MOLECULAR ORBITAL THEORY (MOT)

INTERACTION of ATOMIC ORBITALS

MOT predicts the formation of two types of orbitals from the interaction of atomic orbitals. These are the bonding molecule orbital and the antibonding molecule orbital. The fact that atomic orbitals can interact or have an effective interaction between the orbitals depends on three basic conditions:

1. *Atoms should approach each other at a distance that allows orbitals to interact.*
2. *The energy of the orbitals must be equal to or close to each other. The valence orbitals of the electronegative atom have lower energy.*

Element	1s	2s	2p	3s	3p	4s
H	-13.6					
Li		-5.5				
Be		-9.3				
B		-14.0	-8.3			
C		-19.5	-10.7			
N		-25.5	-13.1			
O		-32.4	-15.9			
F		-46.4	-18.7			
Na				-5.2		
Mg				-7.7		
Al				-11.3	-6.0	
Si				-15.0	-7.8	
P				-18.7	-10.0	
S				-20.7	-12.0	
Cl				-25.3	-13.7	
K						-4.3

3. *The overlap integral of atomic orbitals must be different from zero. Orbitals must be of the same type of symmetry.* ψ_1 *and* ψ_2 *are wave functions of atomic orbitals and overlapping integral is*

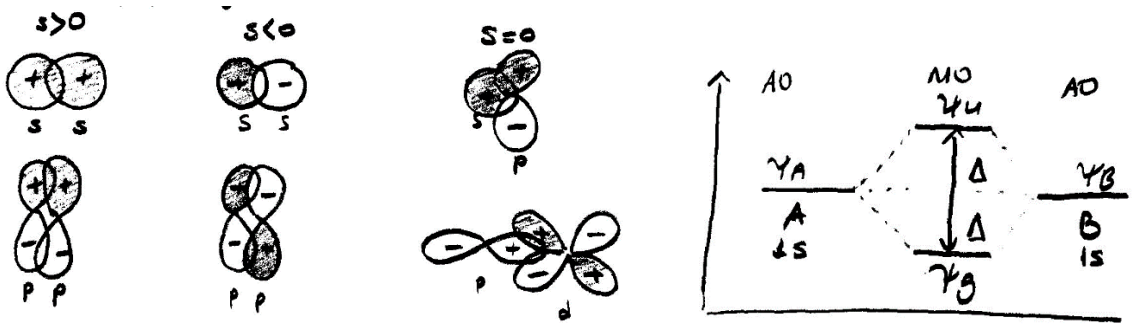
$$S = \int \psi_1 . \psi_2 \, d\tau$$

In the positive overlap (S>0), ''bonding molecular orbital (BMO)''.

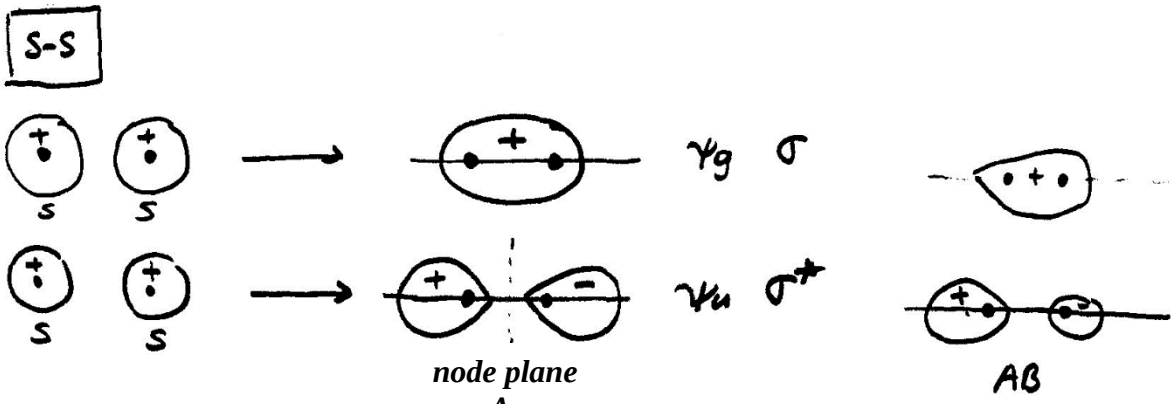
In the negative overlap (S<0), ''antibonding molecular orbital (AMO)''.

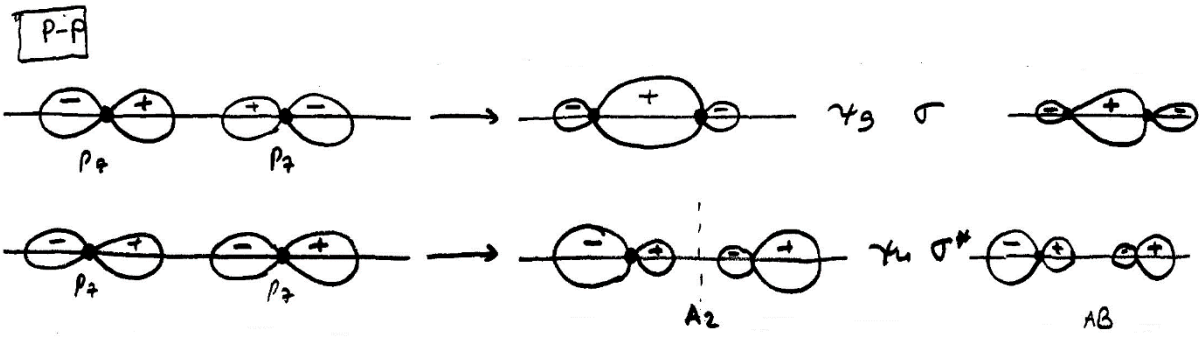
In the S=0 overlap, ''non-bonding molecular orbital'' (NMO).

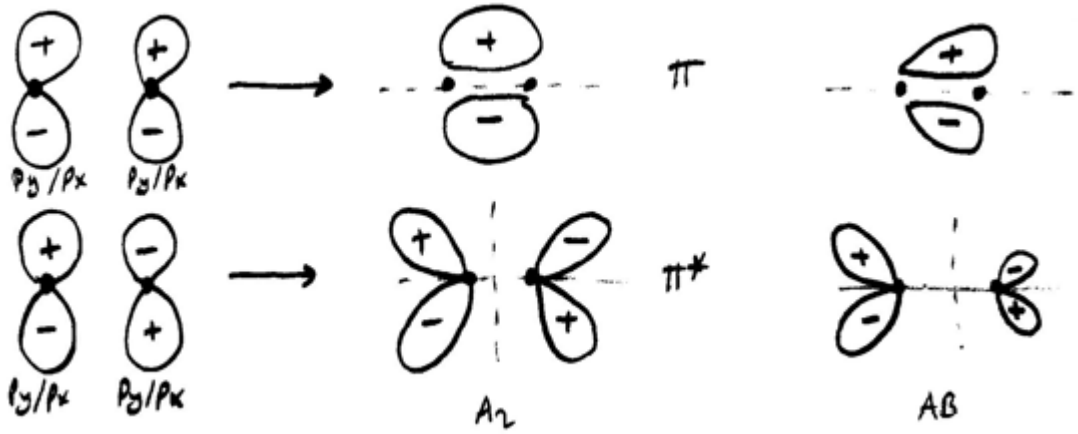
Energy of BMO is lower than the energy of atomic orbitals. The energy of AMO is higher than the energy of atomic orbitals. The energy of MOSs is less than that of the AMOs. The energy of AMOs is higher than BMOs.



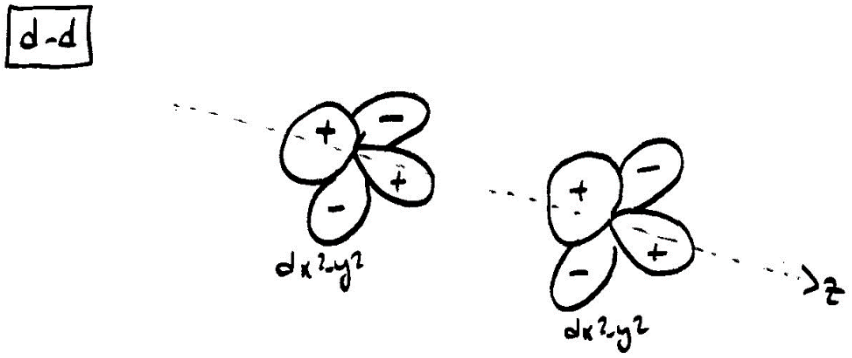
There are overlaps, such as s-s, p-p, d-d, s-p and p-d.

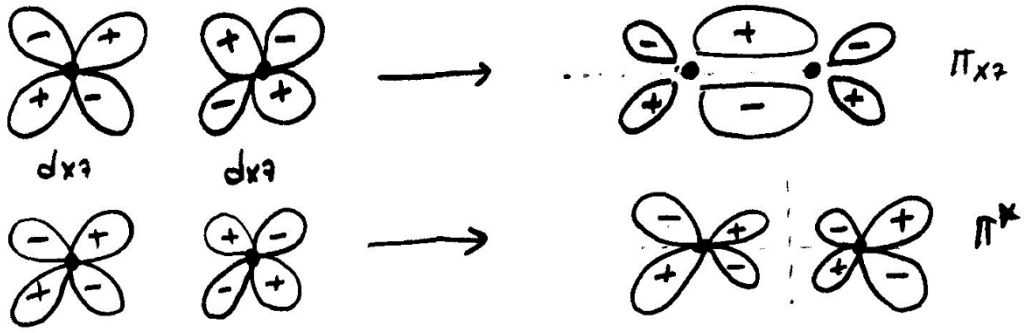


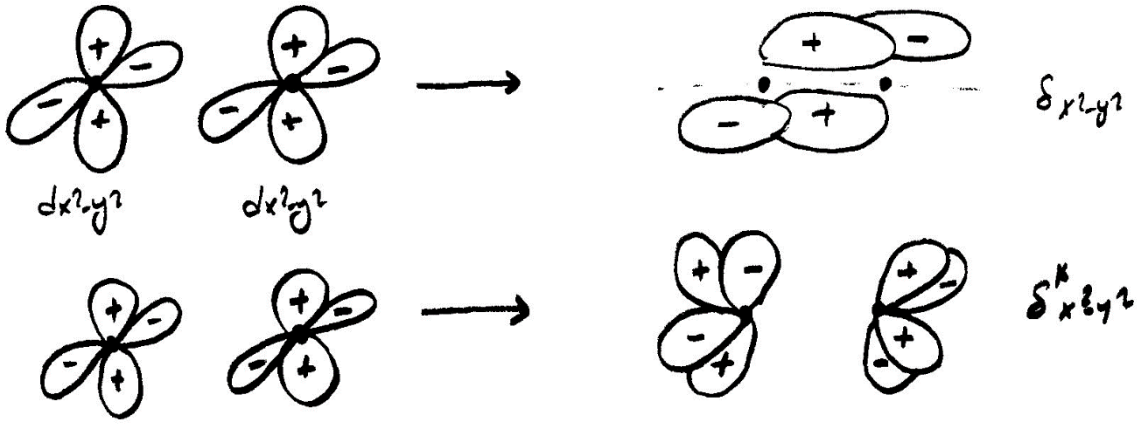


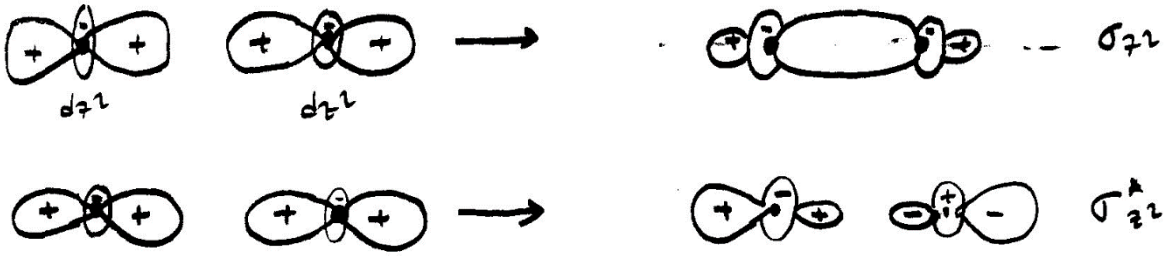


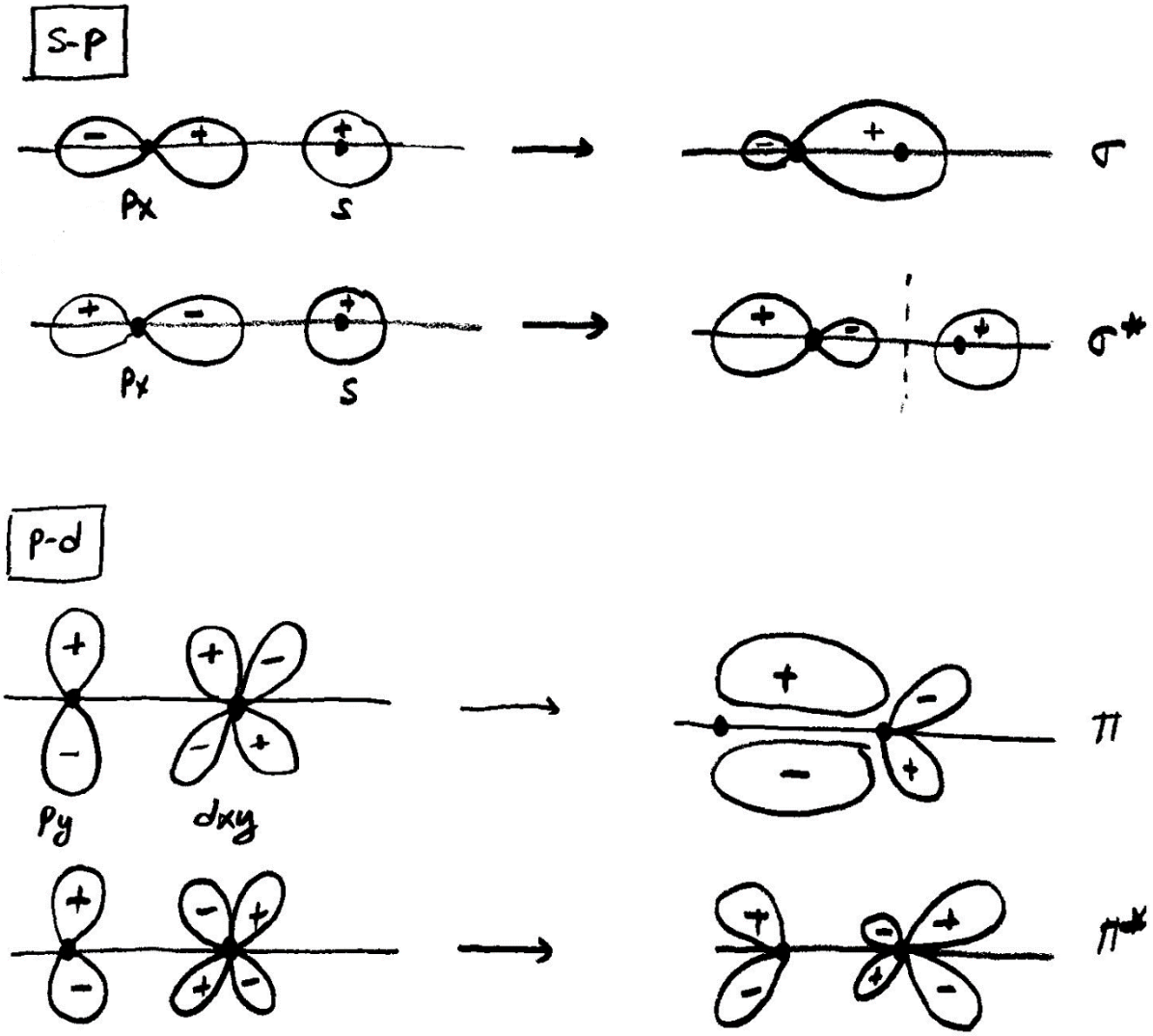
d-d


$d_{x^2-y^2}$
$d_{x^2-y^2}$
z


d_{xz}
d_{xz}
π_{xz}
π^*

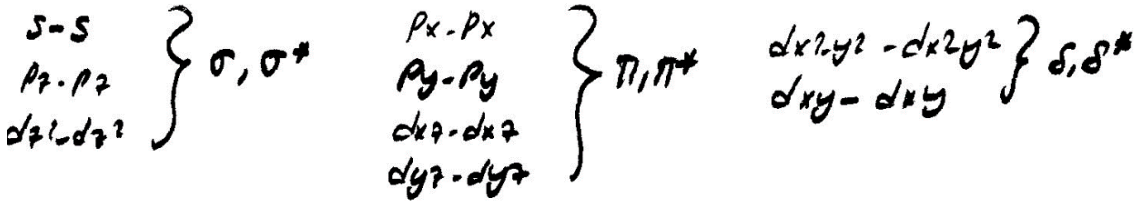

$d_{x^2-y^2}$
$d_{x^2-y^2}$
$\delta_{x^2-y^2}$
$\delta^*_{x^2-y^2}$


d_{z^2}
d_{z^2}
σ_{z^2}
$\sigma^*_{z^2}$


S-P
Px
S
σ
Px
S
σ*
P-d
Py
dxy
π
π*

MOLECULAR ORBITAL ENERGY DIAGRAMS

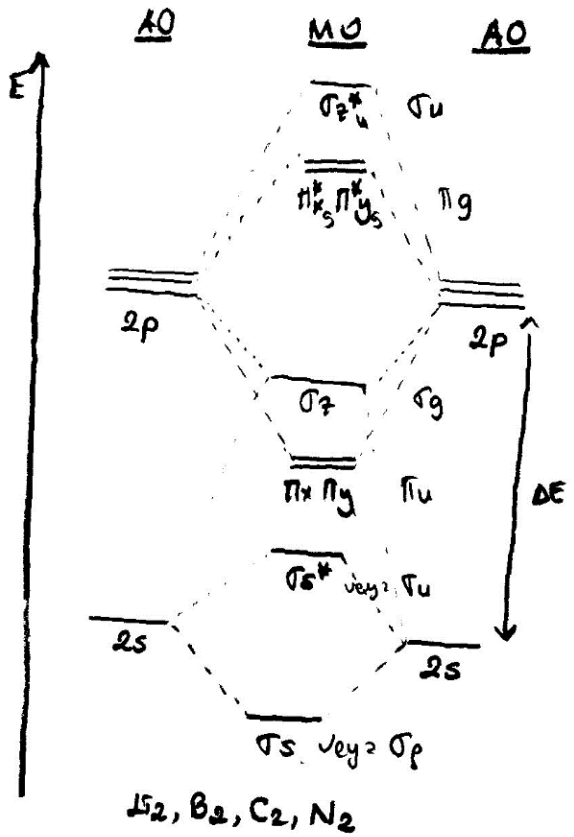
1. *It is a diagram which is sorted molecular orbitals of a molecule according to the increasing energies of the molecular orbitals. In the energy diagrams of the AX_n (n=1,2,…) molecules, the energy levels of the orbitals of the central atom are located on the left side of the molecular orbitals and the bound atoms (X) are located on the right side. Electrons are placed in molecular orbitals according to the Aufbau principle (this principle states that those molecular orbitals which have the lowest energy are filled first) and Pauli's exclusion principle (according to this principle, each molecular orbital can accommodate a maximum of two electrons having opposite spins).*

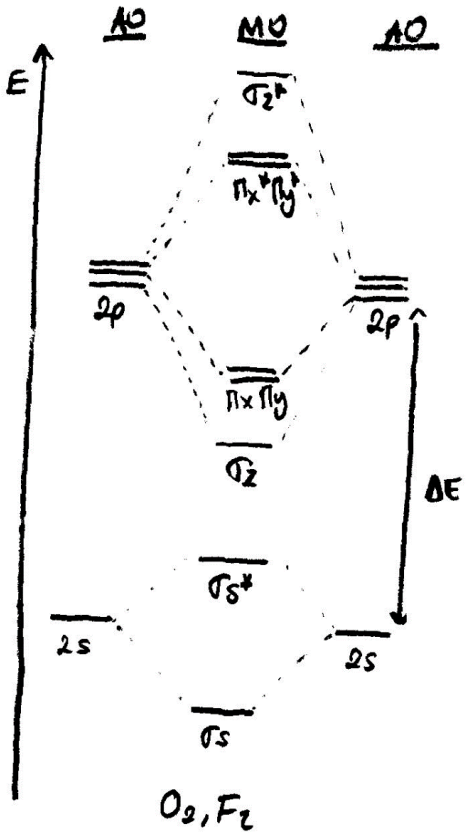


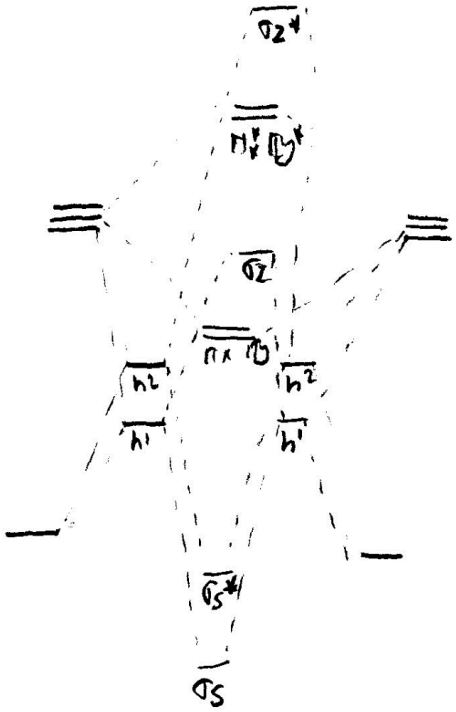
2. *Energy of BMO is lower than that of AMO.*
3. *The energy level of the lower shell where the atomic orbitals form the molecular orbitals, are the main factor determining the energy level of the molecular orbitals. For example, σ_{2s} and σ_{2s}*, which consist of 2s-2s overlap, are lower energy than σ_z, n_x, n_y, n_x* and σ_z* which are composed of 2p-2p overlap.*
4. *Energy sequence of molecular orbitals of orbitals in the same sub-shell;*
   $\sigma<n<\delta<\delta^*<n^*<\sigma^*$
5. *Since the n and Δ symmetry types correspond to the binary degenerative representation, the molecular orbitals in these symmetry types have degenerated energy levels. For example, n_x and n_y; n_x* and n_y*; δ_{xy} and δ_{x2-y2}; δ_{xy}* and δ_{x2-y2}* are degenerate molecular orbitals.*
6. *The energy of the NMO is almost the same as that of the atomic orbitals. The NMO is the atomic orbital that does not interfere with the interaction. For example, the energy of σ_s^n in HF is equal to the energy of F's 2s orbital, the energy of n_x^n is equal to the energy of $2p_x$ orbital F.*

MOLECULAR ORBITAL ENERGY DIAGRAMS of A_2 TYPE MOLECULES

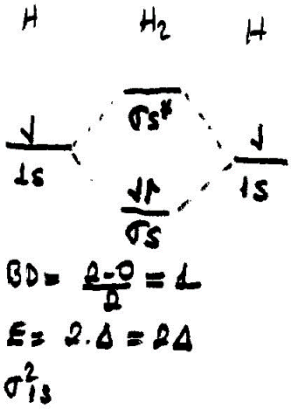
	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond lenght (pm)	267	–	159	124	110	121	142	–
Bond energy (kJ.mol^{-1})	110	–	272	602	941	493	138	–
Bond order	1	0	1	2	3	2	1	0



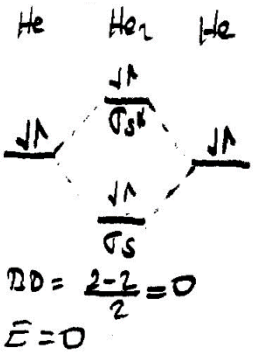




H_2

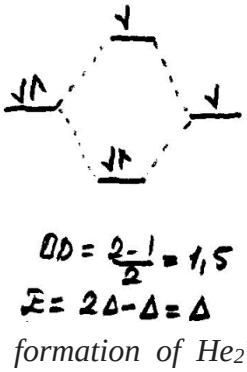


He_2

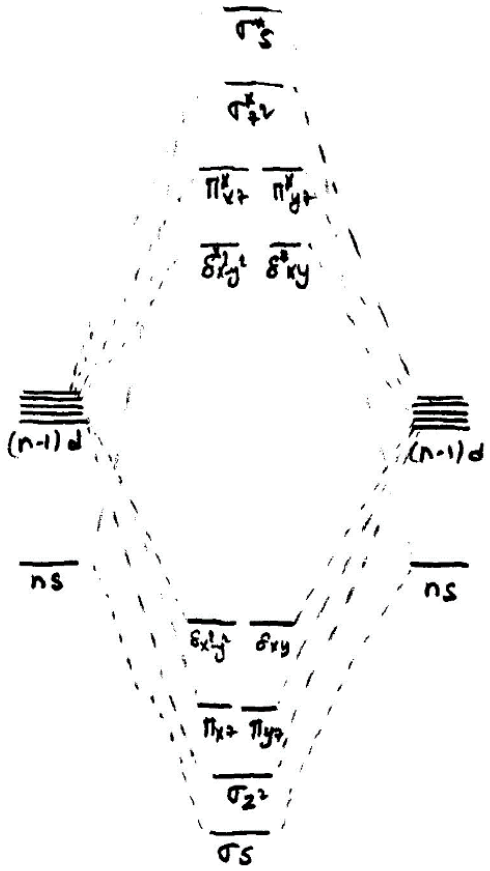


He_2 does not occur

He_2^+



The formation of He_2^+ was determined

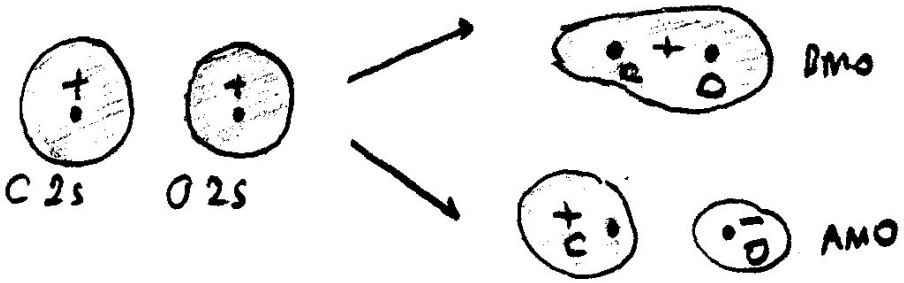


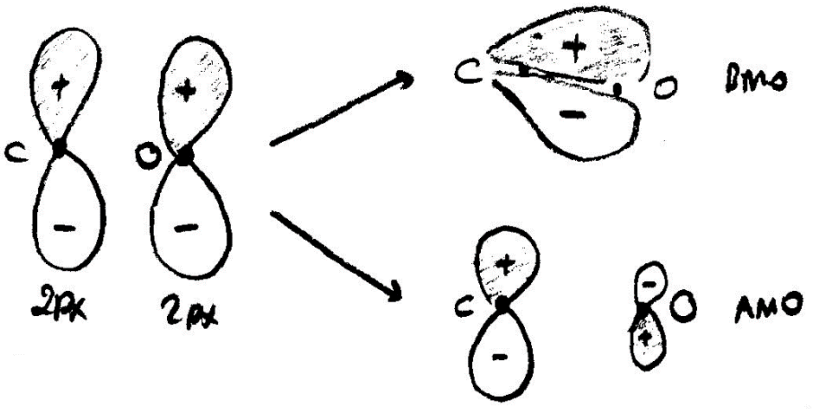
***Cr*$_2$**: *BO=6 (2σ, 2n, 2δ bonds)*

***Cu*$_2$**: *BO=1 (1σ bond)*

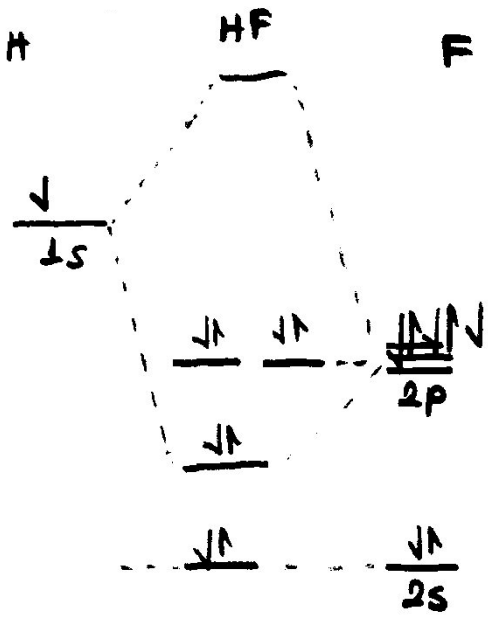
MOLECULAR ORBITAL ENERGY DIAGRAMS of AB TYPE MOLECULES

The contribution of atomic orbitals to AB type molecules is different. If the electronegativity of the B-atom is greater than the electronegativity of the A-atom, since the electron density will be above the B-atom, the bond is drawn on a larger volume around the atomic orbital of the B- atom. The antibonding molecule orbital is drawn on a larger volume around the atomic orbital of the A-atom.

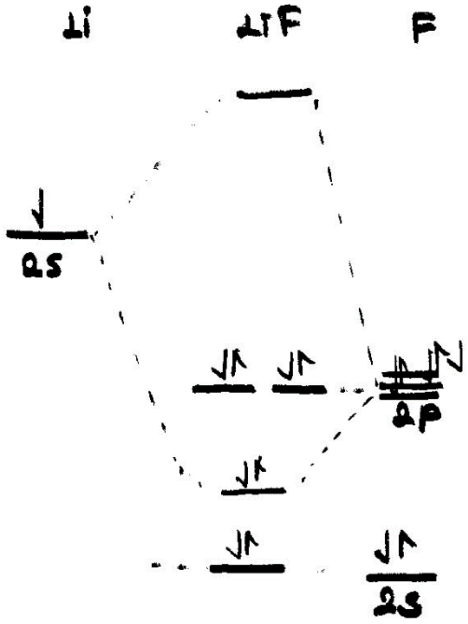


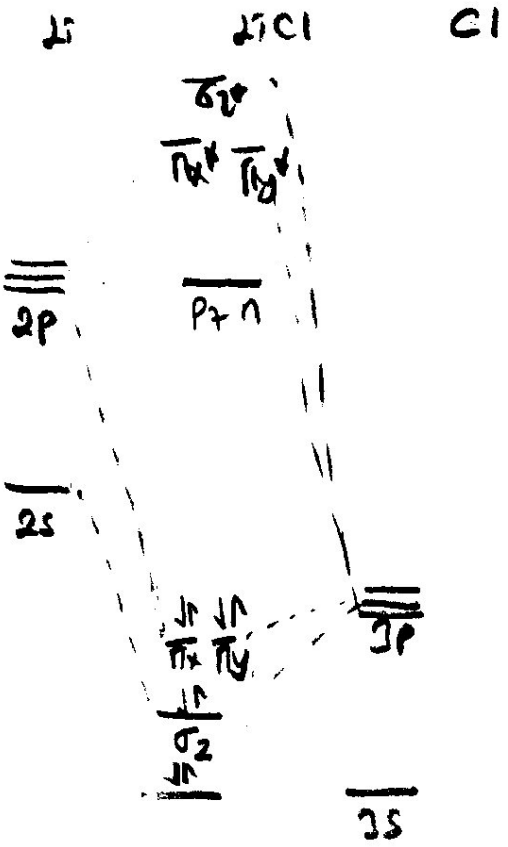


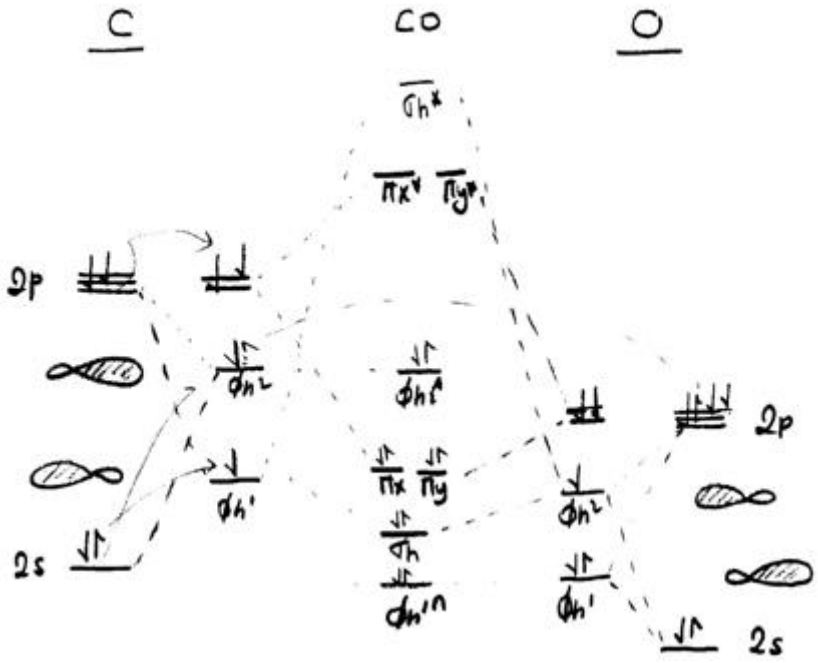
HF



LiF

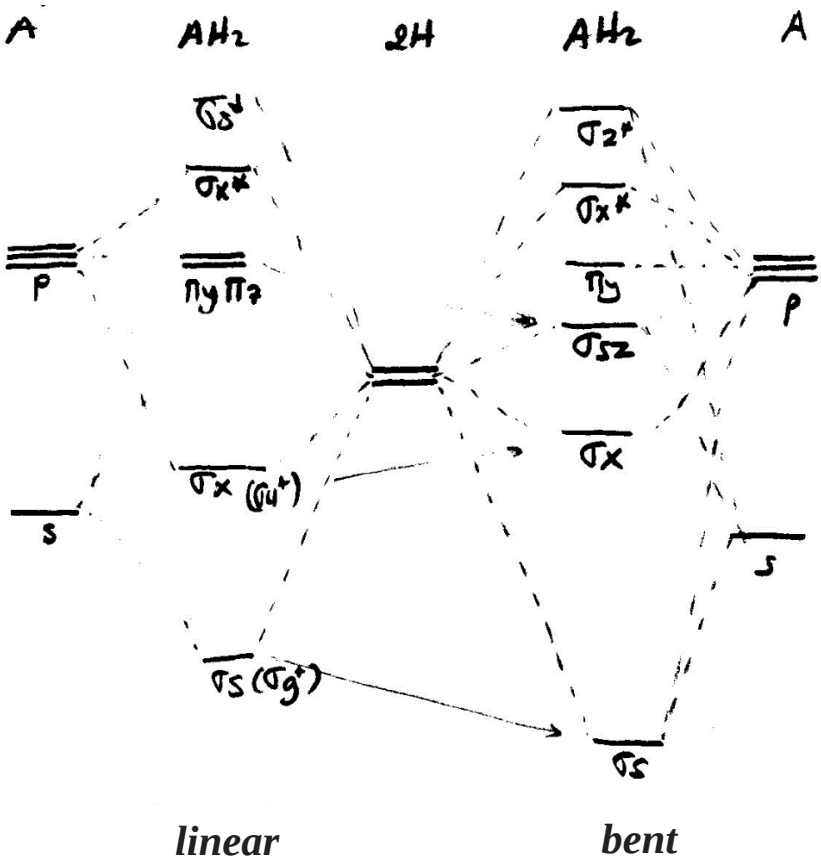





C
CO
O
2p
2s
2p
2s

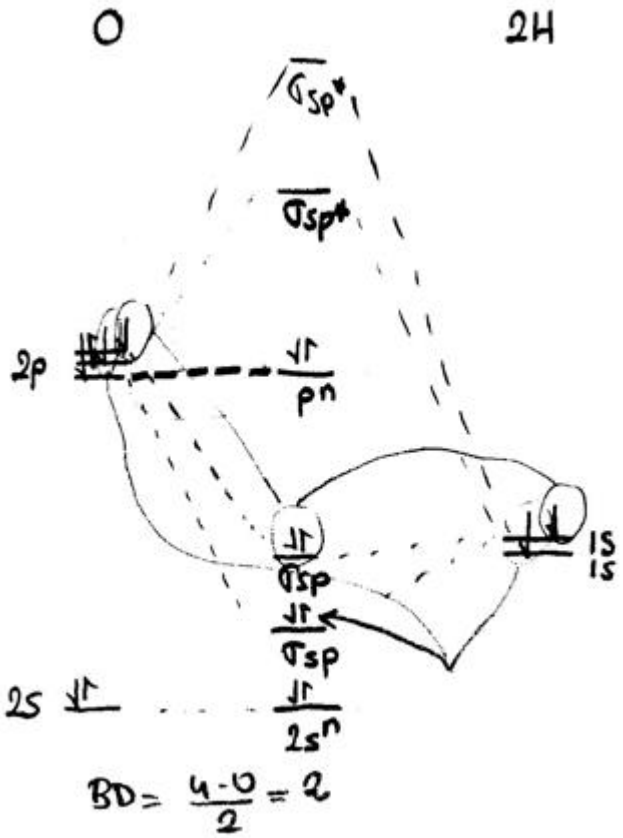
MOLECULAR ORBITAL ENERGY DIAGRAMS of AB_2 TYPE MOLECULES

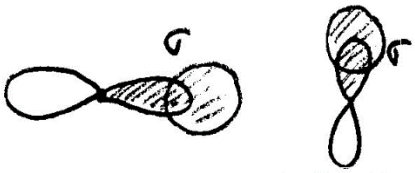
AH_2 Type Molecules (Walsh Rule and Diagrams)



Number of valence electrons	Molecule	Walsh geometry	H-A-H angle
2	LiH_2^+	Bent	
3	BeH_2^+	Linear	
4	BeH_2	Linear	
4	BH_2^+	Linear	
5	BH_2	Bent	131°
5	AlH_2	Bent	
6	CH_2	Bent	136°
6	NH_2^+	Bent	140°-150°
6	BH_2^-	Bent	100°
6	SiH_2	Bent	97°
7	NH_2	Bent	103°
7	PH_2	Bent	92°
8	H_2O	Bent	104°
8	H_2S	Bent	92°
8	H_2F^+	Bent	135°

H_2O

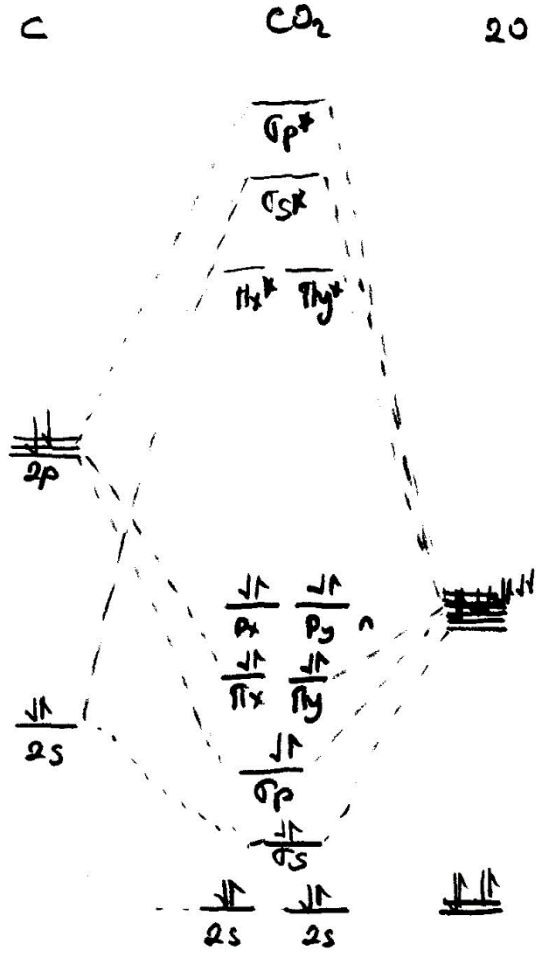


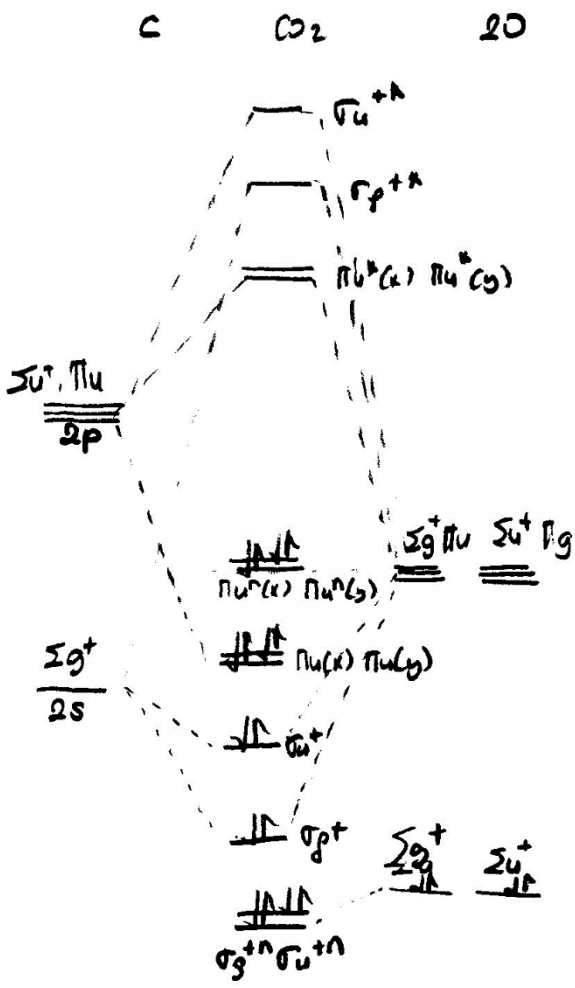


***HOMO**: Highest occupied molecular orbital (p^n for H_2O).*

***LUMO**: Lowest unoccupied molecular orbital (σ_{sp} for H_2O).*

***SOMO**: Highest singly occupied molecular orbital or highest semi occupied molecular orbital.*

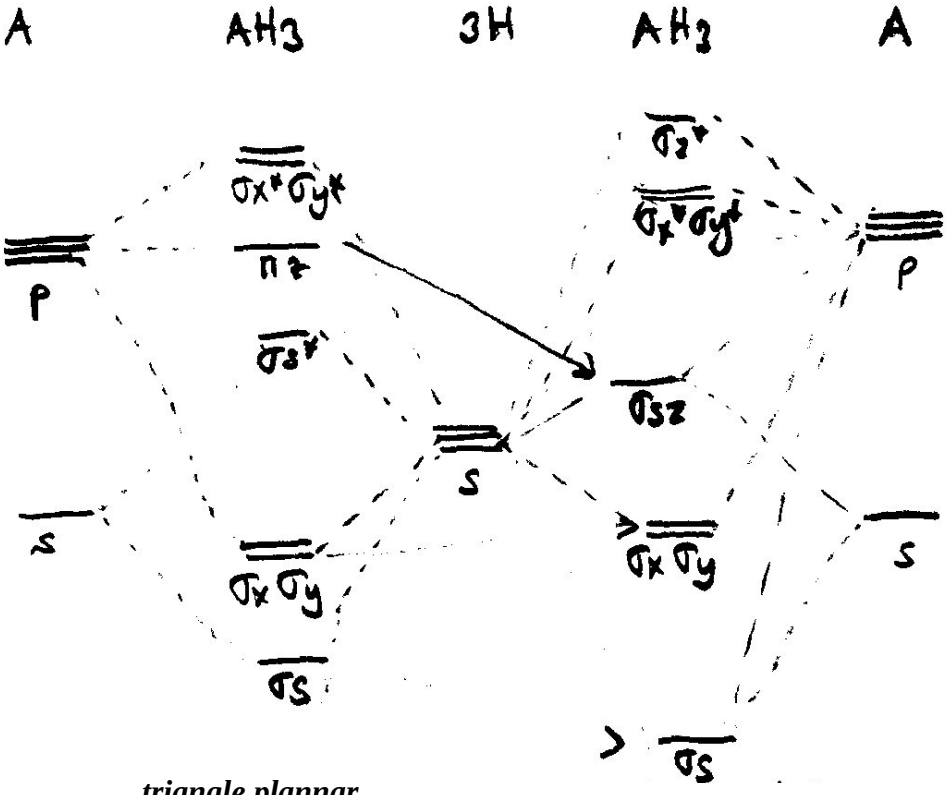

C
CO2
2O
σp*
σs*
πx* πy*
2p
πx πy
2s
σp
σs
2s 2s


C
CO2
2O
σu+*
σg+*
πu*(x) πu*(y)
Σu+, Πu
2p
Σg+Πu Σu+Πg
πu(x) πu(y)
Σg+
2s
σu+
σg+
Σg+
Σu+
σg+ σu+

MOLECULAR ORBITAL ENERGY DIAGRAMS of AB_3 TYPE MOLECULES

AH_3 Type Molecules (Walsh Rule and Diagrams)

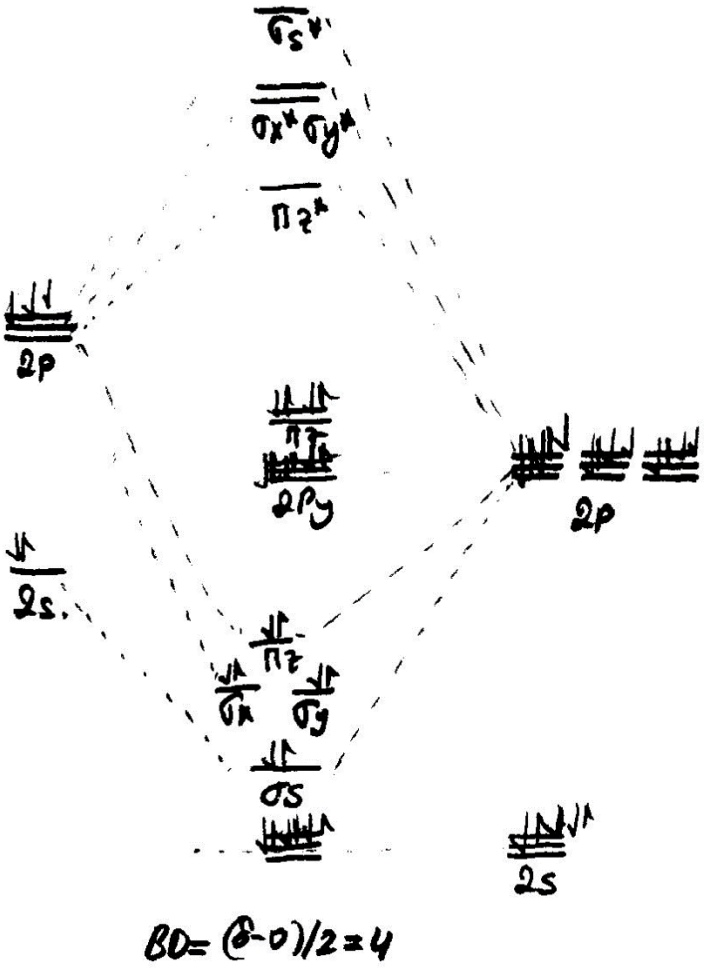
BH_3 (triangle Plannar) and NH_3 and H_3O^+ (triangle Pyramida) can be given as examples.



triangle plannar ***triangle pyramidal***

AB_3 Type Molecules

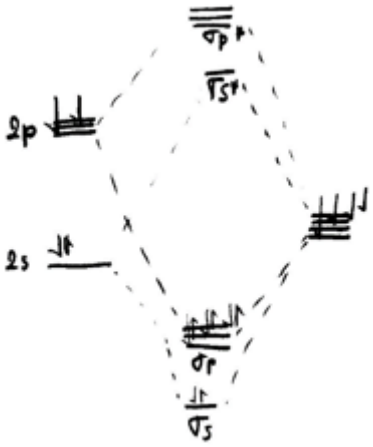
NO_3^-



For each N-O bond. BO=1σ+n/3

MOLECULAR ORBITAL ENERGY DIAGRAMS of AB_4 TYPE MOLECULES

CH_4



SiH_4