Quantum Mechanical Approaches to Molecular Bonding

☺ In principle, it is possible to construct a Schrödinger equation, $\mathcal{H}\Psi = E\Psi$, to describe the electronic structure of a molecule.

☹ In practice, seeking exact solutions to the Schrödinger equation for molecules is an insurmountable mathematical problem.

☞ Two principal approaches have been taken to construct approximate wave functions for molecules, starting with the atomic orbitals of the atoms comprising the molecules.

1. Valence Bond (VB) theory - developed by Linus Pauling and co-workers, essentially puts the Lewis notion of electron pairs on a quantum mechanical footing, in which each shared or lone pair of electrons about an atom occupies a localized orbital.

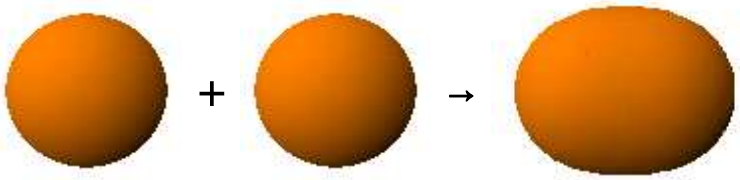
2. Molecular orbital (MO) theory, developed by Robert S. Mulliken and co-workers, constructs new orbitals that are *delocalized* (i.e., "spread out") across the molecule.

☞ VB and MO theories take different mathematical approaches to constructing wave functions for the molecule, but their results are often equivalent.

Valence Bond (VB) Theory

- A chemical bond forms by sharing a pair of electrons through overlap of atomic orbitals on the bonded atoms.

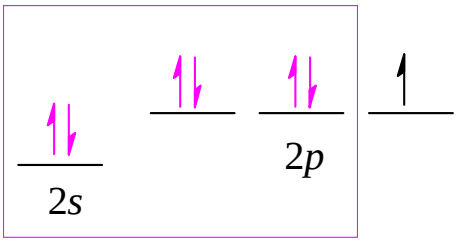
- When overlap creates an increase in electron density in the region between the two nuclei a **sigma bond** (σ bond) is formed.



Formation of sigma (σ) bond in H_2 from 1*s* orbitals

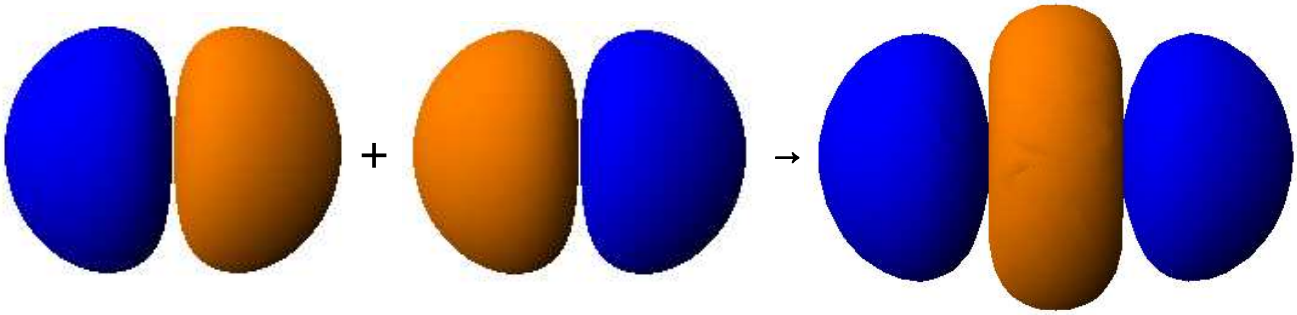
Sigma Bond Formation in F_2

Valence configuration:



Non-bonding electrons

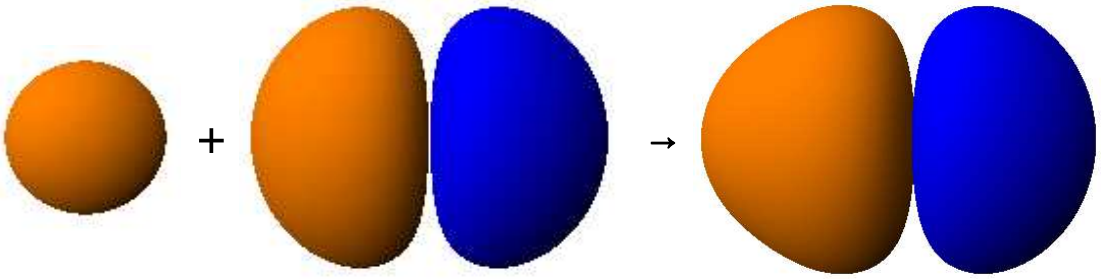
- The single bond in F_2 can be seen as a sigma bond formed by overlap of two 2*p* orbitals.



Formation of sigma (σ) bond in F_2 from 2*p*

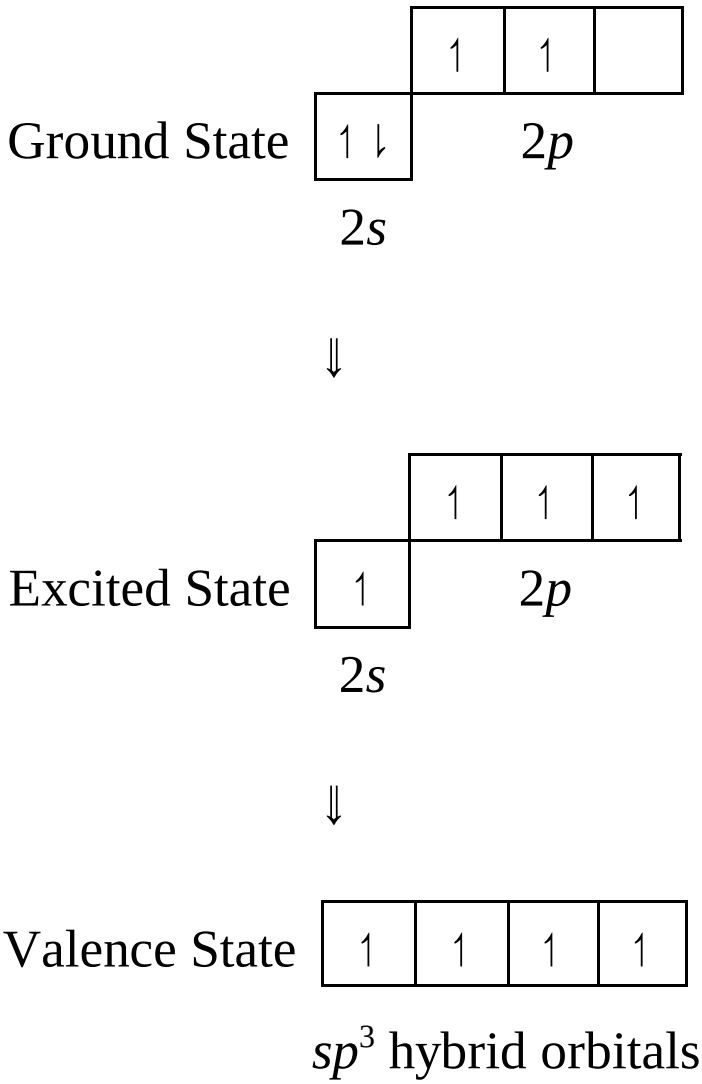
Heteronuclear Diatomic Molecules

- In heteronuclear diatomic molecules, the overlap may involve two different types of orbitals.

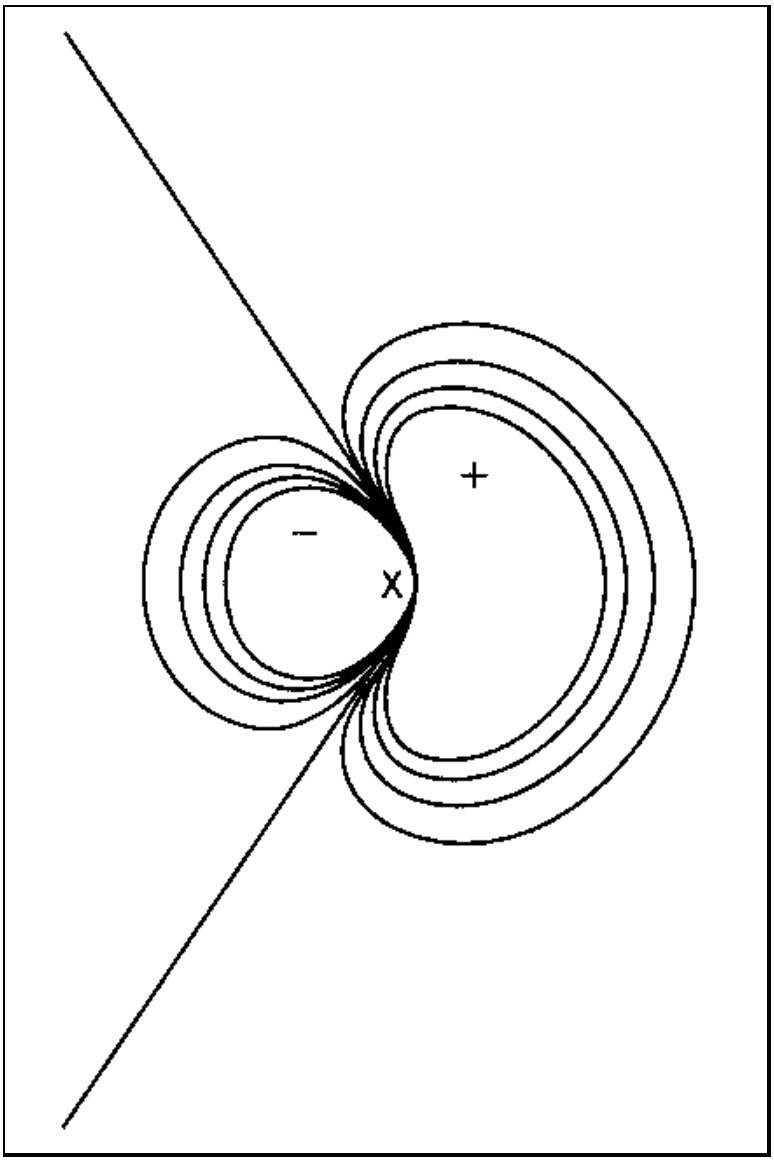


Formation of sigma (σ) bond in HF from H 1*s* and F 2*p*

Hybrid Orbital Formation in CH_4
A Hypothetical Process



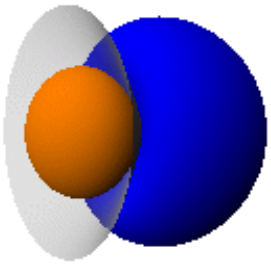
Contour Diagram of a Single sp^3 Hybrid Orbital



X marks the position of the nucleus

Boundary Surface Model of a Single sp^3 Hybrid

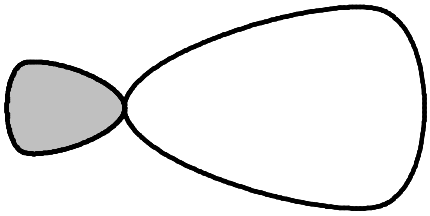
Three-dimensional model (rotated 30^o about a vertical axis):



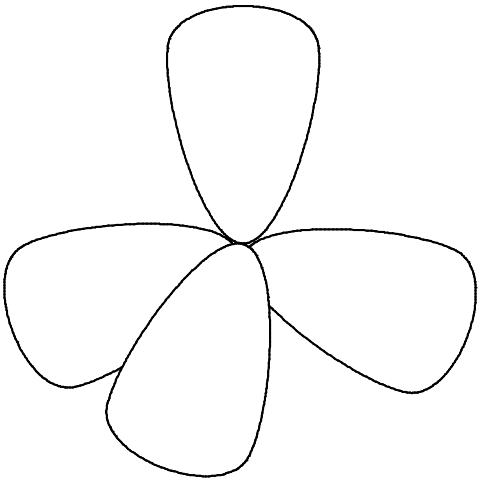
Cut-away rendering:

sp^3 Hybrid Orbitals - Simplified Sketches

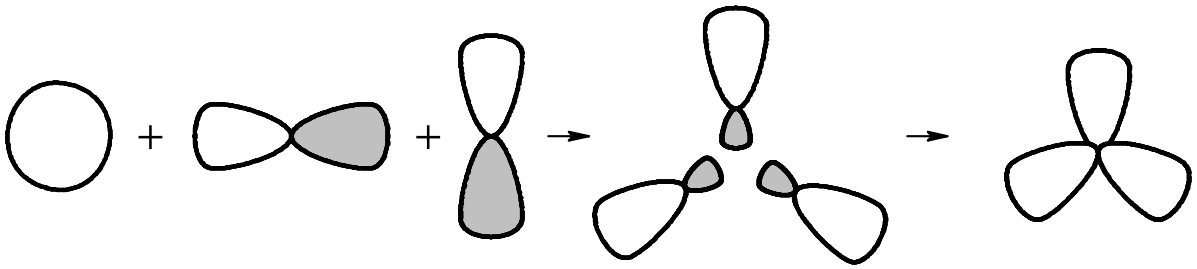
Shape of an individual sp^3 hybrid orbital:



Set of four sp^3 hybrid orbitals in a tetrahedral arrangement:

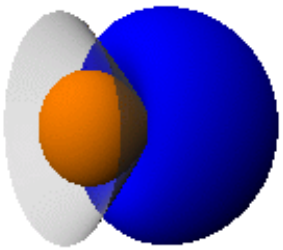


Hybrids for 3 Electron Domains



s *p*$_x$ *p*$_y$ *sp*^{2} orbitals (3)

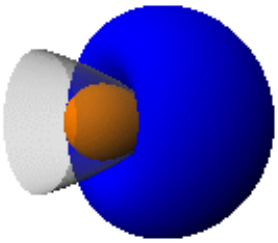
Boundary surface model of one *sp*^{2} hybrid:



Hybrids for 2 Electron Domains

s *p* *sp* orbitals (2)

Boundary surface model of one *sp* hybrid:

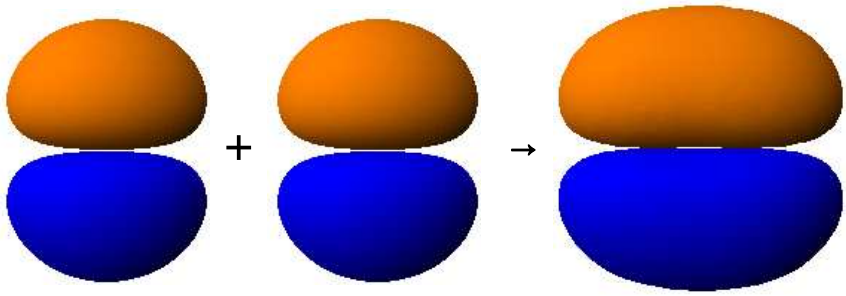


Summary of Hybrid Orbital Types

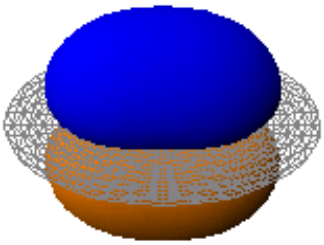
Domains	Geometry	Orbitals Used	Hybrids
2	linear	s, p	sp
3	trigonal planar	s, p_x, p_y	sp^2
4	tetrahedral	s, p_x, p_y, p_z	sp^3
5	trigonal bipyramidal	s, p_x, p_y, p_z, d_{z^2}	sp^3d
6	octahedral	s, p_x, p_y, p_z,d_{z^2}, $d_{x^2-y^2}$	sp^3d^2

Orbital Overlap in Double and Triple Bonds
Pi Bonding (π bonds)

☞ Pi bonding results from side-by-side overlap of two orbitals, such as two $2p_x$ or two $2p_y$ orbitals.

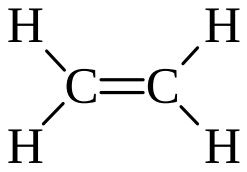


Rotated about bond axis to show nodal plane:

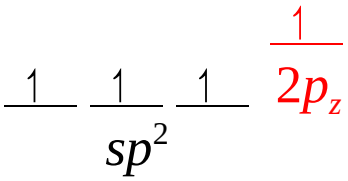


☞ In the VB approach, there is never a π bond without a σ bond, too.

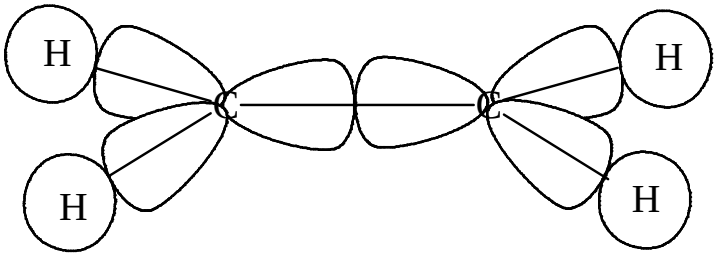
Sigma and Pi Bonding in C_2H_4



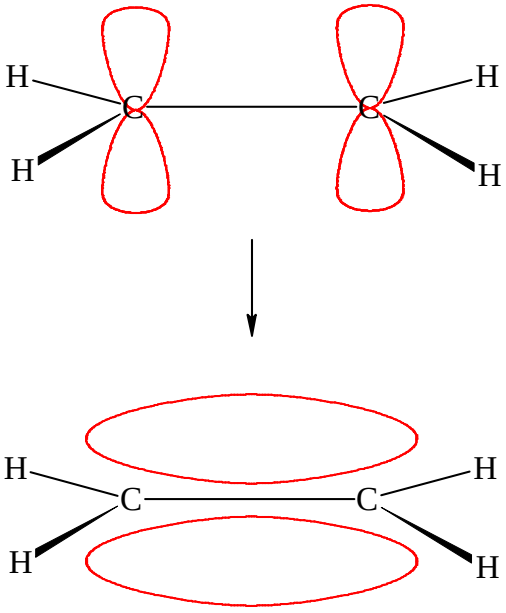
C sp^2 hybridized



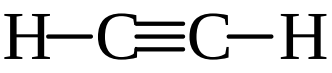
Sigma Bonding:



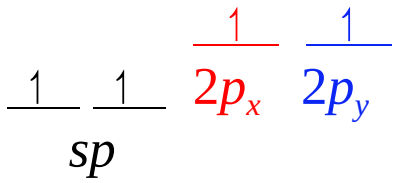
Pi Bonding:



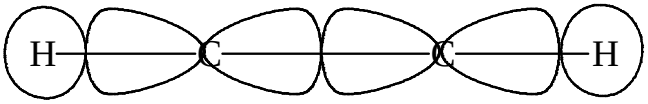
Triple Bond in C_2H_2



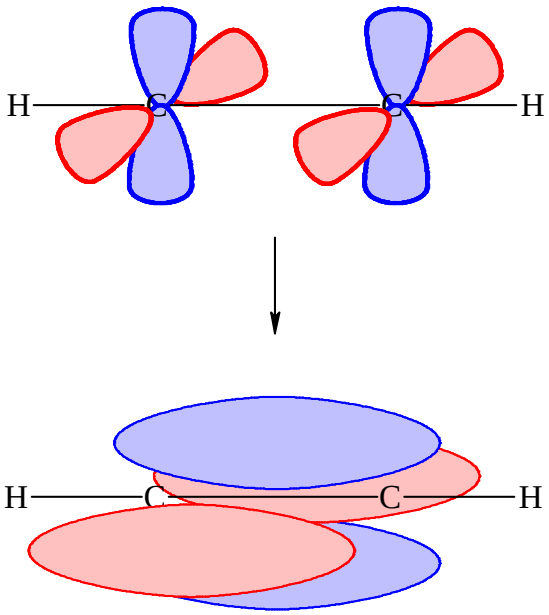
C *sp* hybridized



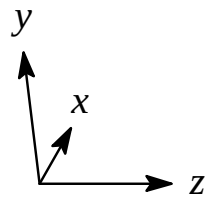
Sigma Bonding:



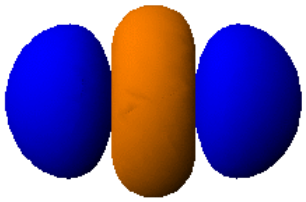
Pi Bonding:



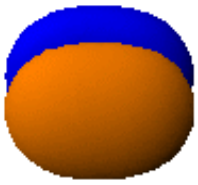
Boundary Surface Models of the Sigma and Two Pi Bonds in C_2H_2



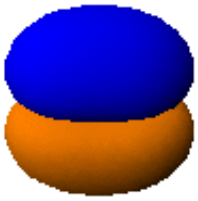
$\sigma(z)$



$\pi(xz)$



$\pi(yz)$



Molecular Orbital Theory of Diatomic Molecules

- MO theory seeks to formulate orbitals that extend over the entire molecule as linear combinations of atomic orbitals (LCAOs) on the individual atoms.

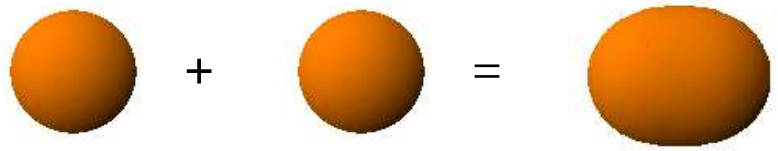
- For diatomic molecules the MOs are positive and negative combinations of the wave functions for pairs of atomic orbitals (AOs) on the two atoms, A and B:

$$\Psi^{+} = a\psi_{A} + b\psi_{B}$$

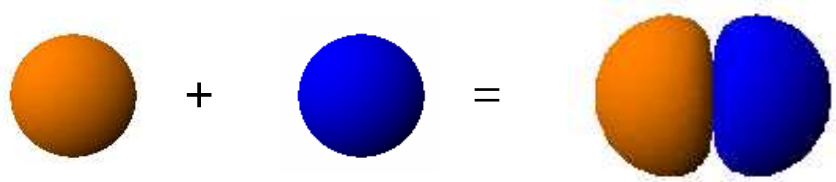
$$\Psi^{-} = a\psi_{A} - b\psi_{B} = a\psi_{A} + (-b\psi_{B})$$

where a and b are mixing constants, which indicate the degree of overlap of the two orbitals.

MOs from 1*s* Orbitals
Homonuclear Diatomic Molecules



σ bonding MO



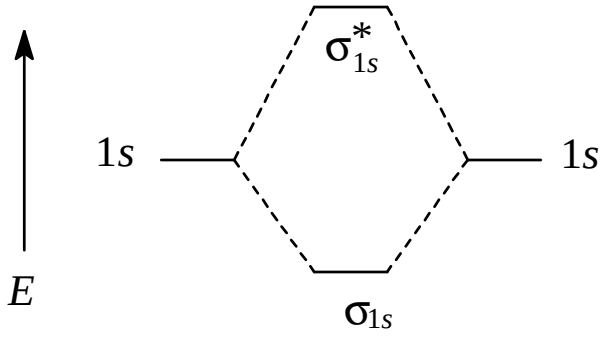
σ* antibonding MO

- Positive combination causes a build-up of electron density between the nuclei, resulting in a **sigma bonding MO (σ)**.

- Negative combination results in a nodal plane between the nuclei, which works against bonding, resulting in a **sigma antibonding MO (σ^*)**.

- In general, number of MOs formed as LCAOs equals number of AOs used.

MO Energy Level Scheme
First Period Homonuclear Diatomic Cases



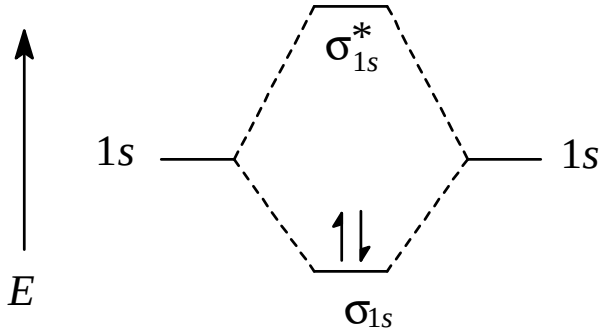
- Scheme is filled in the usual aufbau manner, following the Pauli exclusion principle and Hund's rule of maximum multiplicity (for the ground state).

- Bond order is defined as follows:

bond order = ½ (bonding *e*'s – antibonding *e*'s)

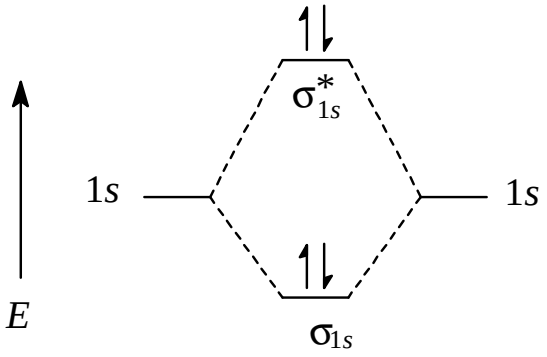
H_2 and He_2

H_2



bond order = ½(2 – 0) = 1

He_2

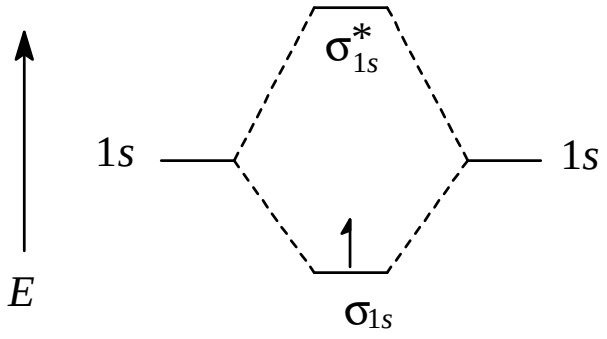


bond order = ½(2 – 2) = 0

(He_2 does not exist.)

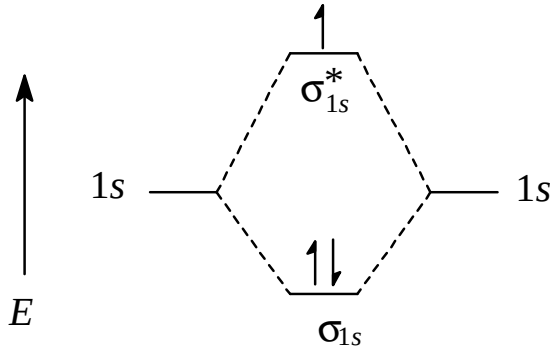
H_2^+ and He_2^+ Ions

H_2^+



bond order = ½(1 – 0) = ½

He_2^+



bond order = ½(2 – 1) = ½

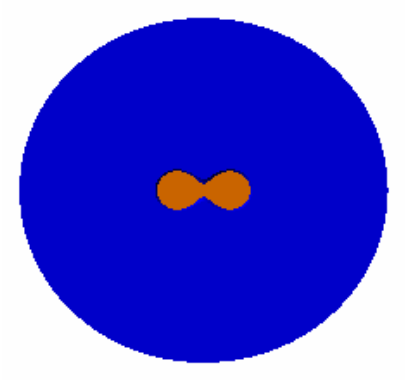
MOs for Second Period
Homonuclear Diatomic Molecules

- In general, atomic orbitals that are most similar in energy interact most effectively in forming MOs.

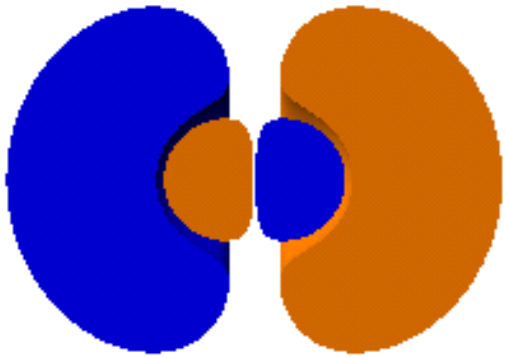
- MOs for second period diatomic molecules are combinations of the type $2s \pm 2s$ and $2p \pm 2p$.

Sigma MOs from 2*s* ± 2*s*

(cutaway views)

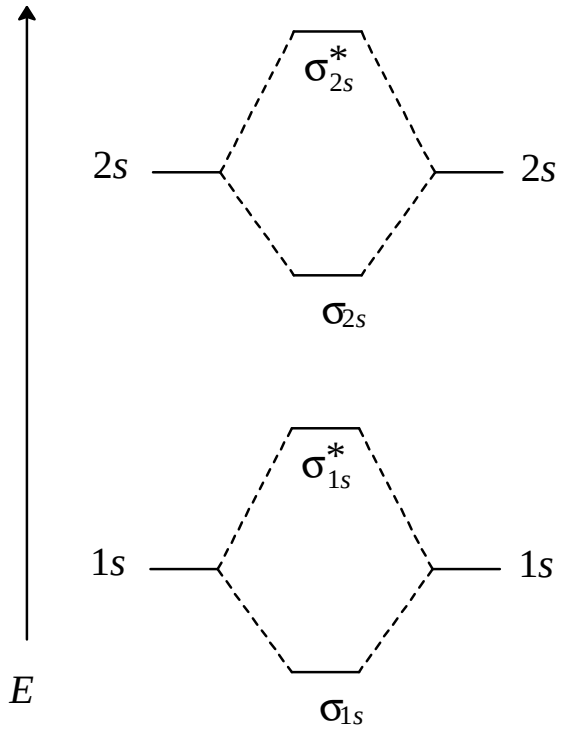


σ_{2s}

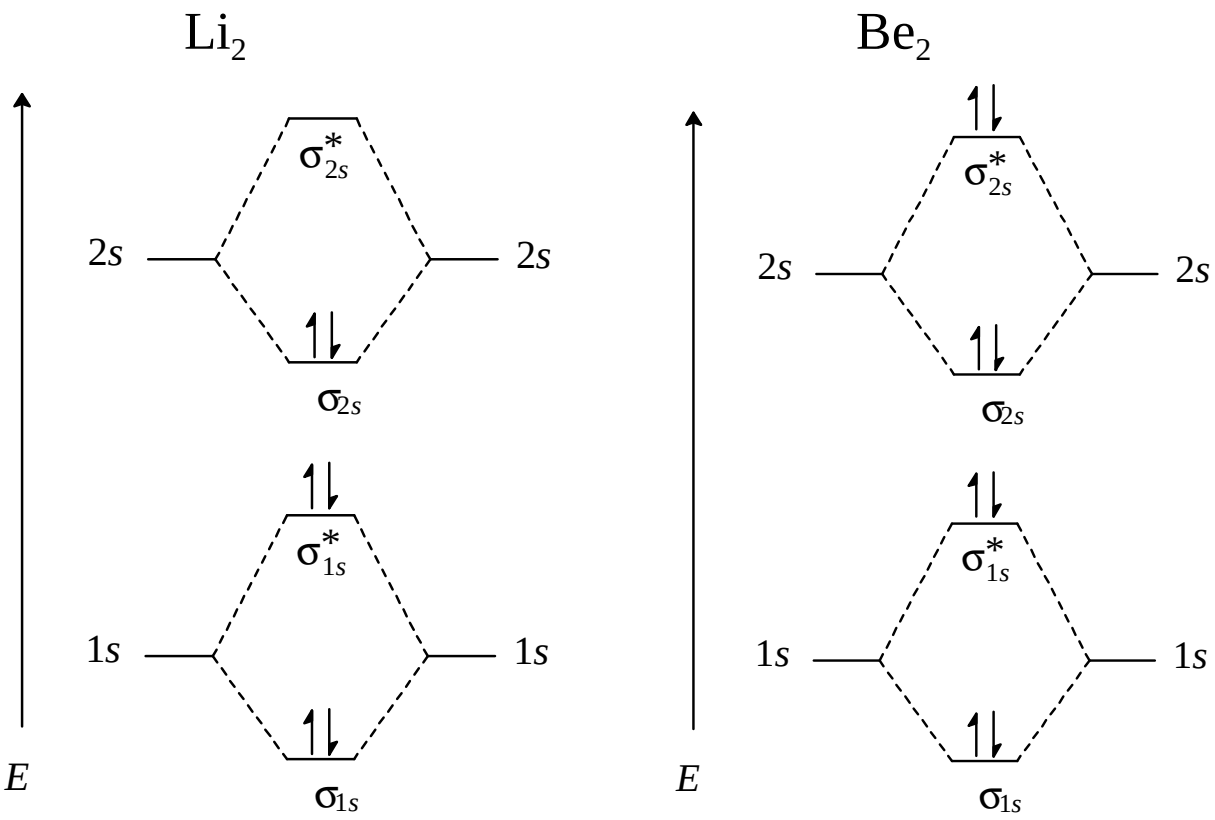


σ^*_{2s}

MO Energy Level Scheme
Li_2, Be_2, and Related Ions



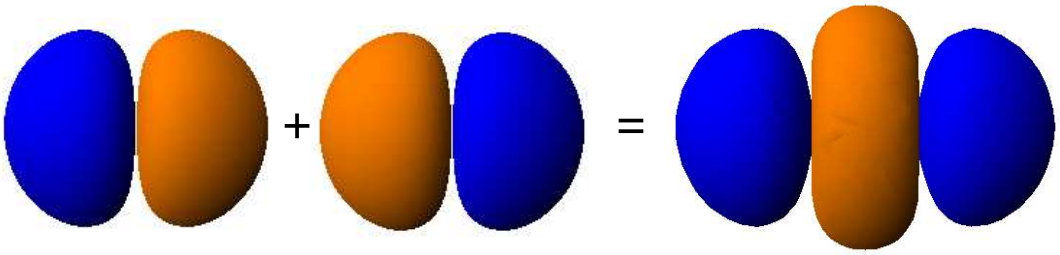
Configurations of Li_2 and Be_2



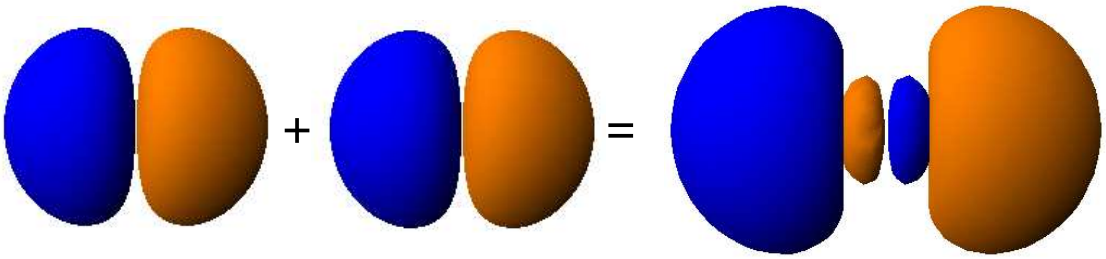
bond order = 1

bond order = 0

Sigma Orbitals from 2*p* ± 2*p*



σ_{2p}



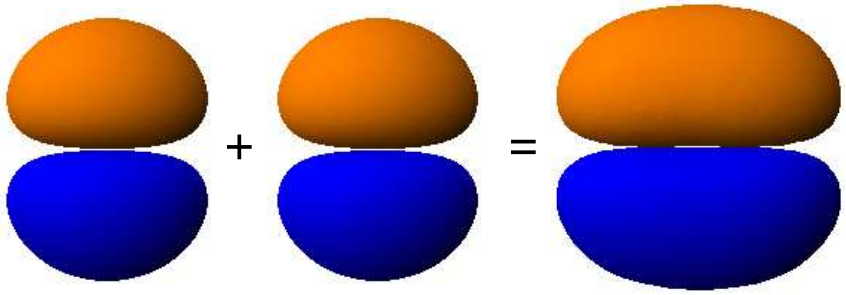
σ^*_{2p}

Pi MOs from $2p \pm 2p$

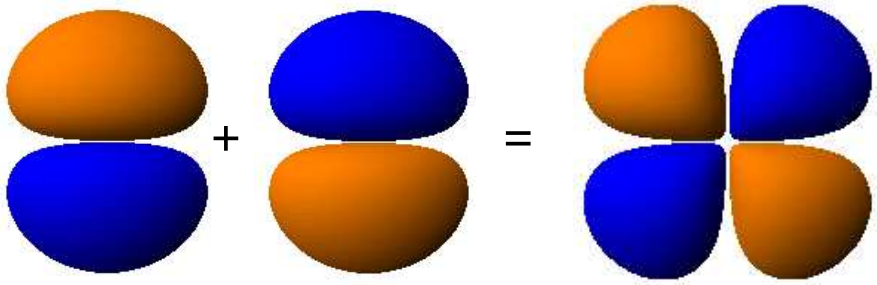
- Two degenerate π_{2p} bonding MOs, one from $2p_x + 2p_x$ and one from $2p_y + 2p_y$.

- Two degenerate π^*_{2p} antibonding MOs, one from $2p_x - 2p_x$ and one from $2p_y - 2p_y$.

$2p_y \pm 2p_y$ Combinations



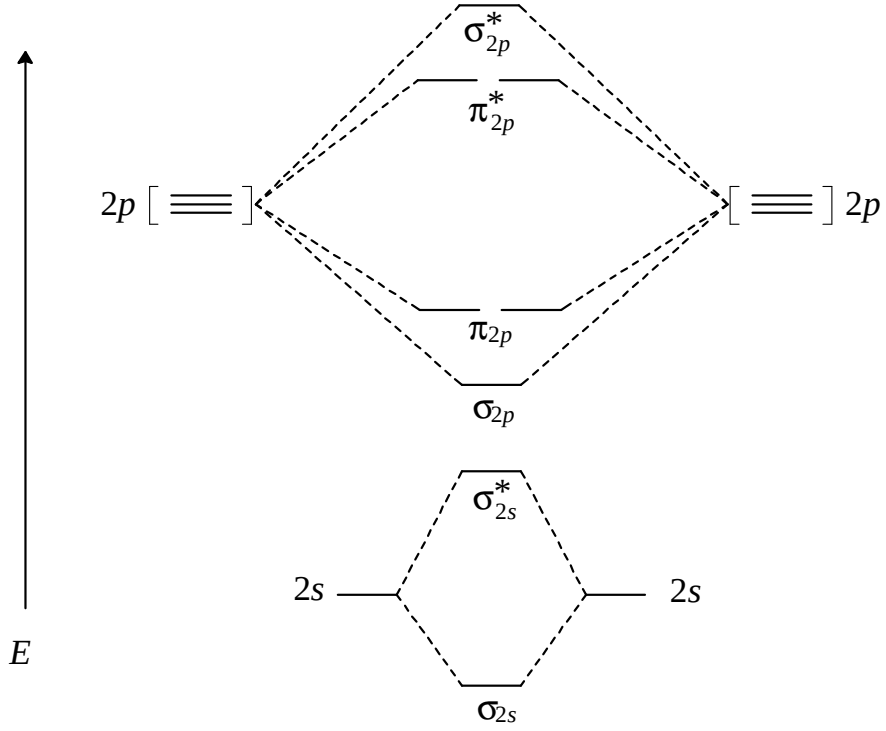
π_{2p}



π^*_{2p}

MO Scheme for O_2 through Ne_2 and Related Ions

☞ The core configuration levels σ_{1s} and σ^*_{1s} are omitted.

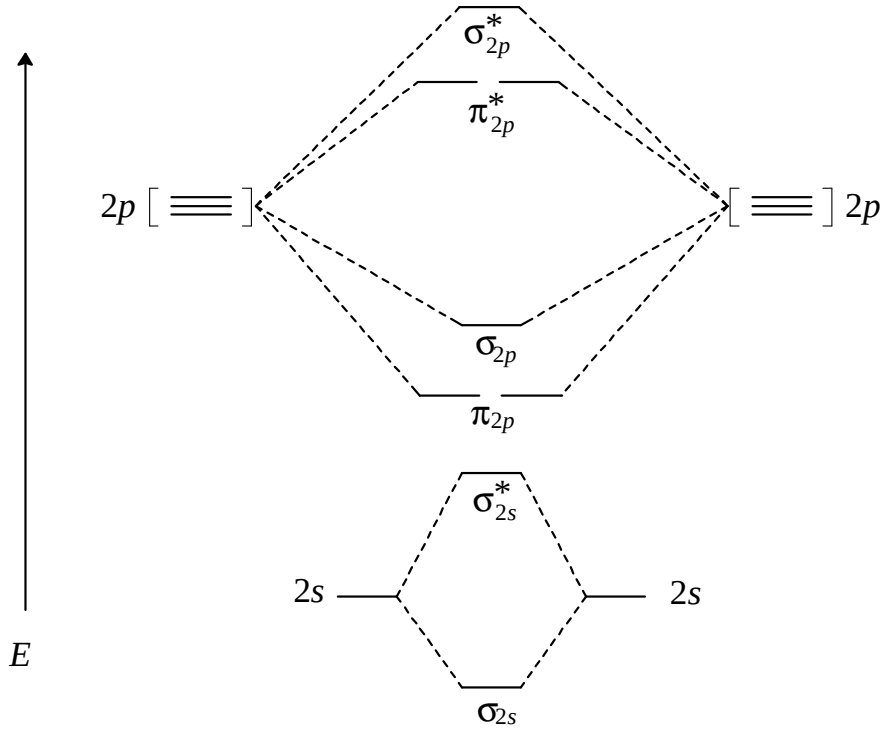


MO Scheme for B_2 through N_2 and Related Ions

- In diatomic molecules of the lighter elements B_2, C_2, and N_2, mixing between sigma-type MOs causes the σ^*_{2s} level to move down and the σ_{2p} level to move up in energy.

- The σ_{2p} level rises above that of π_{2p}.

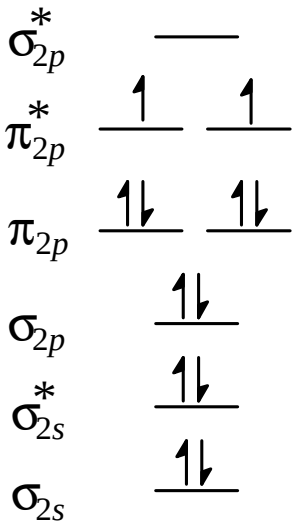
- This results in the following scheme, in which the relative ordering $\pi_{2p} < \sigma_{2p}$ occurs:



Configurations of Second Period Homonuclear Diatomic Molecules

X_2	Configuration	Bond Order	$D(X_2)$ kJ/mol	d(X–X) pm	Magnetic Property
Li_2	$(\sigma_{2s})^2$	1	101	267.3	dia
Be_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0	n/a	n/a	n/a
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^2$	1	291	159	para
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4$	2	599	124.3	dia
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$	3	942	109.77	dia
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	155	141	dia
Ne_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4\ (\sigma^*_{2p})^2$	0	n/a	n/a	n/a

MO Description of O_2 and Its Ions



☞ MO model predicts the observed paramagnetism, which VB theory cannot explain easily.

Formula	Configuration	Bond Order	$D(X_2)$ kJ/mol	d(X–X) pm	Magnetic Property
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
O_2^-	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$	1.5	395	135	para
O_2^{2-}	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	126	149	dia
O_2^+	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^1$	2.5	643	111.6	para

Second Period Heteronuclear Diatomic Molecules

- MO scheme for homonuclear diatomic molecules can be adapted to describe bonding in heteronuclear diatomic molecules.

- The two atoms do not contribute equally to each MO.

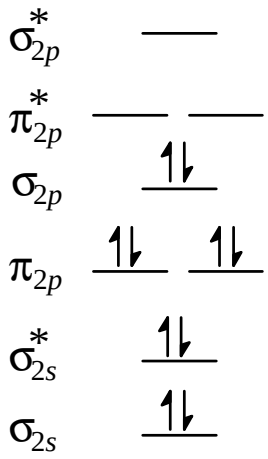
    - More electronegative element has lower energy AOs and makes a greater contribution to bonding MOs.

    - Less electronegative atom makes a greater contribution to antibonding MOs.

- Ordering of MOs energies in heteronuclear cases tends to be like lighter homonuclear cases: i.e., $\pi_{2p} < \sigma_{2p}$

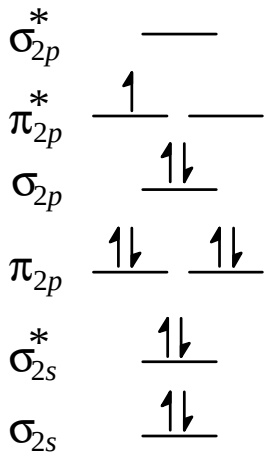
Heteronuclear Diatomic Molecules
Examples

CO, CN^-, NO^+ (10 valence electrons, like N_2)



bond order = 3

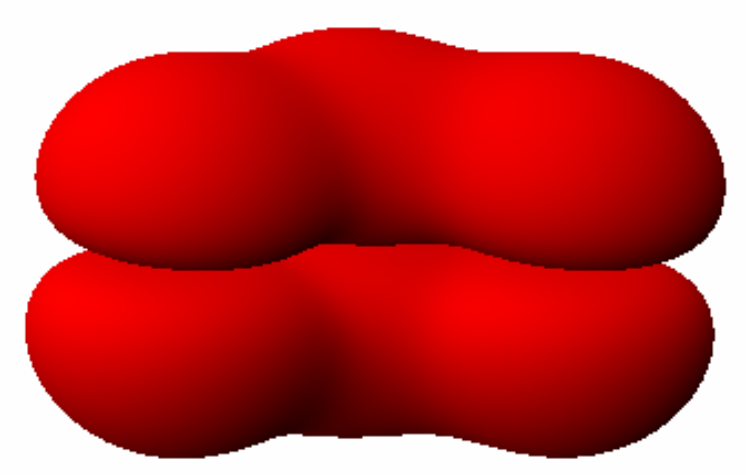
NO (11-electron free radical, like O_2^+)



bond order = 2.5

MO Description of Pi-Delocalized Systems

☞ MO theory has no difficulty explaining the π-delocalized electron density implied by resonance forms, which VB theory cannot easily represent.



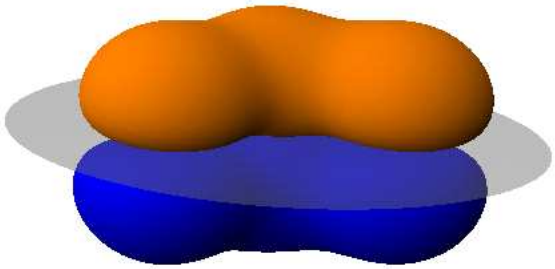
π electron density of O_3

Pi MOs of Ozone, O_3

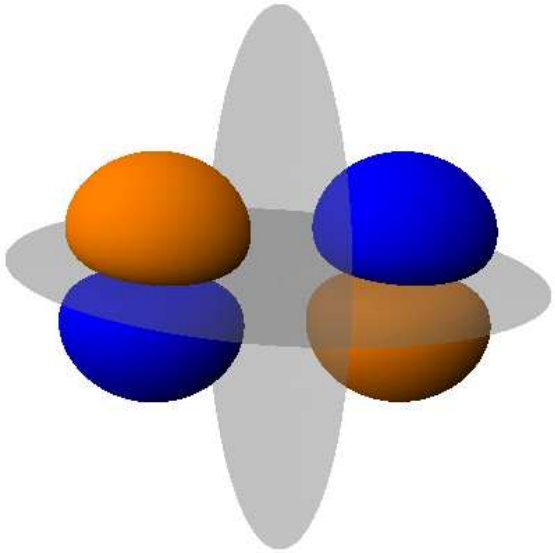
- ✔ The three 2*p* orbitals perpendicular to the molecular plane combine to form three π MOs:
  1. π – bonding MO
  2. π^n – nonbonding MO
  3. π* – antibonding MO

- ✔ A non-bonding MO neither builds nor destroys bonding between the oxygen atoms.

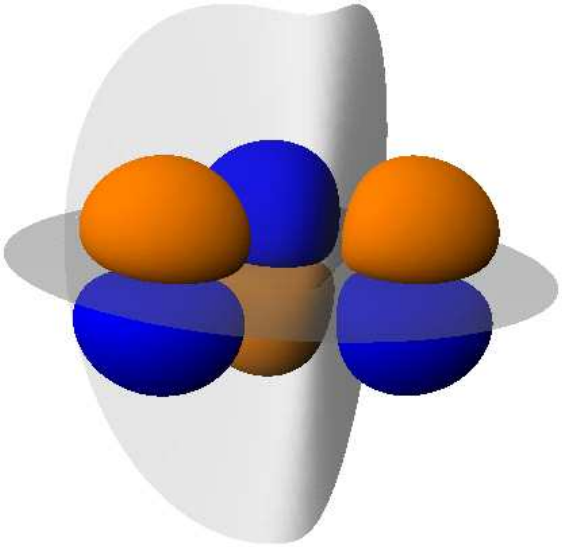
Pi MOs of Ozone, O_3



π (bonding)



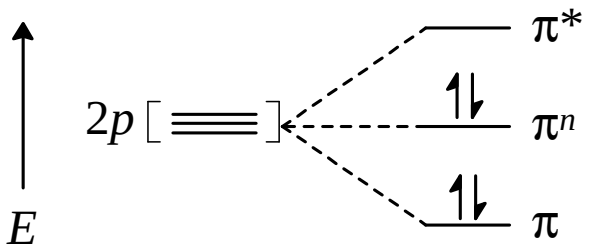
π^n (nonbonding)



π* (antibonding)

Pi MO Energy Level Scheme for O_3

- ✔ The π system has two pairs of electrons, one pair in the π MO, and the other in the π^n non-bonding MO.



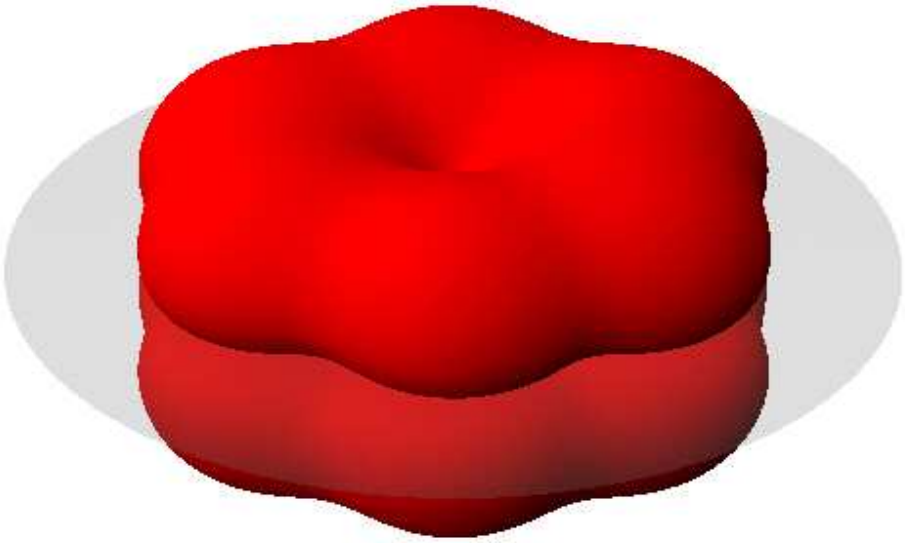
- ✔ The configuration $(\pi)^2$ adds a bond order of 1 across the two O–O bonds (i.e., 0.5 to each bond).

- ✔ When this is added to the sigma bond between each oxygen pair, the O–O bond order becomes 1.5.

- ✔ The configuration $(\pi^n)^2$ neither adds nor subtracts from the overall strength of the bonds.

Pi MOs of Benzene, C_6H_6

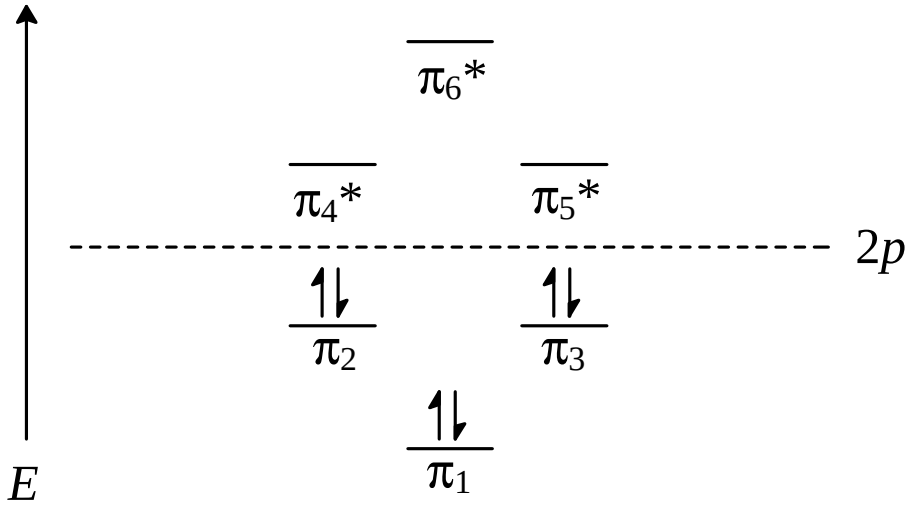
- ✔ C_6H_6, has three pairs of electrons delocalized in a π system extending around the hexagonal ring.



π electron density of benzene

- ✔ The six 2*p* orbitals perpendicular to the ring on the six carbon atoms combine to form three bonding (π_1, π_2, π_3) and three antibonding (π_4*, π_5*, π_6*) MOs.

Pi MO Energy Level Scheme for Benzene, C_6H_6

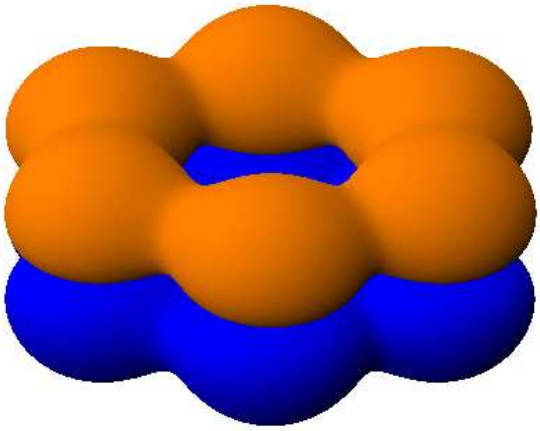


- ✔ Three pairs in bonding MOs add a total of three bond orders over six C–C linkages, or 0.5 for each.

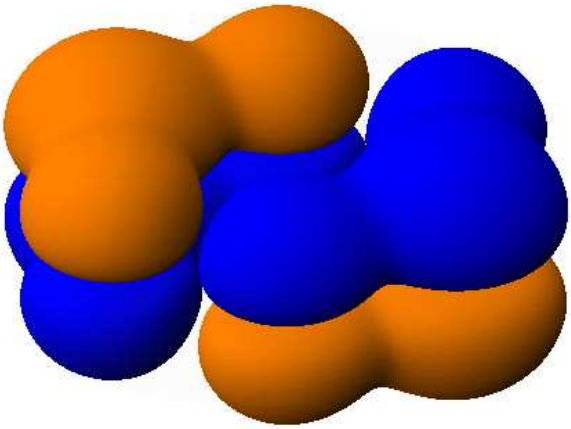
- ✔ When this is added to the sigma bond between each carbon pair, the C–C bond order becomes 1.5.

Occupied Bonding π MOs of Benzene, C_6H_6

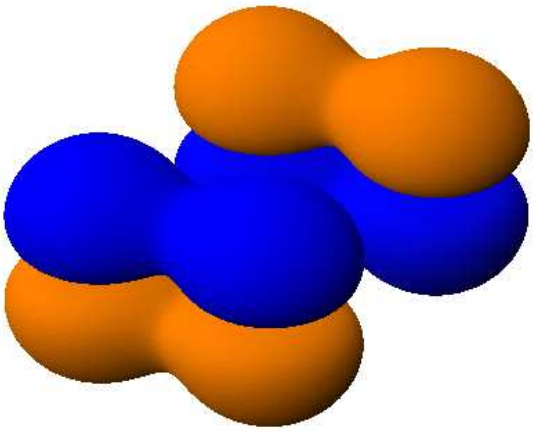
π_1



π_2

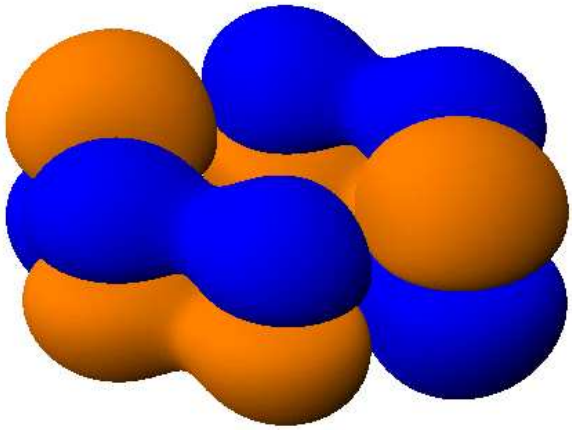


π_3

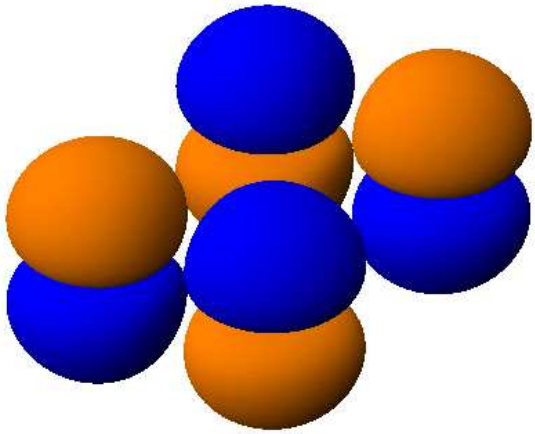


Unoccupied Antibonding π* MOs of Benzene, C_6H_6

π_4^*



π_5^*



π_6^*