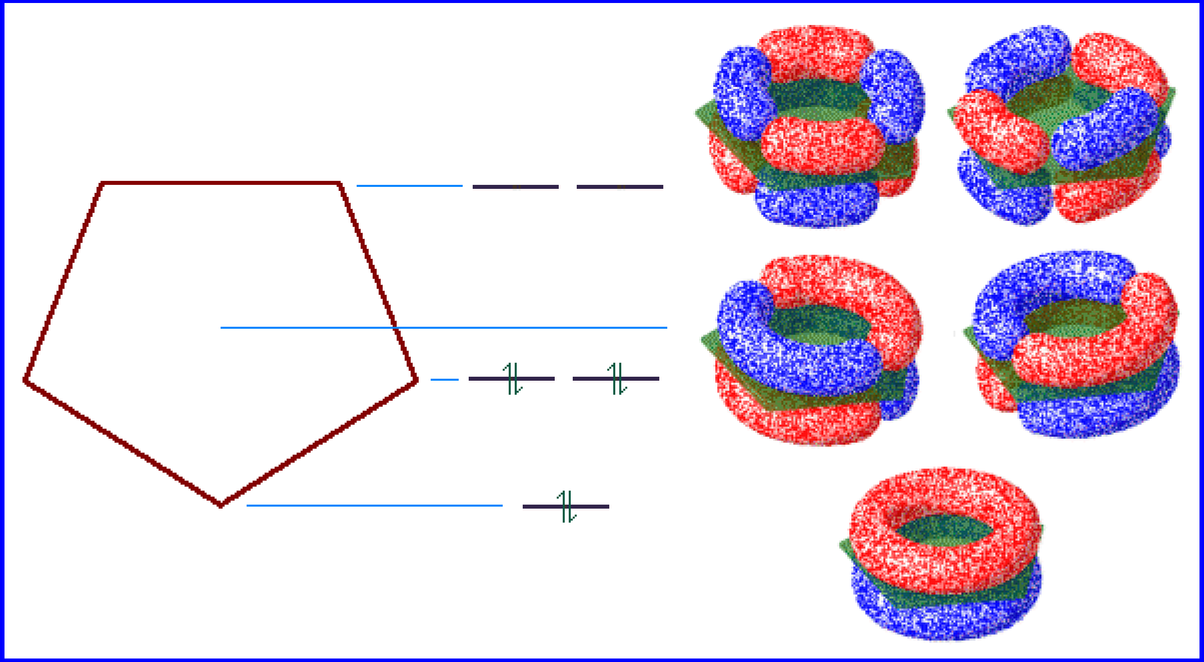
$C_3H_3^+$



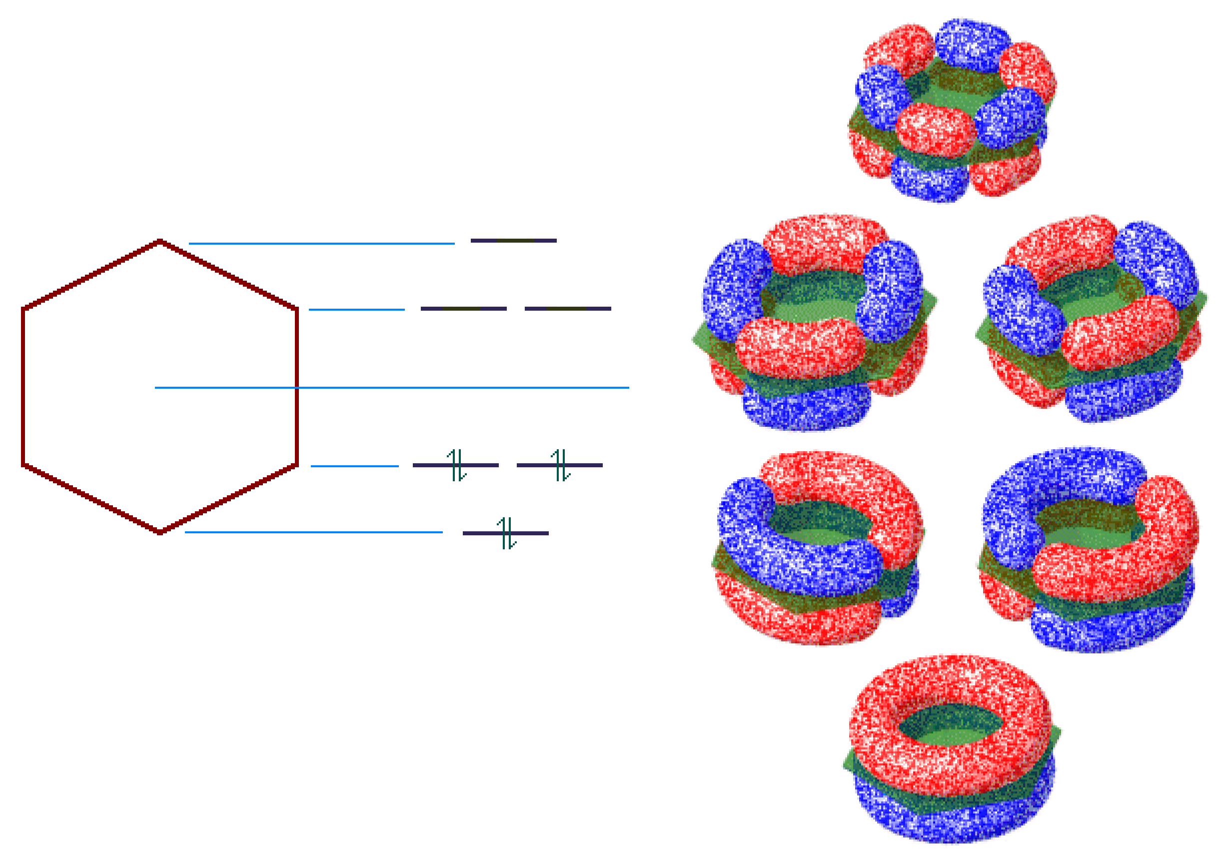
$C_4H_4^{2+}$



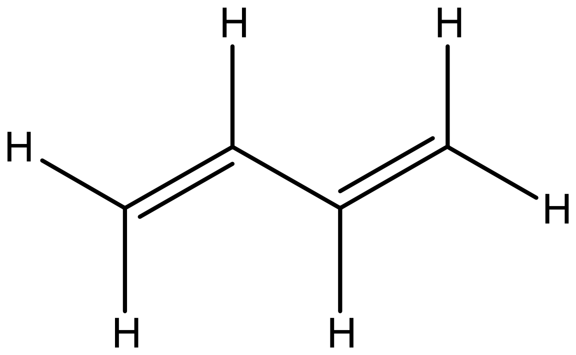
$C_5H_5^-$

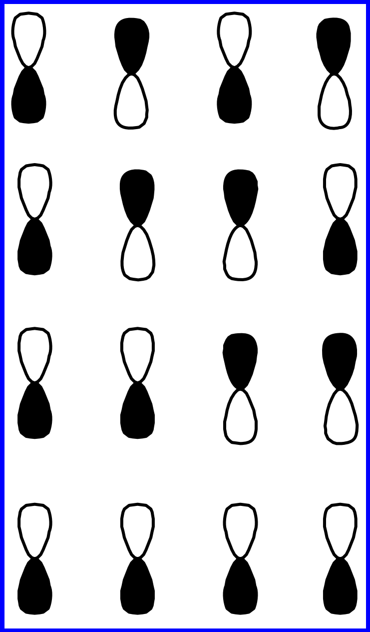


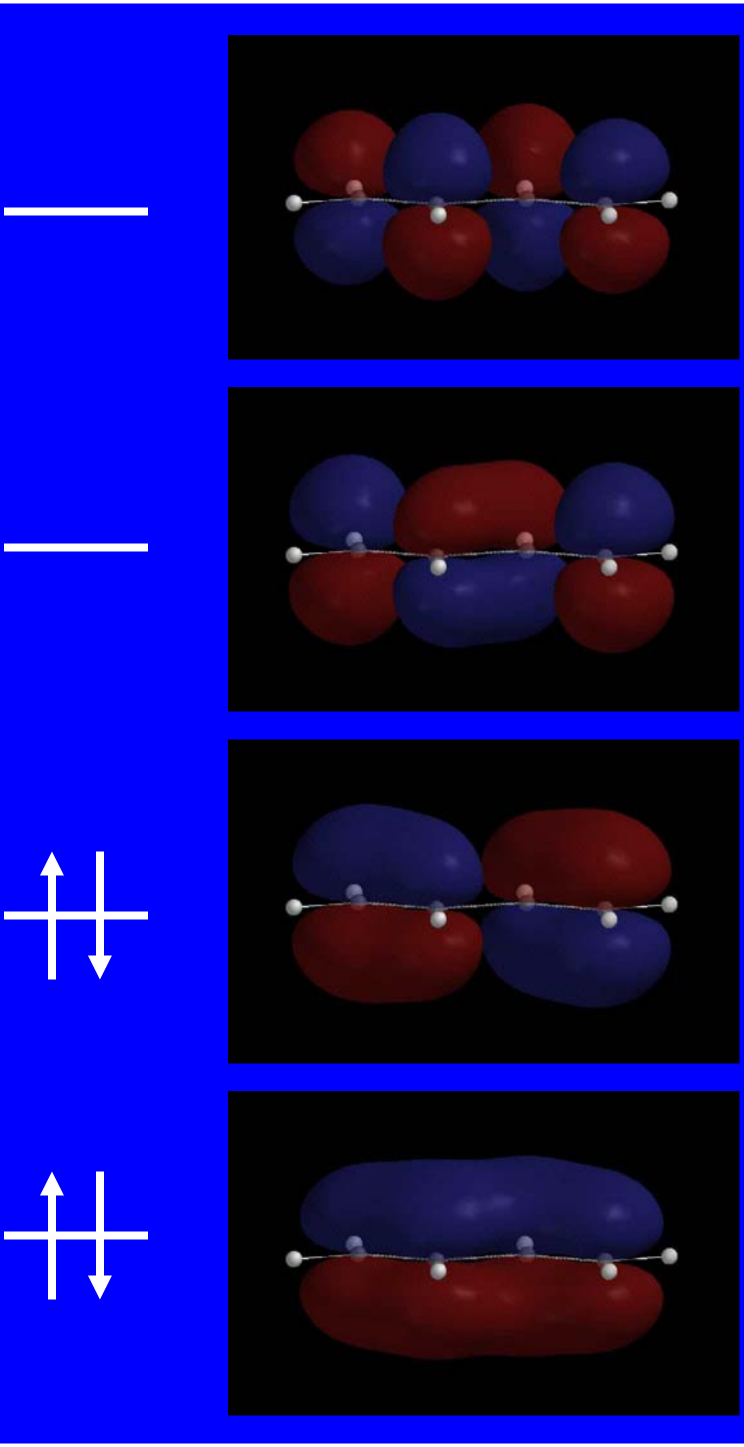
C_6H_6



1,3-butadiene



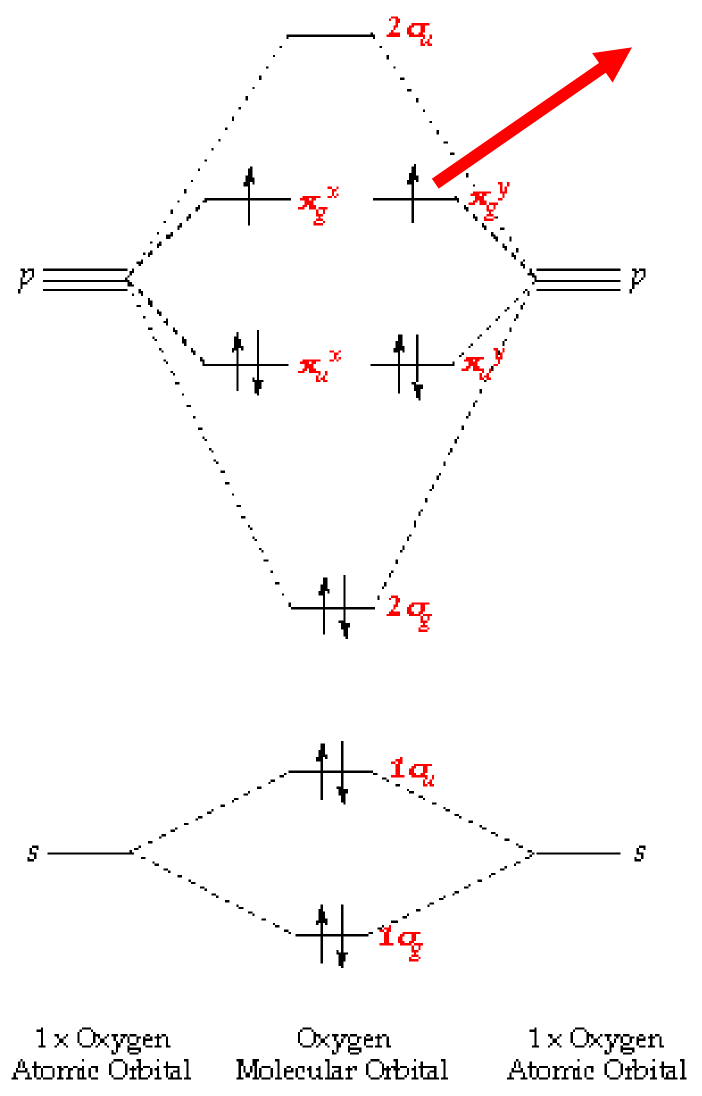




LUMO

HOMO

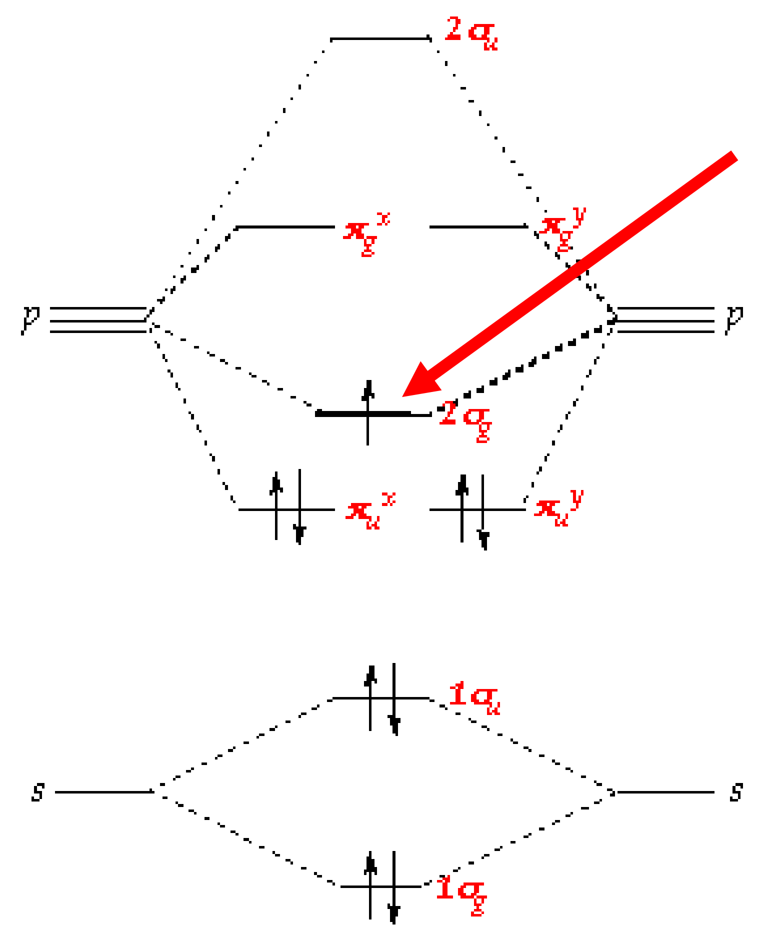
Molecular Ions



$$O_2 \xrightarrow{IE} O_2^+ + e^-$$

Splitting off the weakest bound e in HOMO

Molecular Ions



$CN + e^- \rightarrow CN^-$

Adding e to HOMO

Excitation of Molecules

$E_{tot} = E(\text{electronic}) + E(\text{vibrat}) + E(\text{rotat}) + E_{other}$

Individual parts of E_{tot} are independent – very different magnitudes (Bornova-Oppenheimmer approximation)

E(electron)	100 kJ mol^{-1}	UV and visible
E(vibrat)	1.5 – 50 kJ mol^{-1}	Infrared (IR)
E(rotat)	0.1 – 1.5 kJ mol^{-1}	Microwave and far IR

Rotational Energy

Quantization of rotational energy

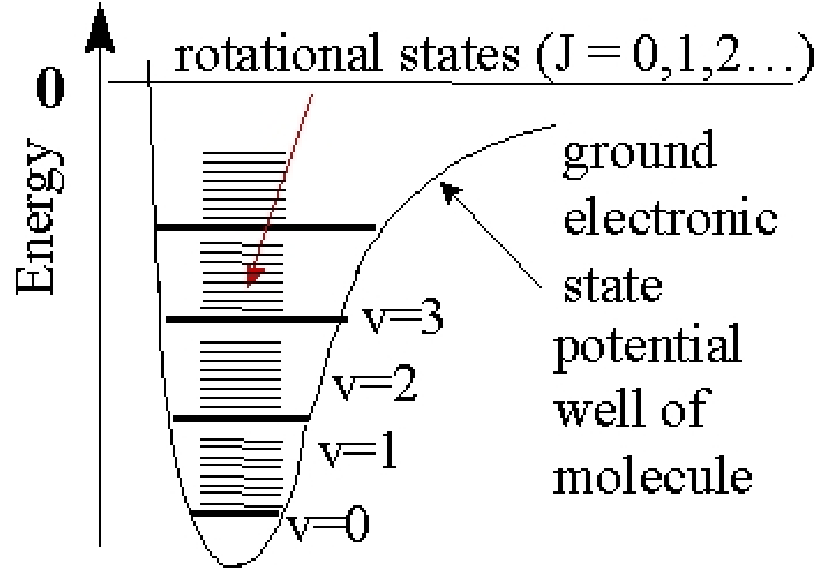
$E(\text{rotat}) = (\hbar^2/2I)\, J(J+1)$

J = rotat quantum number

I = moment of inertia ($m\,r^2$)

$m = m_1 m_2/(m_1 + m_2)$

Selection Rule $\Delta J = \pm 1$



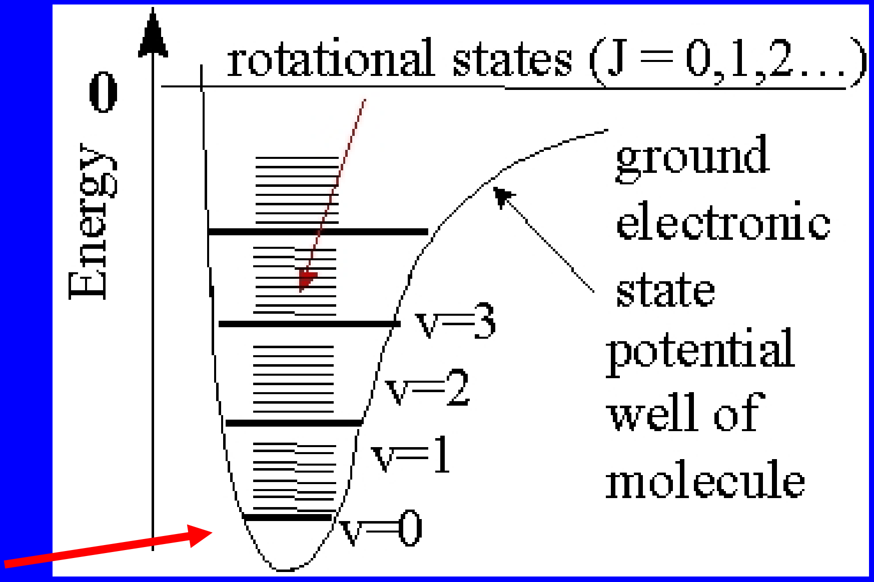
At normal temperature, molecules are in many excited rotational states, rotational energy is comparable to thermal energy of molecular motion

Vibrational Energy

Quantization of vibrational energy

$E(vibrat) = k\,\hbar^2\,(v + ½)$
v = vibrat quantum number

Selection Rule $\Delta v = \pm 1$

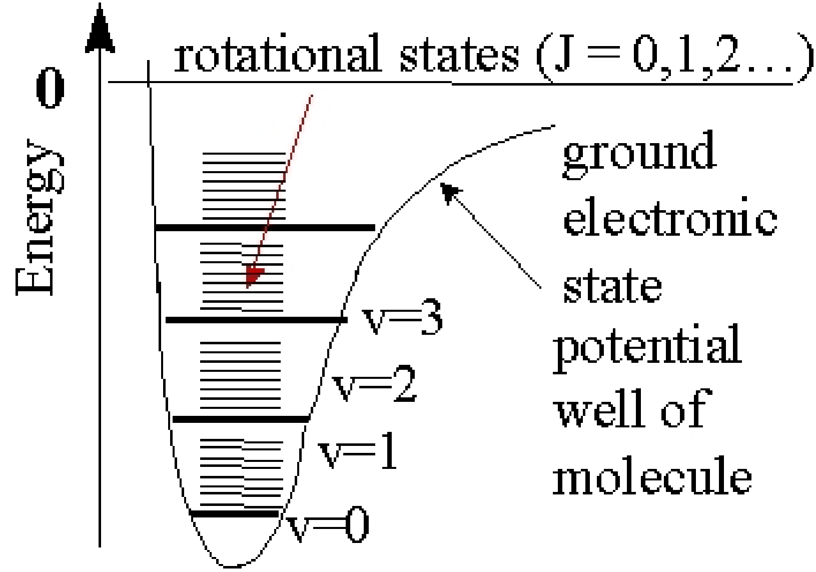


Zero Point Energy:
for v = 0 $E(vibrat) = ½\,k\,\hbar^2$
H_2 $E(disoc) = 432\ kJ\ mol^{-1}$
$E(v = 0) = 25\ kJ\ mol^{-1}$

At normal temperature, molecules are in ground vibrational state v = 0

Vibrational Energy

Molecule	Vibrational energy, cm^{-1}
H_2	4159.2
D_2	2990.3
H_2^+	2173



$$ΰ = 1/2\pi\ (k\ /m)^{½}$$

Rotational – Vibrational Spectrum of $HCl_{(g)}$

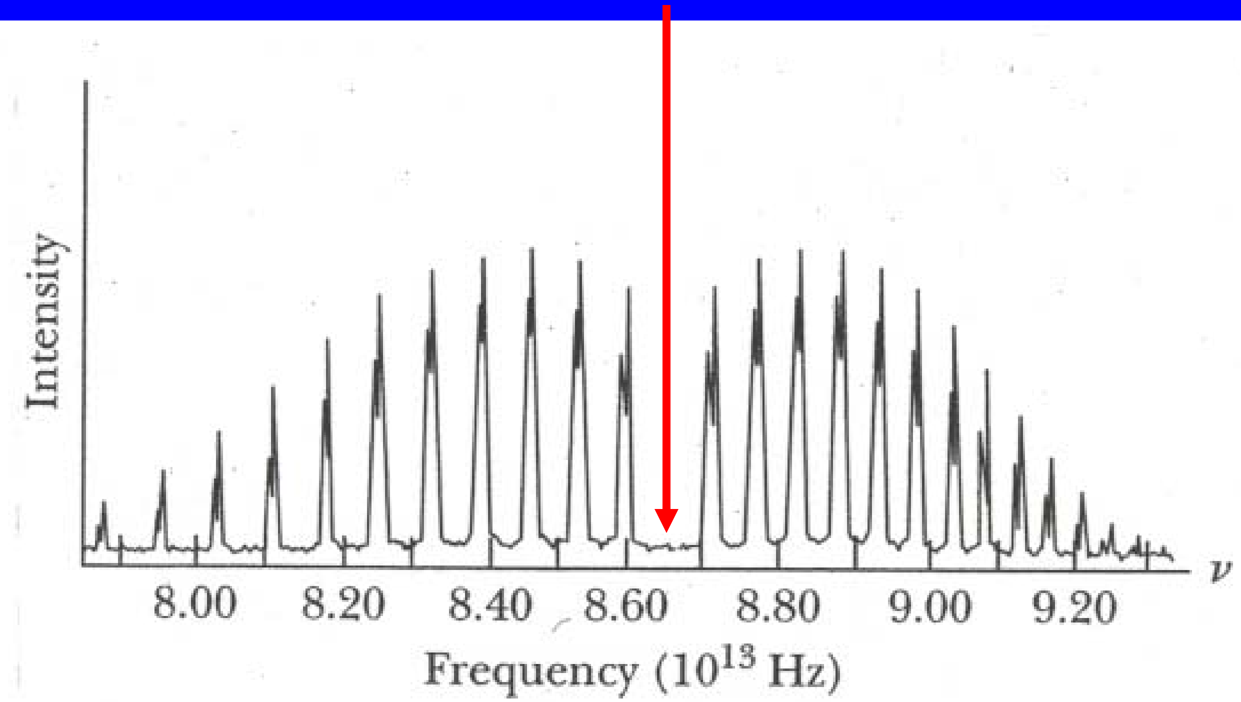
IR region

$\nu_0 = 2886\ cm^{-1}$

$\Delta v = \pm 1$

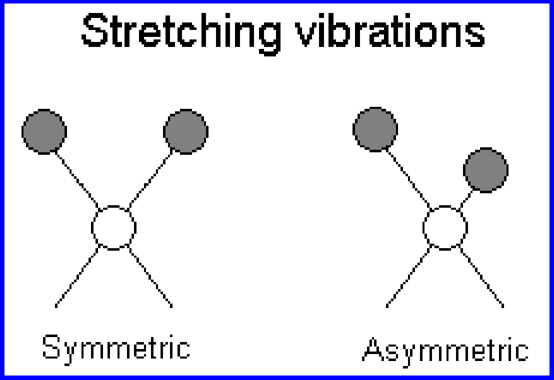
$\Delta J = \pm 1$

ν_0

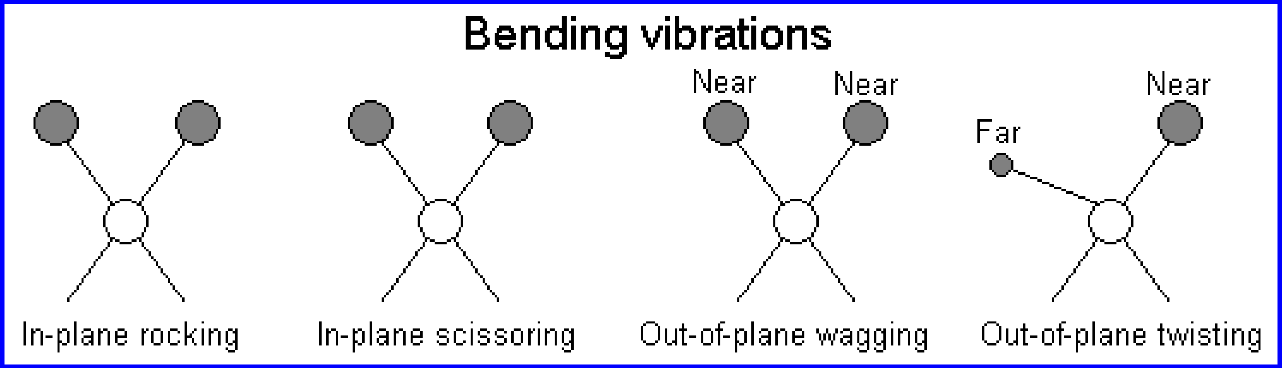


Types of Vibrations

Valence



Deformation



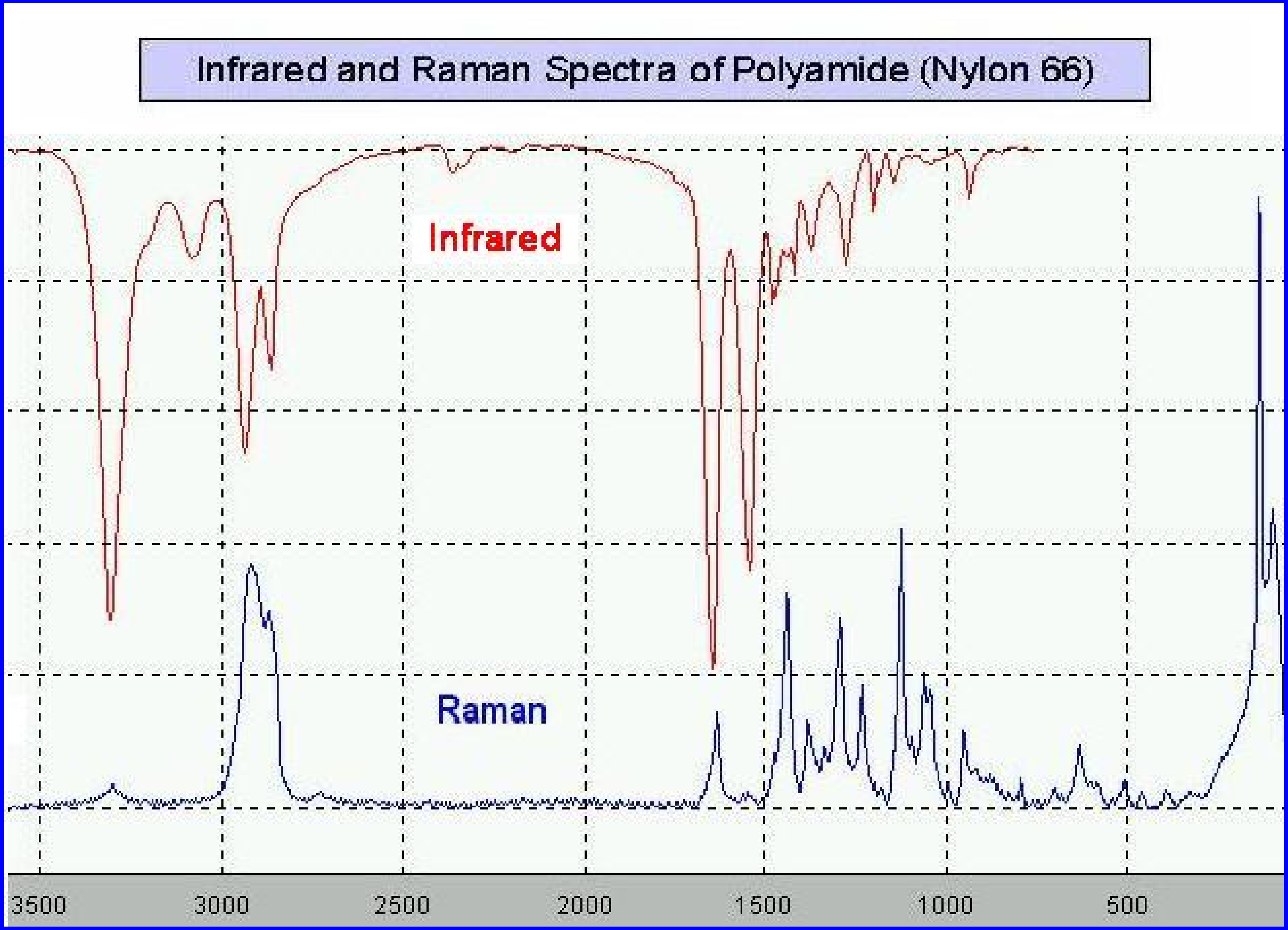
Infrared and Raman Spectroscopies

Infrared spectroscopy

Vibration must change dipole moment of a molecule (HCl, H_2O)

Raman spectroscopy

Vibration must change polarization of a molecule (H_2)



$$\ddot{\upsilon} = 1/2\pi\ (k\ /m)^{1/2}$$