

# *Molecular orbital theory*

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# Molecular Orbital Theory

The goal of molecular orbital theory is to describe molecules in a similar way to how we describe atoms, that is, in terms of orbitals, orbital diagrams, and electron configurations.

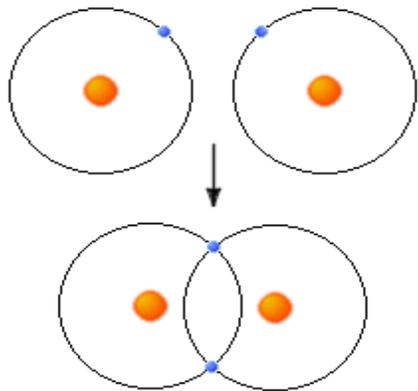
Molecules can form bonds by sharing electron - *Two shared electrons form a single bond*

Atoms can share one, two or three pairs of electrons - *Forming single, double and triple bonds*

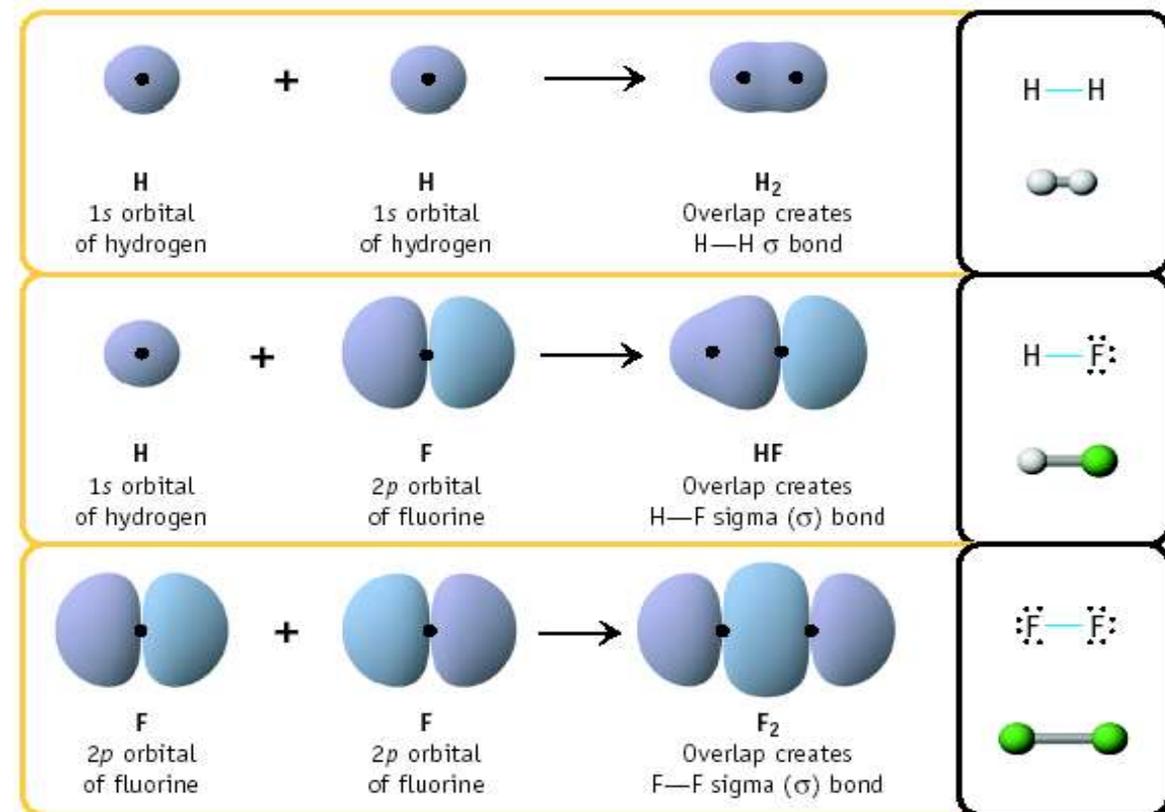
Other types of bonds are formed by **charged atoms** (ionic) and **metal atoms** (metallic).

**Orbital Mixing:** When atoms share electrons to form a bond, their *atomic orbitals mix* to form molecular bonds. In order for these orbitals to mix they must:

- Have similar energy levels.
- Overlap well.
- Be close together.



The two atoms share one electron each from their outer shell. In this case both 1s orbitals overlap and share their valence electrons.



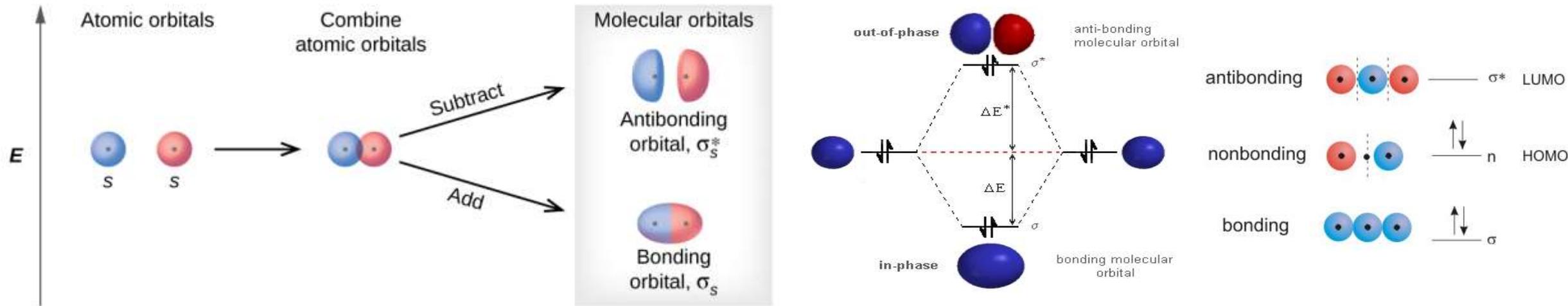
# Molecular Orbital Theory

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mullikan in 1932

- ❑ In valence bond theory, **orbitals in a molecule are thought to be localized on atoms**, with some overlap of the orbitals between bonded nuclei. In the molecular orbital view, **orbitals in a molecule are thought to be spread out (delocalized) over many atoms**.
- ❑ Valence bond theory is often referred to as a **localized bonding theory** while molecular orbital theory is referred to as a **delocalized bonding theory**.
- ❑ The molecular orbital theory is used **to predict the shapes and energies of orbitals that contain no electrons**.

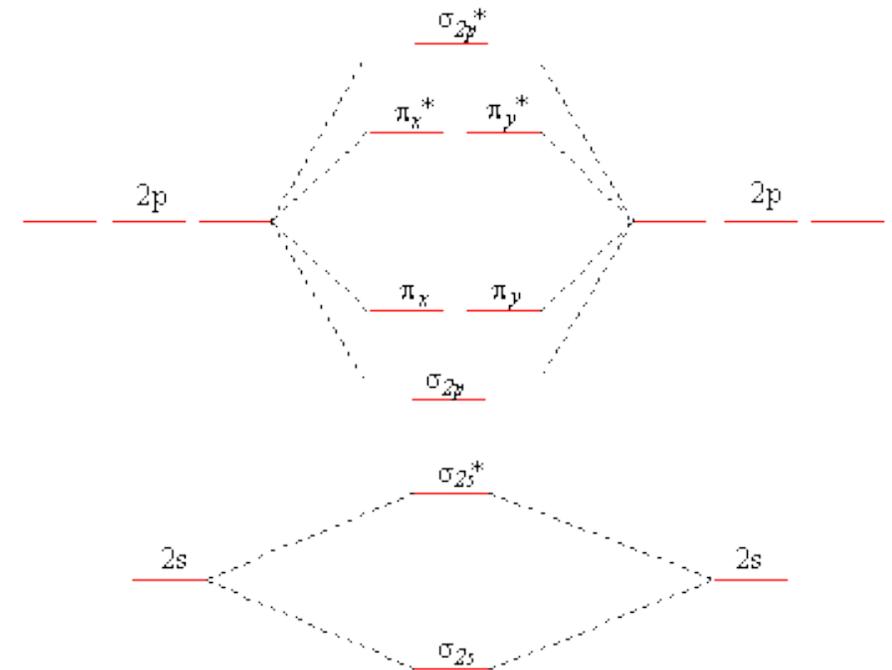
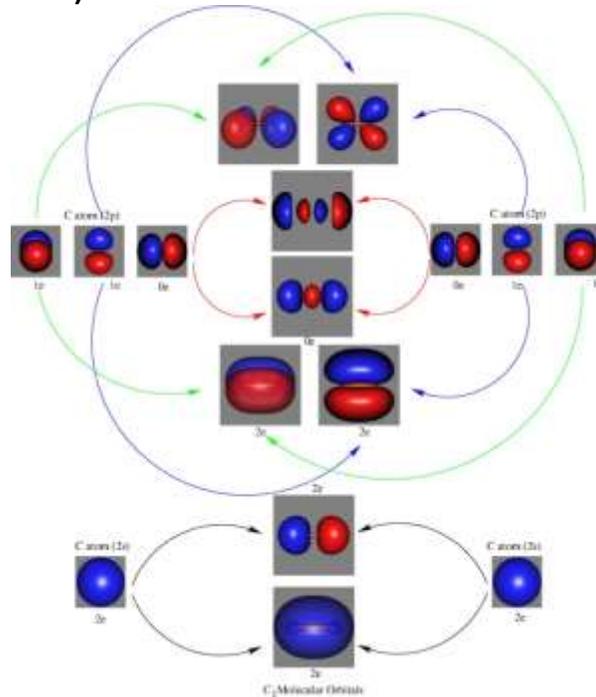
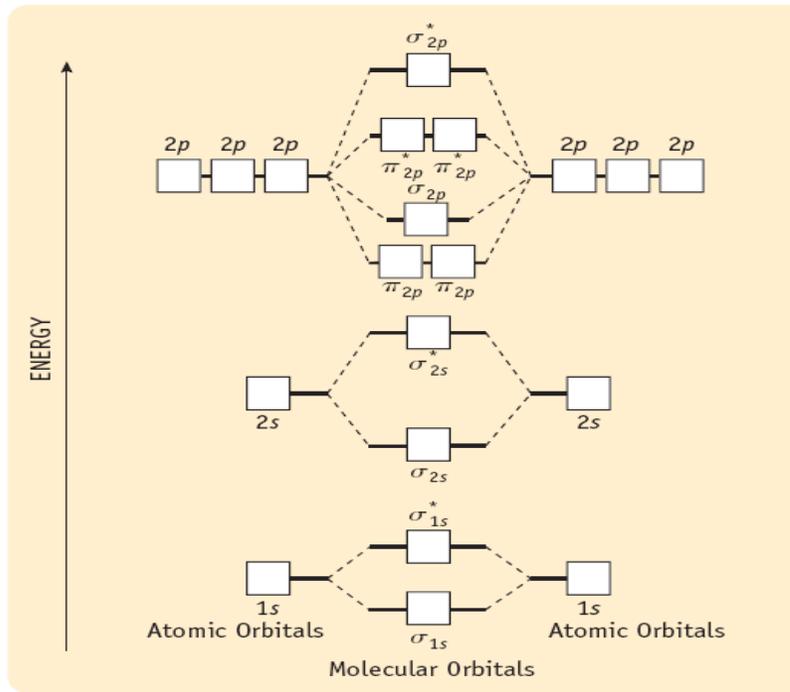
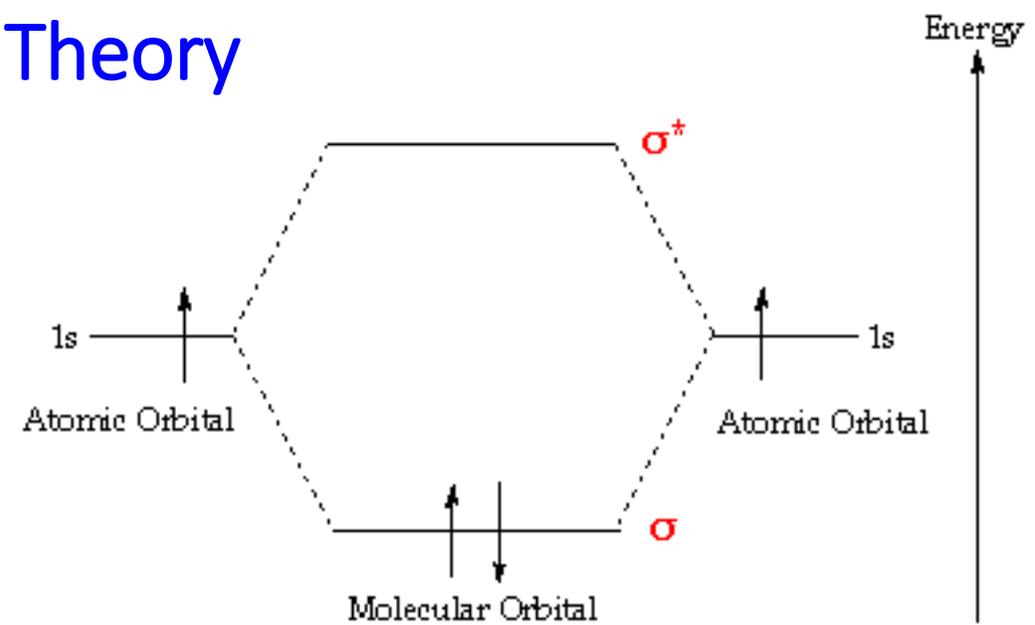
## Principle of MOT

“ Any number of atomic orbitals overlaps to form molecular orbitals, an **equal number** of molecular orbitals are formed. When two s orbitals overlap, they form two new orbitals: one at lower energy than the original s orbitals and one at higher energy than the original s orbitals”.



# Molecular Orbital Theory

- ❑ Each line in the diagram represents an orbital.
- ❑ The electrons fill the molecular orbitals of molecules like electrons fill atomic orbitals in atoms
- ❑ Electrons go into the lowest energy orbital available to form lowest potential energy for the molecule.
- ❑ The maximum number of electrons in each molecular orbital is two. (Pauli exclusion principle)
- ❑ One electron goes into orbitals of equal energy, with parallel spin, before they begin to pair up. (Hund's Rule.)



# Molecular Orbital Theory

• Atomic orbitals mix together and make: • Molecular Orbitals can:

– **Bonding Orbitals**

Electrons in these orbitals help hold atoms near each other

– **Antibonding Orbitals**

Electrons in these orbitals push atoms apart from each other

– **Nonbonding Orbitals**

Electrons in these orbitals have no effect on bonding

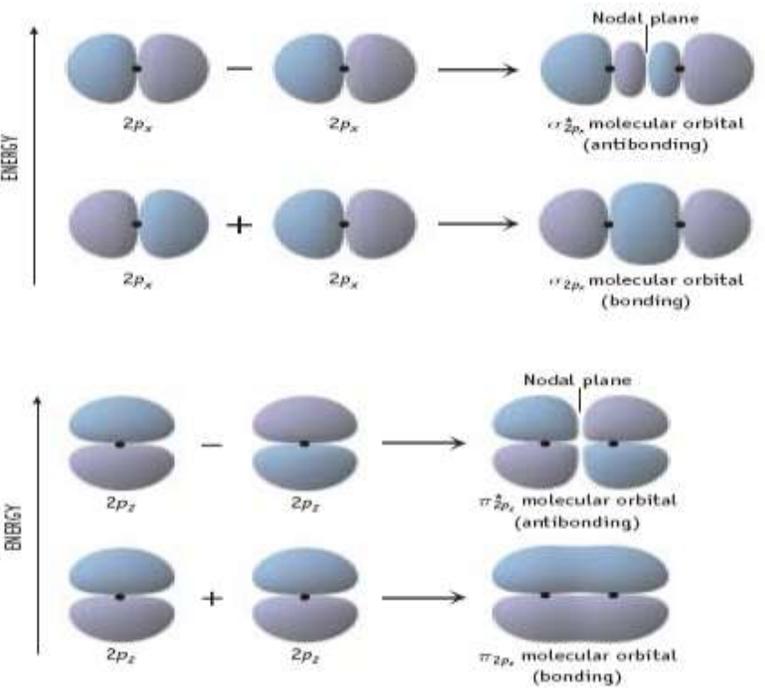
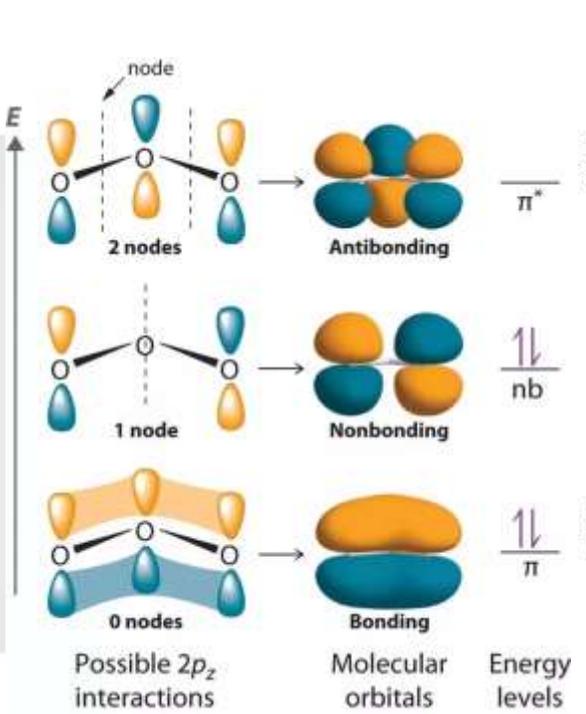
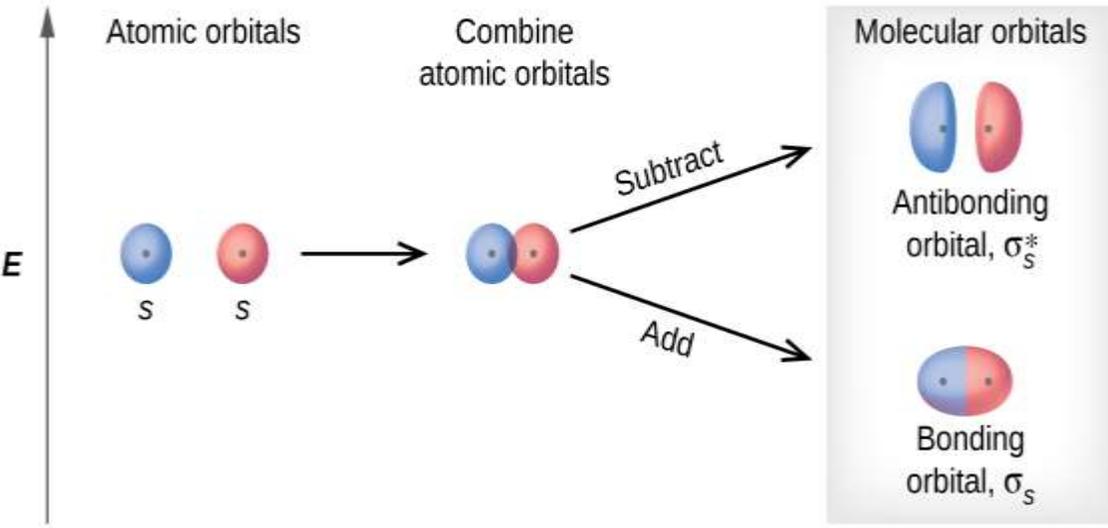
– be **Sigma or Pi**

– be **spread over multiple atoms**

– **Paramagnetic:** a compound with any unpaired electrons

– **Diamagnetic:** no unpaired electrons.

	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>
$\sigma_{2p}^*$					
$\pi_{2p}^*$					
$\sigma_{2p}$					
$\pi_{2p}$					
$\sigma_{2s}^*$					
$\sigma_{2s}$					



# Molecular Orbital Theory

## Comparison of bonding theories:

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (s, p, d...) and hybrid orbitals (sp, sp <sup>2</sup> , sp <sup>3</sup> ...)	combines atomic orbitals to form molecular orbitals ( $\sigma$ , $\sigma^*$ , $\pi$ , $\pi^*$ )
forms $\sigma$ or $\pi$ bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	No needs multiple structures to describe resonance

# Molecular Orbital Theory

## Linear combination of atomic orbitals to give molecular orbitals LCAO-MO approach

The technique used to construct **molecular wave functions** is known as the **linear combination of atomic orbitals** (denoted as LCAO-MO). The linear combination of atomic orbitals can be written mathematically as –

$$\varphi = \sum a_i \phi_i \quad (1)$$

Where,  $\varphi$  is the molecular wave function,  $\phi$  is atomic wave function, and  $a$  is a weighting coefficient that gives the relative weight in the “mix” of the atomic wave functions.

For diatomic molecule,  $i = 2$ , then –

$$\varphi = a_1 \phi_1 + a_2 \phi_2$$

The **average value for a dynamical variable  $a$**  whose **operator** is  $\alpha$ , is calculated by using following relationship ( $r, \theta, \varphi$ ) are polar co-ordinates and energy is -

$$\langle a \rangle = \frac{\int \varphi^* \alpha \varphi dr}{\int \varphi^* \varphi dr} \quad E = \frac{\int \varphi^* \hat{H} \varphi dr}{\int \varphi^* \varphi dr}$$

Where,  $\hat{H}$  is the Hamiltonian operator, the operator for total energy. Substituted equation (1) for  $\varphi$  in the equation -

$$E = \frac{\int (a_1 \phi_1^* + a_2 \phi_2^*) \hat{H} (a_1 \phi_1 + a_2 \phi_2) dr}{\int (a_1 \phi_1^* + a_2 \phi_2^*) (a_1 \phi_1 + a_2 \phi_2) dr}$$

Simply above equation –

$$E = \frac{a_1^2 \int \phi_1^* \hat{H} \phi_1 dr + 2 a_1 a_2 \int \phi_1^* \hat{H} \phi_2 dr + a_2^2 \int \phi_2^* \hat{H} \phi_2 dr}{a_1^2 \int \phi_1^* \phi_1 dr + 2 a_1 a_2 \int \phi_1^* \phi_2 dr + a_2^2 \int \phi_2^* \phi_2 dr}$$

# Molecular Orbital Theory

it is assumed that –

$$\int \phi_1^* \hat{H} \phi_2 dr = \int \phi_2^* \hat{H} \phi_1 dr$$

$$\int \phi_1^* \phi_2 dr = \int \phi_2^* \phi_1 dr$$

These assumptions are valid for a **diatomic molecule composed of identical atoms** (*homonuclear* diatomic) because  $\phi_1$  and  $\phi_2$  are identical and real.

According to the definition of  $H_{11}$  and  $H_{12}$ , we have –

$$H_{11} = \int \phi_1^* \hat{H} \phi_1 dr$$

$$H_{12} = \int \phi_1^* \hat{H} \phi_2 dr$$

$\hat{H}$  is the operator for total energy,  $H_{11}$  represents the binding energy of an electron in atom 1 to its nucleus. If the subscripts on the wave functions are both 2, the binding energy of electron in atom 2 to its nucleus. Such integrals represent the energy of an electrostatic interaction so they are known as **Coulomb integrals**.

$H_{12}$  represents the energy of the interaction of the electron in atom 1 with the nucleus of atom 2 and vice versa. Therefore, they are known as **exchange integrals**. Interactions of this type must be related to the distance separating the nuclei.

# Molecular Orbital Theory

The equation (6) can be simplified as -

$$E = \frac{a_1^2 H_{11} + 2 a_1 a_2 H_{12} + a_2^2 H_{22}}{a_1^2 + 2 a_1 a_2 S_{12} + a_2^2}$$

To find a minimum in the energy expression, we take the partial derivatives with respect to  $a_1$  and  $a_2$  and set them equal to 0:

$$\left[ \frac{\partial E}{\partial a_1} \right]_{a_2} = 0 \quad \text{and} \quad \left[ \frac{\partial E}{\partial a_2} \right]_{a_1} = 0$$

When the differentiations are carried out with respect to  $a_1$  and  $a_2$  in turn while keeping the other constant, we obtain two equations as -

$$a_1(H_{11} - E) + a_2(H_{12} - S_{12} E) = 0$$

$$a_2(H_{22} - E) + a_1(H_{21} - S_{21} E) = 0$$

These equations are known as the *secular equations*, in which the weighting coefficients  $a_1$  and  $a_2$  are the unknowns.

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

For the homonuclear diatomic molecule,  $H_{12} = H_{21}$ ,  $H_{11} = H_{22}$  and  $S_{12} = S_{21} = S$ , then

$$(H_{11} - E)^2 - (H_{12} - S E)^2 = 0 \quad (H_{11} - E) = \pm (H_{12} - S E)$$

From which we find two values for E -

$$E_b = \frac{H_{11} + H_{12}}{1+S} \quad \text{and} \quad E_a = \frac{H_{11} - H_{12}}{1-S}$$

# Molecular Orbital Theory

In addition to the integrals that represent energies, another integral called as **overlap integrals**, and they represent effectiveness with which the orbitals overlap in a region of space.

$$S_{11} = \int \phi_1^* \phi_1 dr$$

$$S_{12} = \int \phi_1^* \phi_2 dr$$

If the **subscripts are identical**, orbitals on the **same atom are indicated**, and if the atomic wave functions are normalized, the value of such an integral is 1.

$$S_{11} = \int \phi_1^* \phi_1 dr = S_{22} = \int \phi_2^* \phi_2 dr = 1 \quad \text{and}$$

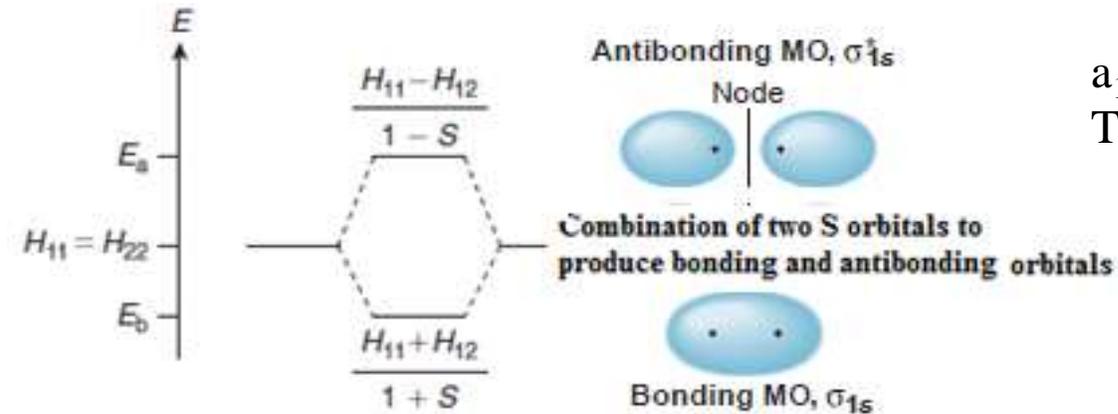
$$S_{12} = \int \phi_1^* \phi_2 dr = S_{21} = \int \phi_2^* \phi_1 dr$$

These integrals are related to the *degree of overlap* of an orbital on atom 1 with an orbital on atom 2. If the two atoms are **separated by a large distance, the overlap integral approaches to 0**. However, if the atoms are closer together, there is some overlap of the orbitals and  $S > 0$ .

Overlap integral lies in between 0 to 1 and is function of the internuclear distance.

# Molecular Orbital Theory

The energy state labeled  $E_b$  is known as the *bonding* or *symmetric* state, whereas that designated as  $E_a$  is called the *antibonding* or *asymmetric* state.

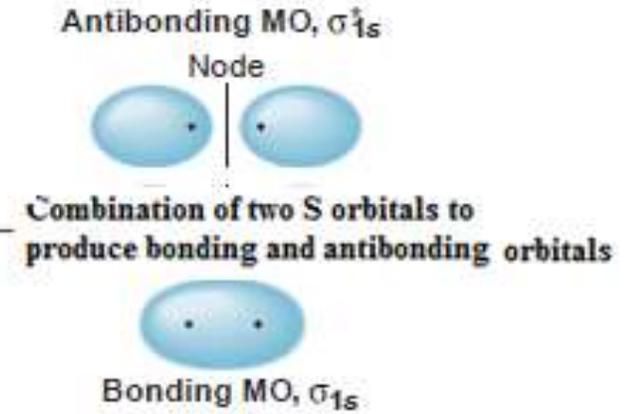
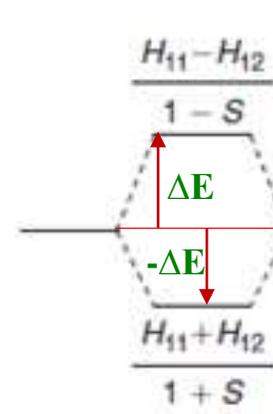
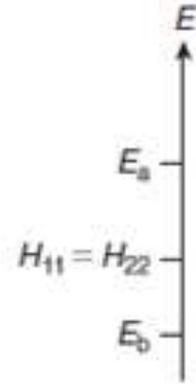
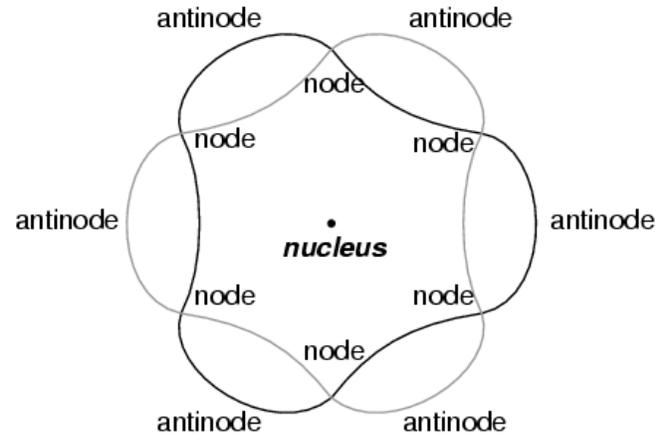
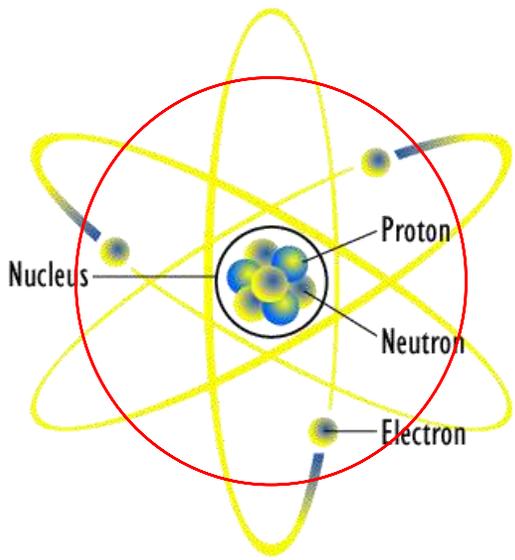


$a_1 = a_2$  (for the *symmetric* state) and  $a_1 = -a_2$  (for the *antisymmetric* state)  
Therefore,

$$\varphi_b = a_1 \phi_1 + a_2 \phi_2 = \frac{1}{\sqrt{2+2S}} (\phi_1 + \phi_2)$$

$$\varphi_a = a_1 \phi_1 - a_2 \phi_2 = \frac{1}{\sqrt{2-2S}} (\phi_1 - \phi_2)$$

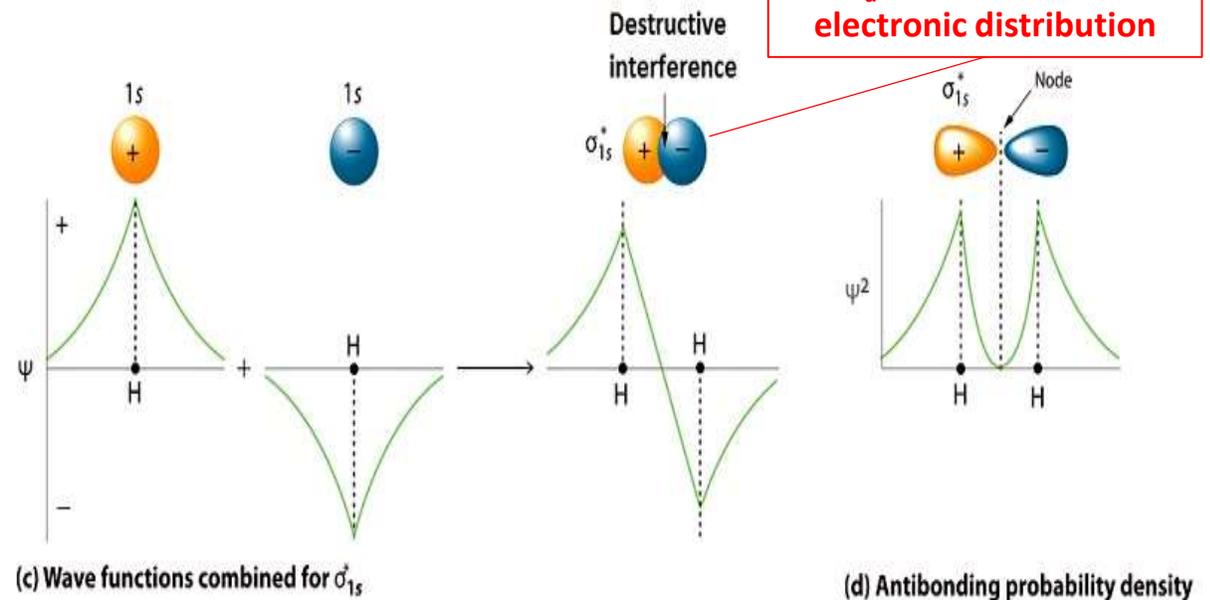
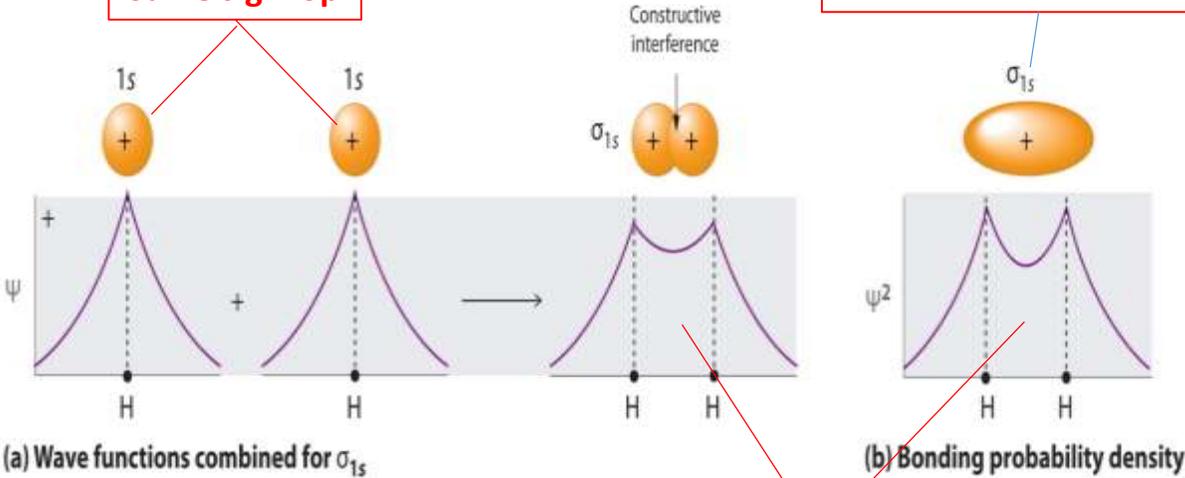
# Molecular Orbital Theory



Same sign lob

**e<sub>g</sub>- symmetrical electronic distribution**

**e<sub>u</sub>- unsymmetrical electronic distribution**



**Electron density is more between two nuclei  
So less nucleus – nucleus repulsion – stable**

(c) Wave functions combined for  $\sigma_{1s}^*$

(d) Antibonding probability density

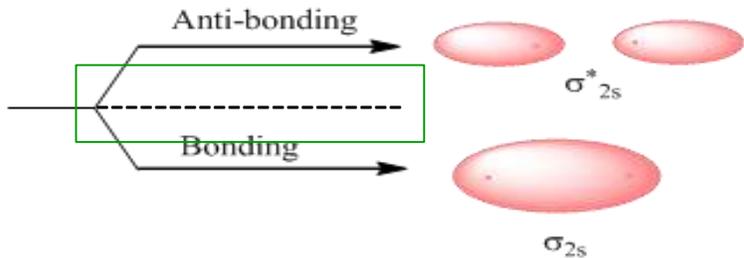
# Molecular Orbital Theory

## Difference between Bonding and Antibonding molecular orbitals

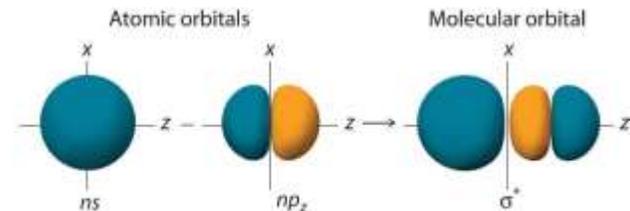
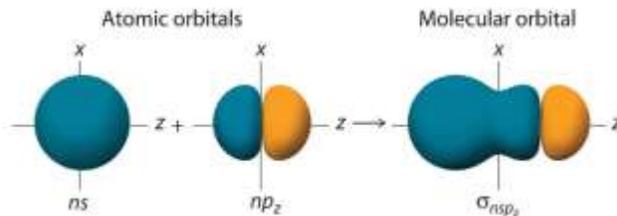
Bonding MO	Antibonding MO
It is formed by <b>addition overlap</b> of atomic orbitals.	It is formed by <b>subtraction overlap</b> of atomic orbitals.
The wave function of a bonding MO is given by $\psi_{(MO)} = \psi_A + \psi_B$	The wave function of an antibonding MO is given by $\psi^*_{(MO)} = \psi_A - \psi_B$
Its formation takes place when the <b>lobes of atomic orbitals have same signs</b> .	Its formation takes place when the <b>lobes of atomic orbitals have different signs</b> .
The <b>energy of bonding MO is lower</b> than that of atomic orbitals from which it is formed.	The <b>energy of antibonding MO is higher</b> than that of atomic orbitals from which it is formed.
The <b>electron density is high</b> in the region between the nuclei of bonded atoms.	The <b>electron density is low</b> in the region between the nuclei of bonded atoms.
Every electron in bonding MO <b>contributes towards the attractive force</b> .	Every electron in antibonding <b>contributes towards repulsive force</b> .

# Molecular Orbital Theory – Orbital overlapping

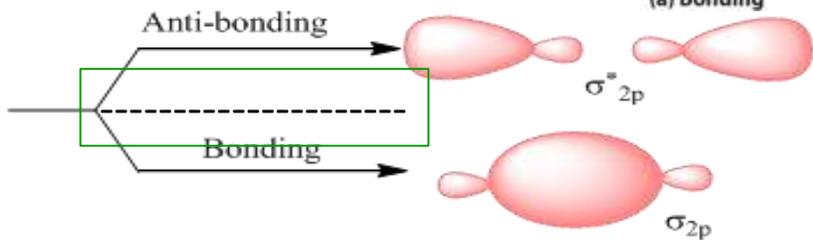
## S – S orbital MO



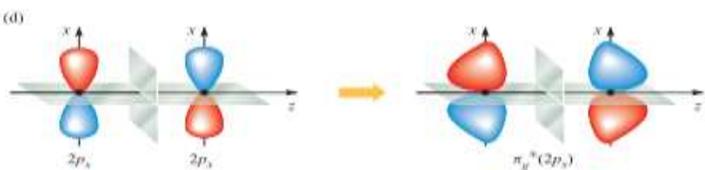
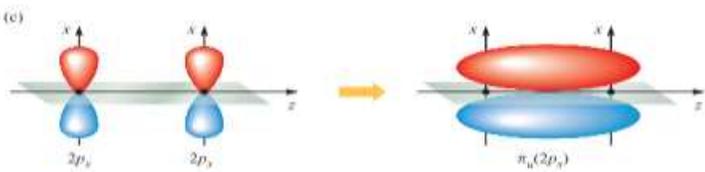
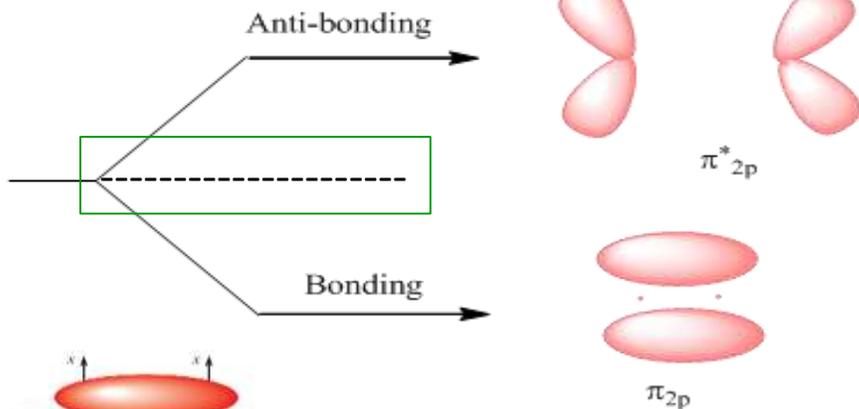
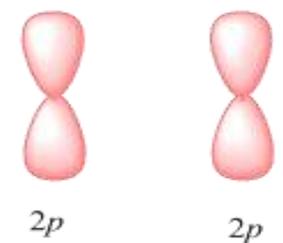
## S – $P_z$ orbital MO



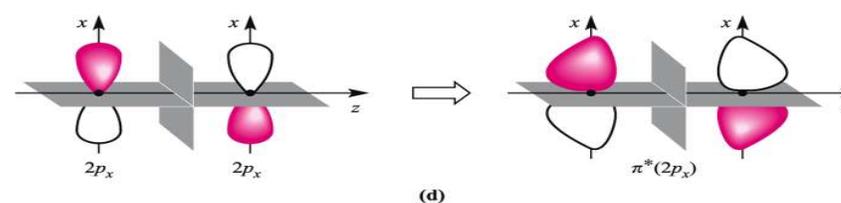
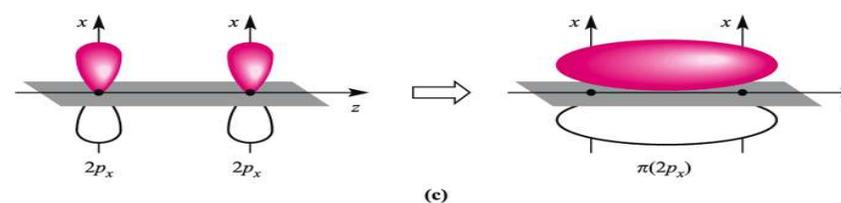
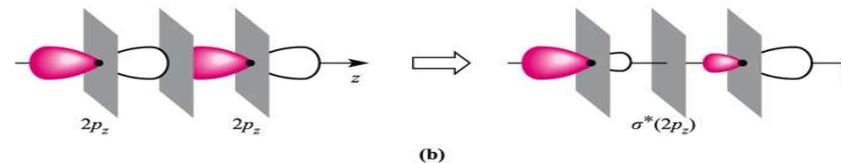
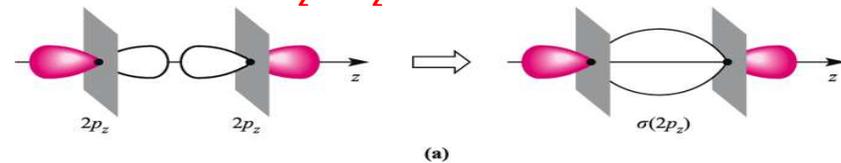
## $P_x$ – $P_x$ orbital MO



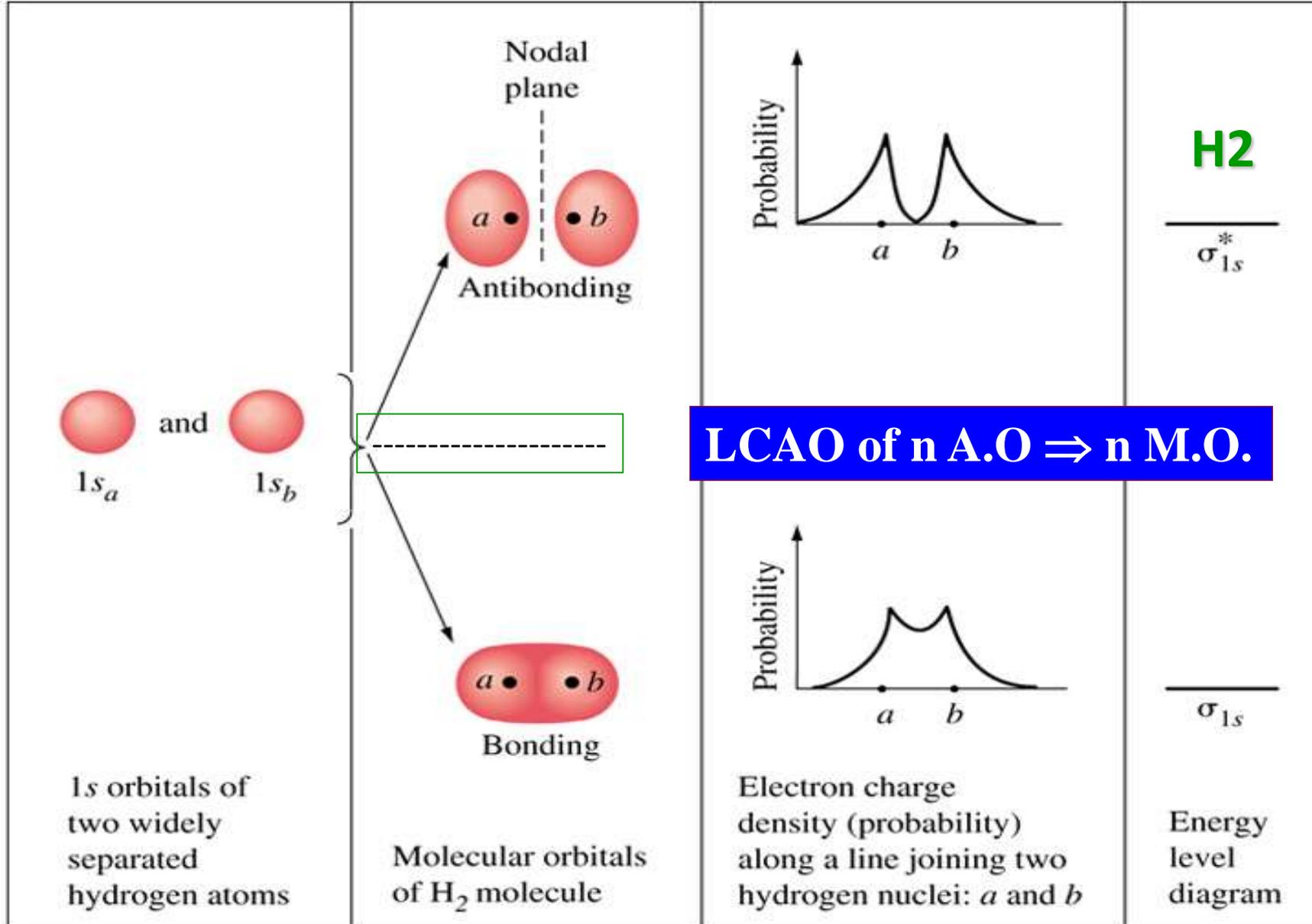
## $P_y$ – $P_y$ orbital MO



## $P_z$ – $P_z$ orbital MO



# Molecular Orbital Theory – Homonuclear diatomic molecules



**LCAO of n A.O  $\Rightarrow$  n M.O.**

$E = 11.4 \text{ eV}$

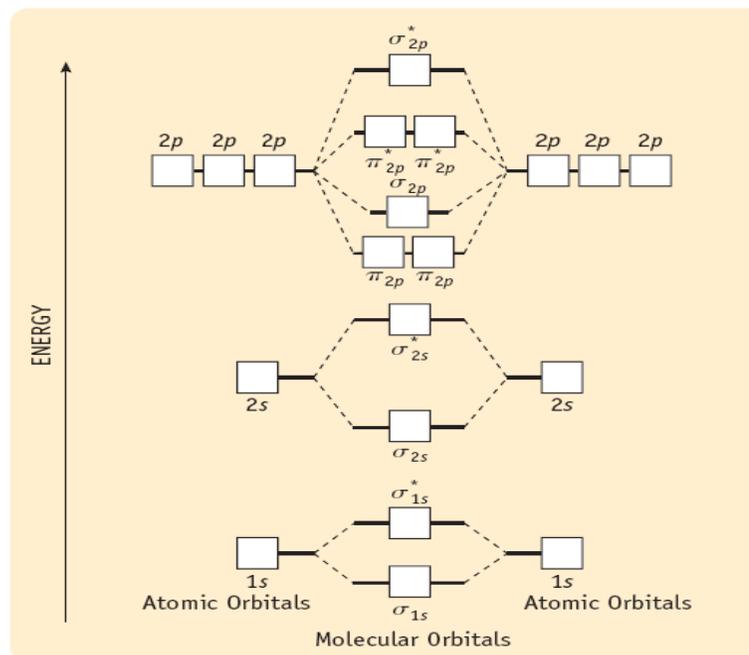
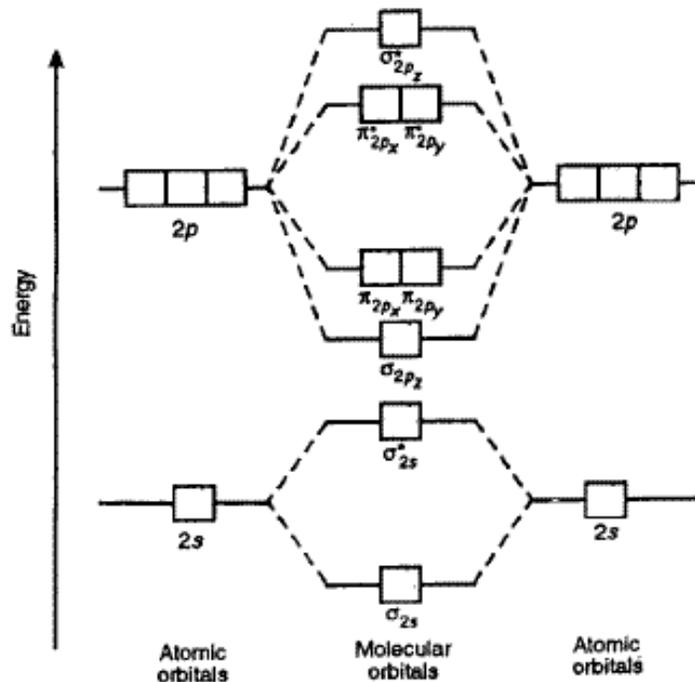
Bond length = 109 nm

Location of Bonding orbital  
 $4.5 \text{ eV}$

# Molecular Orbital Theory – Homonuclear diatomic molecules

When atoms share electrons to form a bond, their *atomic orbitals mix* to form molecular bonds. In order for these orbitals to mix they must:

- ❑ Have similar energy levels.
- ❑ Overlap well.
- ❑ Be close together – positive/in-phase overlap (bonding), negative/out of phase overlap (anti-bonding)



## Advantageous:

1. Electron density in Bonding and anti-bonding Molecular orbitals; bonding electrons stabilizes Molecule while anti-bonding electron destabilizes Bonding.
2. Bond order: As bond order increases, stabilization of the molecule increases with increase in bond order and decrease in bond length.

$$= \frac{1}{2}[(\text{number of bonding electrons}) - (\text{number of antibonding electrons})]$$

All homonuclear diatomic molecules (2<sup>nd</sup> row contain 1s, 2s & 2p orbitals. these molecules are divided in three groups:

1. Use 1s & 2s orbitals – H<sub>2</sub>, He<sub>2</sub>, Li<sub>2</sub> and Be<sub>2</sub>.
2. Use 1s, 2s, and 2p orbitals – O<sub>2</sub>, F<sub>2</sub> and He<sub>2</sub>.
3. Use 1s, 2s & 2p after mixing – B<sub>2</sub>, C<sub>2</sub> & N<sub>2</sub>.

3. Magnetic properties: Diamagnetic (all electrons are paired; Paramagnetic (atleast one electron is unpaired).

# Molecular Orbital Theory – Hydrogen molecule

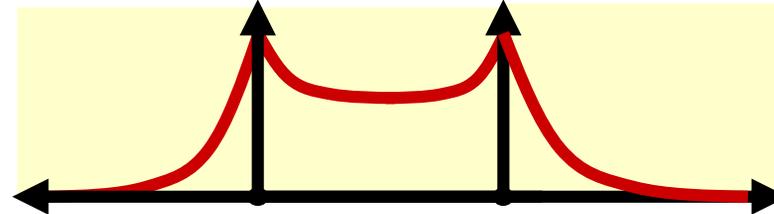
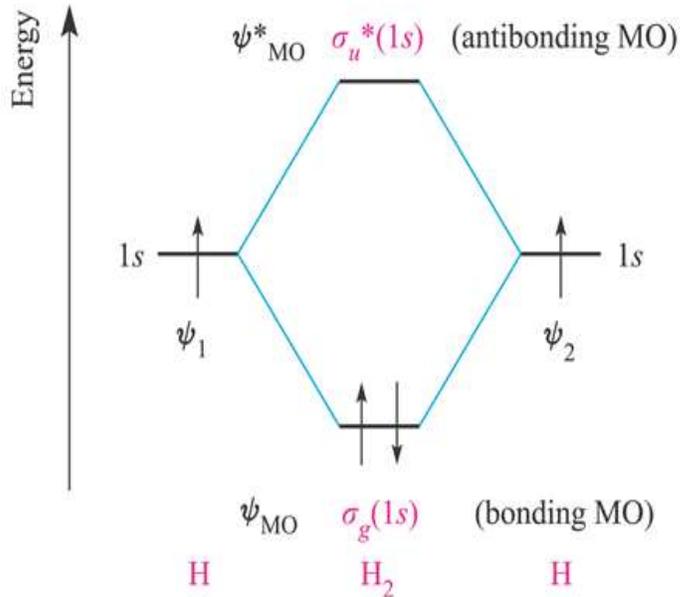
Each of the H atoms has  $1s^1$  atomic orbital with associated wave functions,  $\Psi_1$  and  $\Psi_2$  and the signs of the wave function associated with the  $1s$  orbital may be either + or -.

The possible combinations of the two  $1s$  orbitals are given by equations:

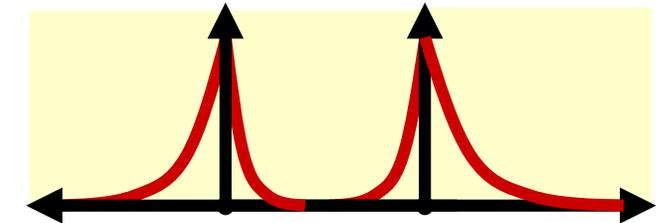
$$\varphi_b = a_1 \phi_1 + a_2 \phi_2 = N(\phi_1 + \phi_2)$$

$$\varphi_a = a_1 \phi_1 - a_2 \phi_2 = N(\phi_1 - \phi_2)$$

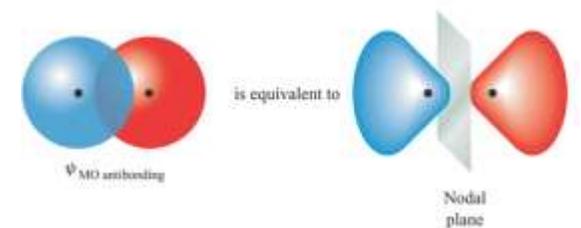
The interaction between the H  $1s$  AOs on forming  $H_2$  may be represented by the MO diagram shown below.



constructive interference  
in-phase (*bonding*) interaction



destructive interference  
out-of-phase (*antibonding*) interaction



The ground state electronic configuration of  $H_2$  may be written as using the notation;  $\sigma_g(1s^2) \sigma_u^*(1s^0)$ .

$$\begin{aligned} \text{Bond order} &= \frac{1}{2}[(\text{number of bonding electrons}) - (\text{number of antibonding electrons})] \\ &= \frac{1}{2}[2 - 0] = 1 \end{aligned}$$

i.e. Hydrogen molecule contain one  $\sigma$ -bond.

$H_2$  molecule is diamagnetic - All electrons are paired.

# Molecular Orbital Theory – Helium molecule

Each of the He atoms has  $1s^2$  atomic orbital with associated wave functions,  $\Psi_1$  and  $\Psi_2$ .

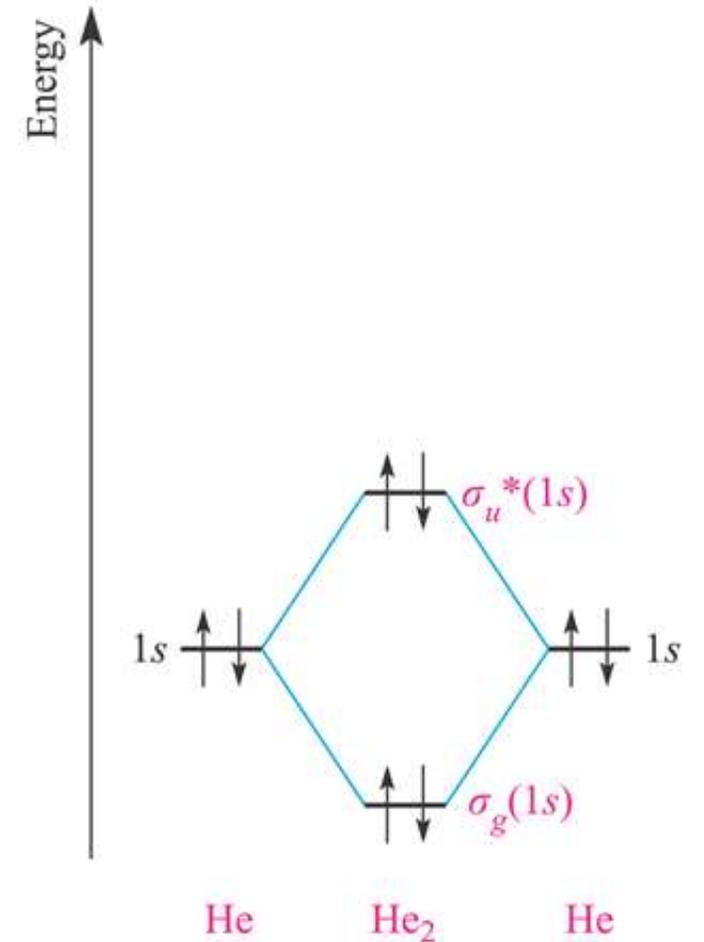
Molecular orbital electronic configuration -  $\sigma_g(1s^2) \sigma_u^*(1s^2)$ .

The bonding effect of the  $\sigma_g(1s^2)$  is cancelled by the anti-bonding effect of  $\sigma_u^*(1s^2)$ .

The  $\text{He}_2$  molecule is not a stable species.

Bond order = 0

$\text{He}_2$  molecule is diamagnetic - All electrons are paired.



# Molecular Orbital Theory

Consider  $\text{H}_2^+$ ,  $\text{H}_2$ ,  $\text{He}_2^+$ ,  $\text{He}_2$ : first row diatomic molecules and ions

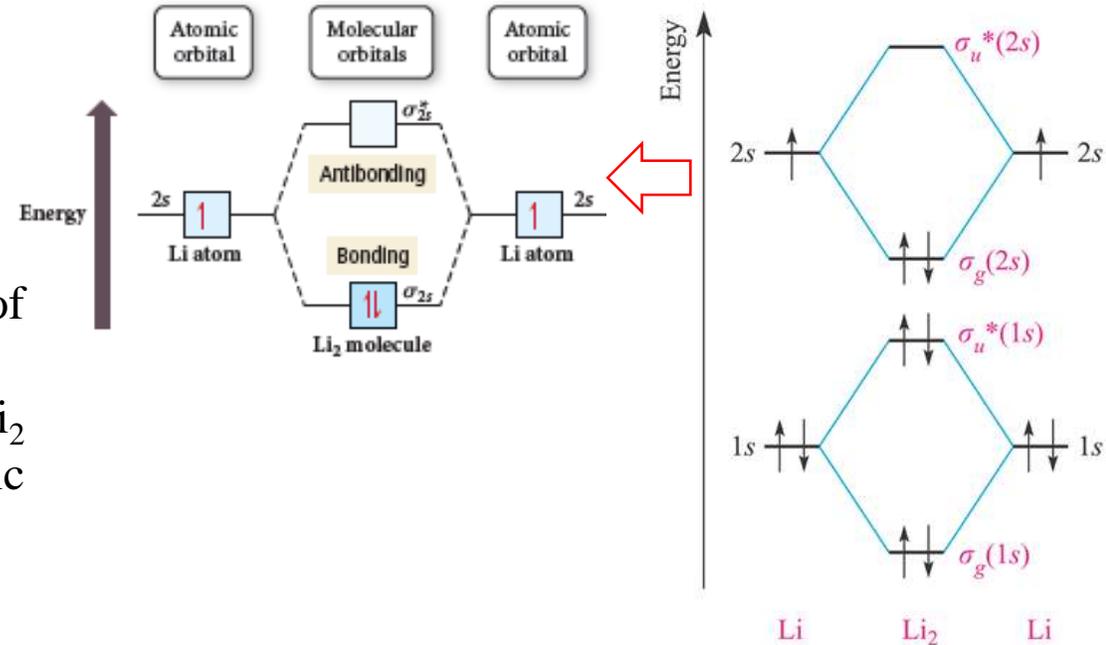
	$\text{H}_2$	$\text{H}_2^+$	$\text{He}_2^+$	$\text{He}_2$
$E \uparrow$ $\sigma_g (1s^2)$ $\sigma_u^* (1s^2)$				
Magnetism	Dia-	Para-	Para-	-
Bond order	1	$\frac{1}{2}$	$\frac{1}{2}$	0
Bond energy (kJ/mol)	436	225	251	-
Bond length (pm)	74	106	108	-

# Molecular Orbital Theory

## Lithium molecule

The ground state electronic configuration of Li ( $Z = 3$ ) is  $1s^2 2s^1$  and when **two Li atoms combine**, orbital overlap occurs efficiently between the 1s atomic orbitals; between the 2s atomic orbitals.

- ❑ The overlapping of 1s orbital with 2s orbital is ignore because of energy difference.
- ❑ Each Li atom provides three electrons and the six electrons in  $\text{Li}_2$  occupy the lowest energy MOs give ground state electronic configuration  $\sigma_g(1s)^2 \sigma_u^*(1s)^2 \sigma_g(2s)^2$  MOs.
- ❑ It suggested that  $\text{Li}_2$  is diamagnetic in nature.



$$\begin{aligned}\text{Bond order} &= \frac{1}{2} [(\text{Number of bonding electrons}) - (\text{number of antibonding electrons})] \\ &= \frac{1}{2} [(2) - (0)] = 1.\end{aligned}$$

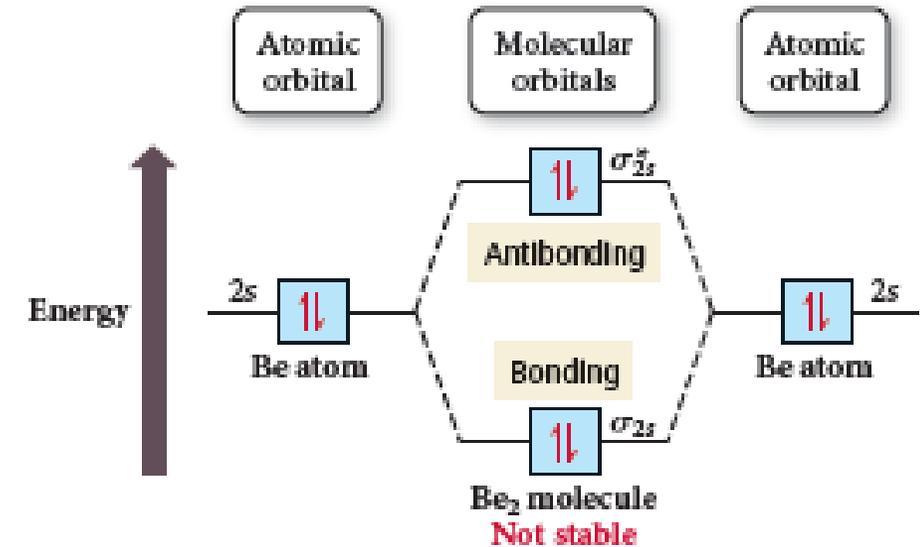
$\text{Li}_2$  molecule is stable with a bond order of 1.

# Molecular Orbital Theory

## Beryllium molecule

The ground state electronic configuration of Be ( $Z = 3$ ) is  $1s^2 2s^2$

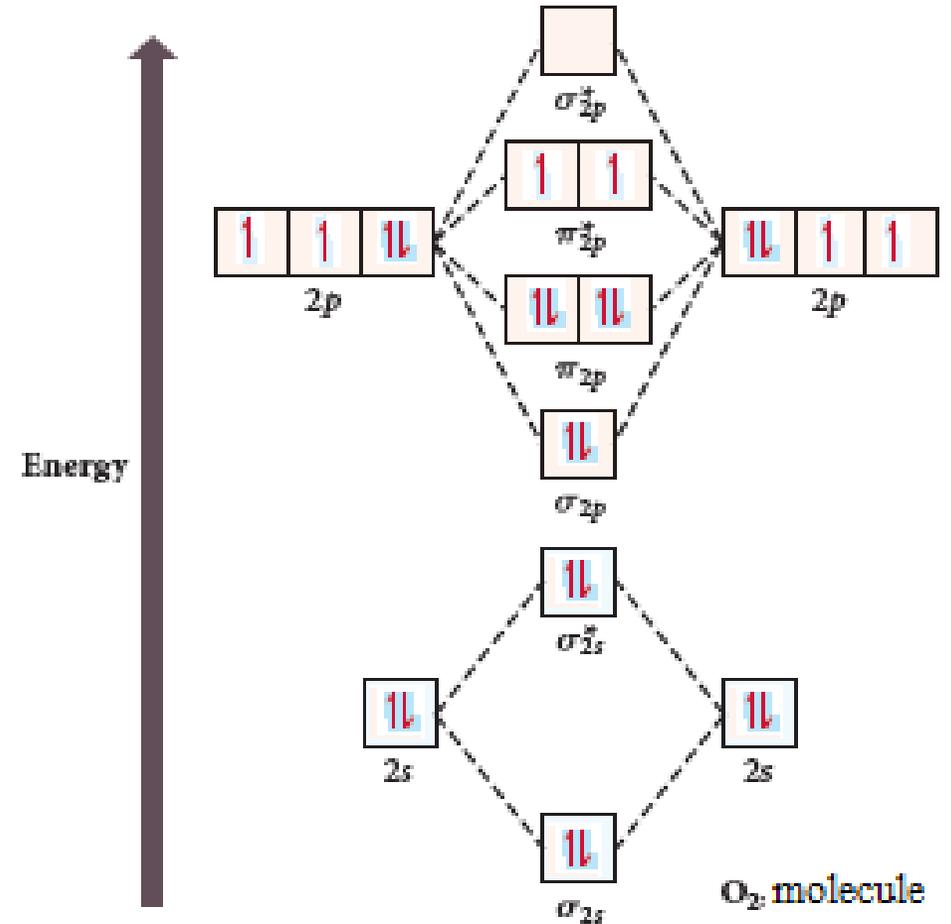
- ❑ The four valence electrons of  $\text{Be}_2$  occupy **one bonding MO** and **one antibonding MO**.
- ❑ The ground state electronic configuration  $\text{Be}_2$  is  $\sigma_g(1s)^2 \sigma_u^*(1s)^2 \sigma_g(2s)^2 \sigma_u^*(2s)^2$  MOs.
- ❑ It is suggested that  $\text{Be}_2$  is **diamagnetic** in nature.
- ❑ The **bond order is 0** and we predict that  $\text{Be}_2$  should not be stable.



# Molecular Orbital Theory

## O<sub>2</sub> molecule

- ❑ The electronic configuration of oxygen is **1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>**
- ❑ The ground electronic configuration of O<sub>2</sub> molecule, therefore, is -  
 $\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^1 \pi^*(2p_y)^1$ .
- ❑ O<sub>2</sub> molecule should be paramagnetic.
- ❑ From the electronic configuration of O<sub>2</sub> molecule, it is clear that **ten electrons are present in bonding molecular orbitals** and **six electrons are present in antibonding molecular orbitals**.
- ❑ Its **bond order**, therefore, is  $= \frac{1}{2} (10 - 6) = 2$ .



# Molecular Orbital Theory

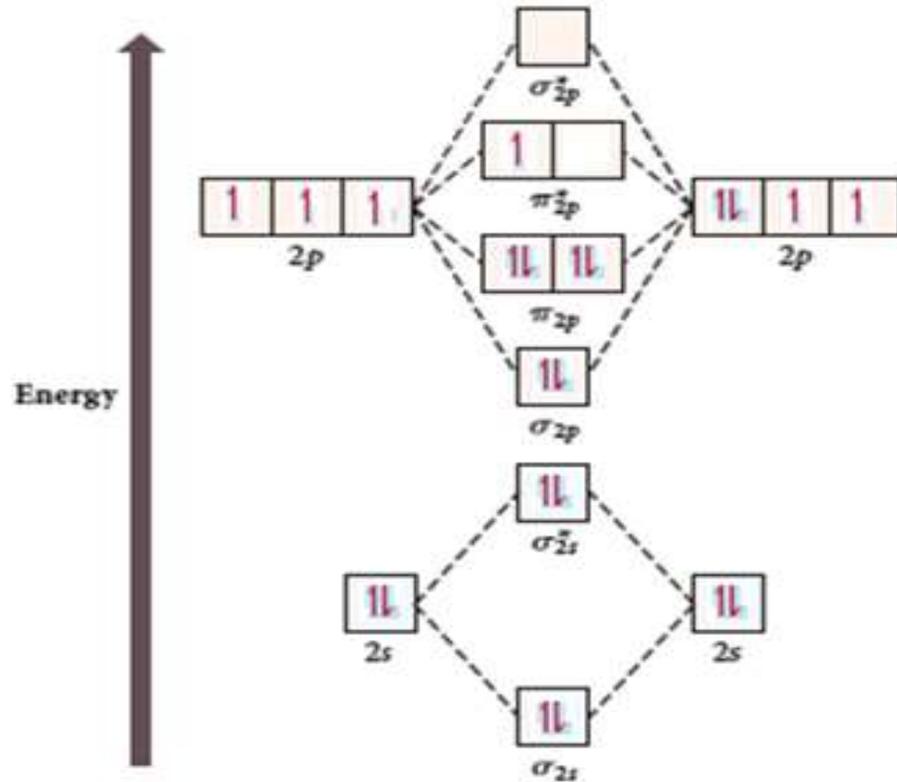
$O_2^+$  molecule

electronic configuration of O-ion is  $1s^2 2s^2 2p^3$ .

$\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^1 \pi^*(2p_y)^0$ .

Bond order =  $\frac{1}{2} (8 - 3) = 2.5$ .

Magnetic property: Paramagnetic



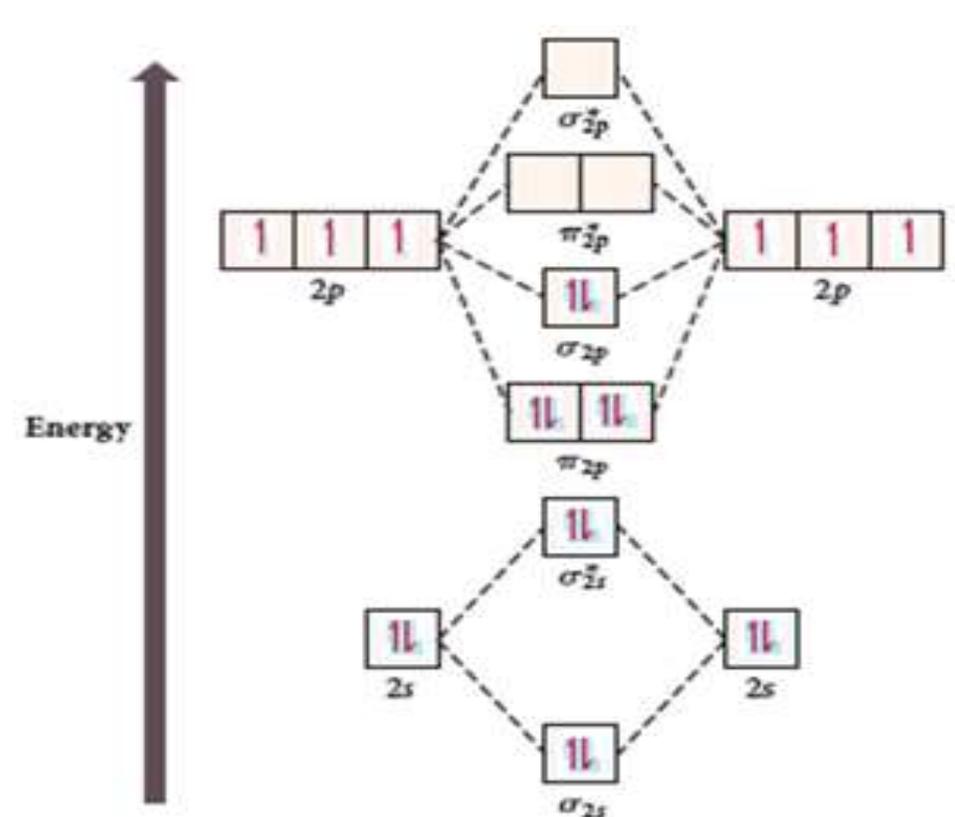
$O_2^{2+}$  molecule

electronic configuration of O-ion is  $1s^2 2s^2 2p^2$ .

$\sigma(2s)^2 \sigma^*(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \sigma(2p_z)^2 \pi^*(2p_x)^0 \pi^*(2p_y)^0$ .

Bond order =  $\frac{1}{2} (8 - 2) = 3$

Magnetic property: Diamagnetic



# Molecular Orbital Theory

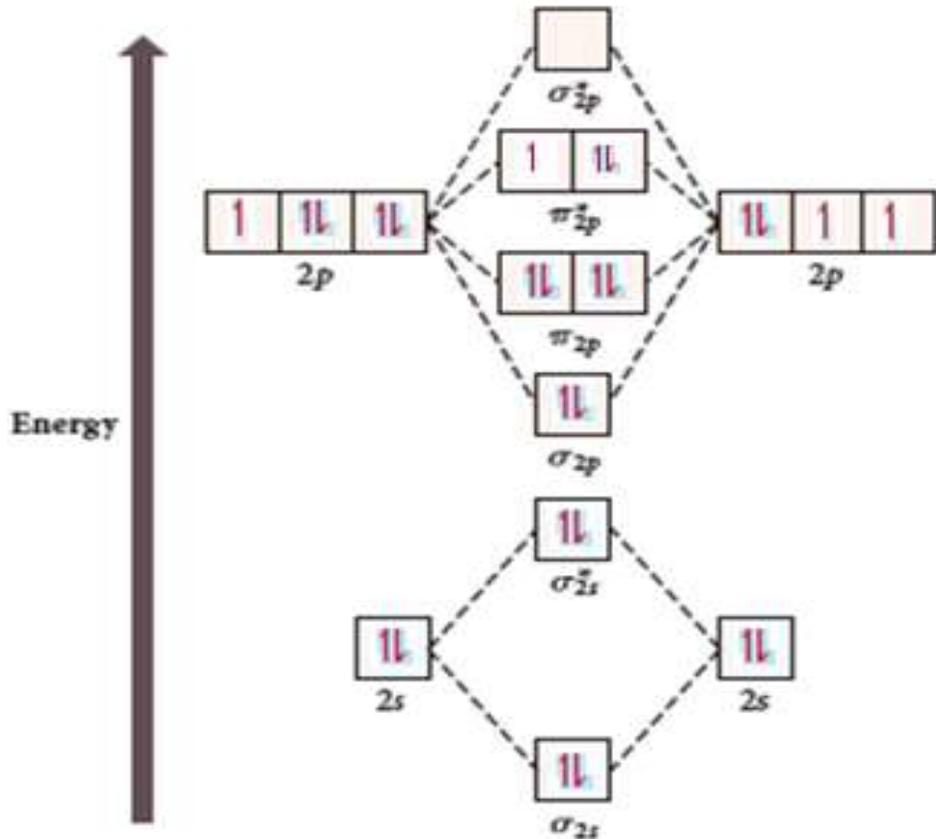
## $O_2^-$ molecule

electronic configuration of O-ion is  $1s^2 2s^2 2p^5$

$\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^2 \pi^*(2p_y)^1$

Bond order =  $\frac{1}{2} (8 - 5) = 1.5$

Magnetic property: Paramagnetic



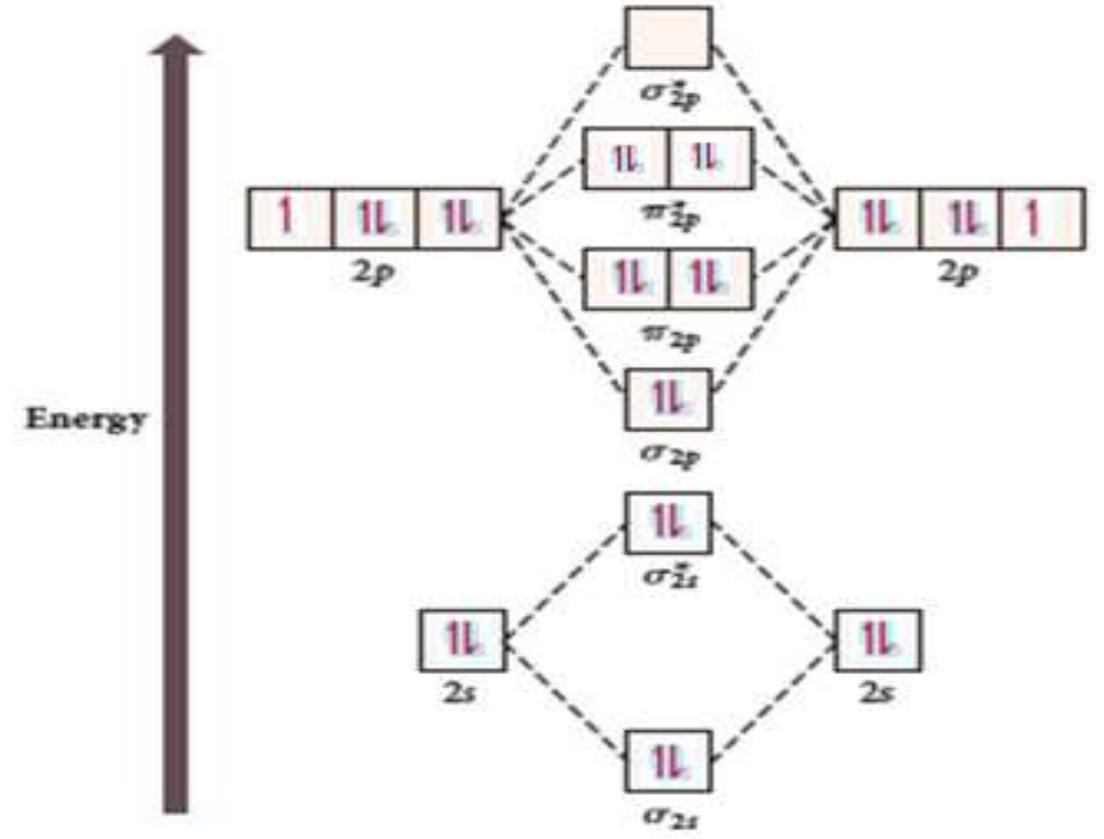
## $O_2^{2-}$ molecule

electronic configuration of O-ion is  $1s^2 2s^2 2p^6$

$\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^2 \pi^*(2p_y)^2$

Bond order =  $\frac{1}{2} (8 - 6) = 1$

Magnetic property: Diamagnetic

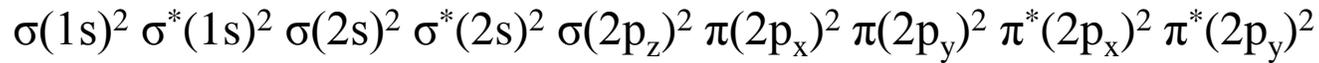


# Molecular Orbital Theory

## F<sub>2</sub> molecule

Electronic configuration of fluorine is  $1s^2 2s^2 2p^5$

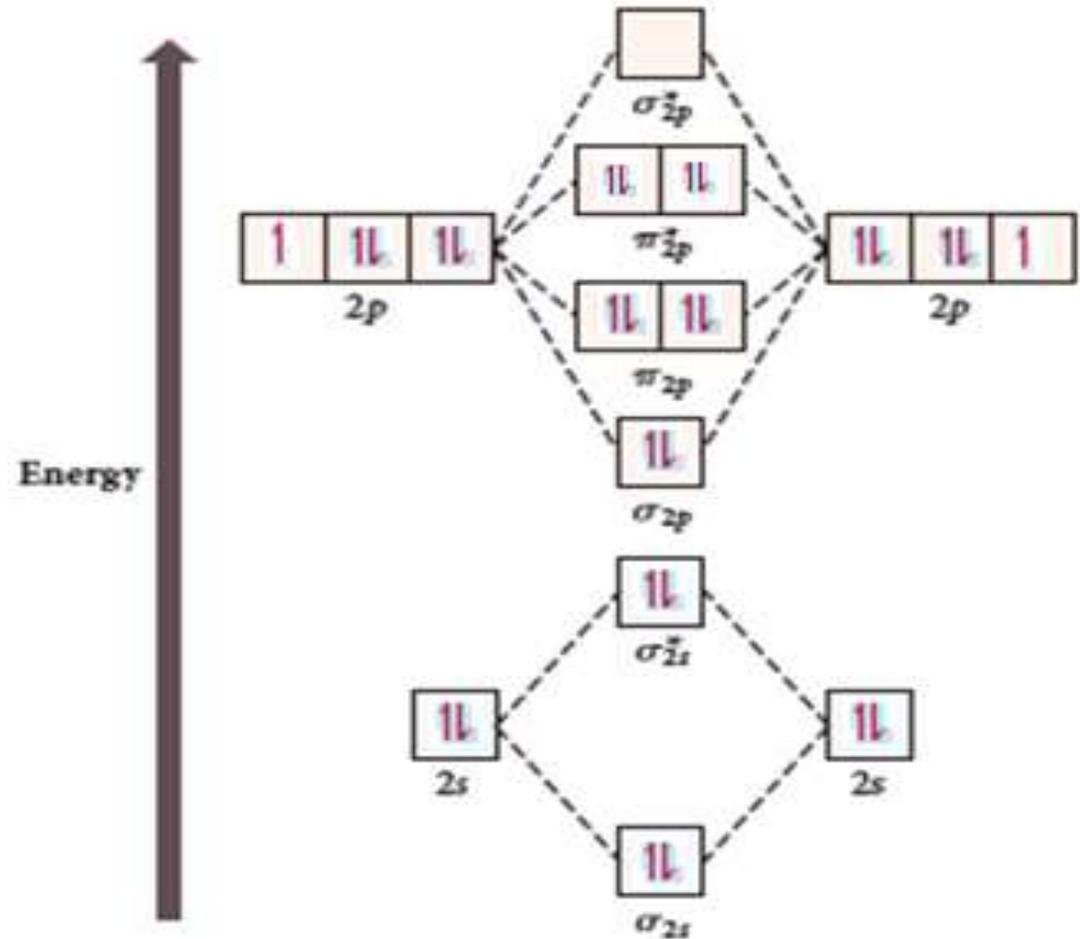
The ground electronic configuration of F<sub>2</sub> molecule, therefore, is -



From the electronic configuration of F<sub>2</sub> molecule, it is clear that **ten electrons are present in bonding molecular orbitals** and **eight electrons are present in antibonding molecular orbitals**.

Its bond order, therefore, is  $= \frac{1}{2} (10 - 8) = 1$

F atoms are held by single bond and it **diamagnetic** in nature.



# Molecular Orbital Theory

## Ne<sub>2</sub> molecule

electronic configuration of neon is  $1s^2 2s^2 2p^6$

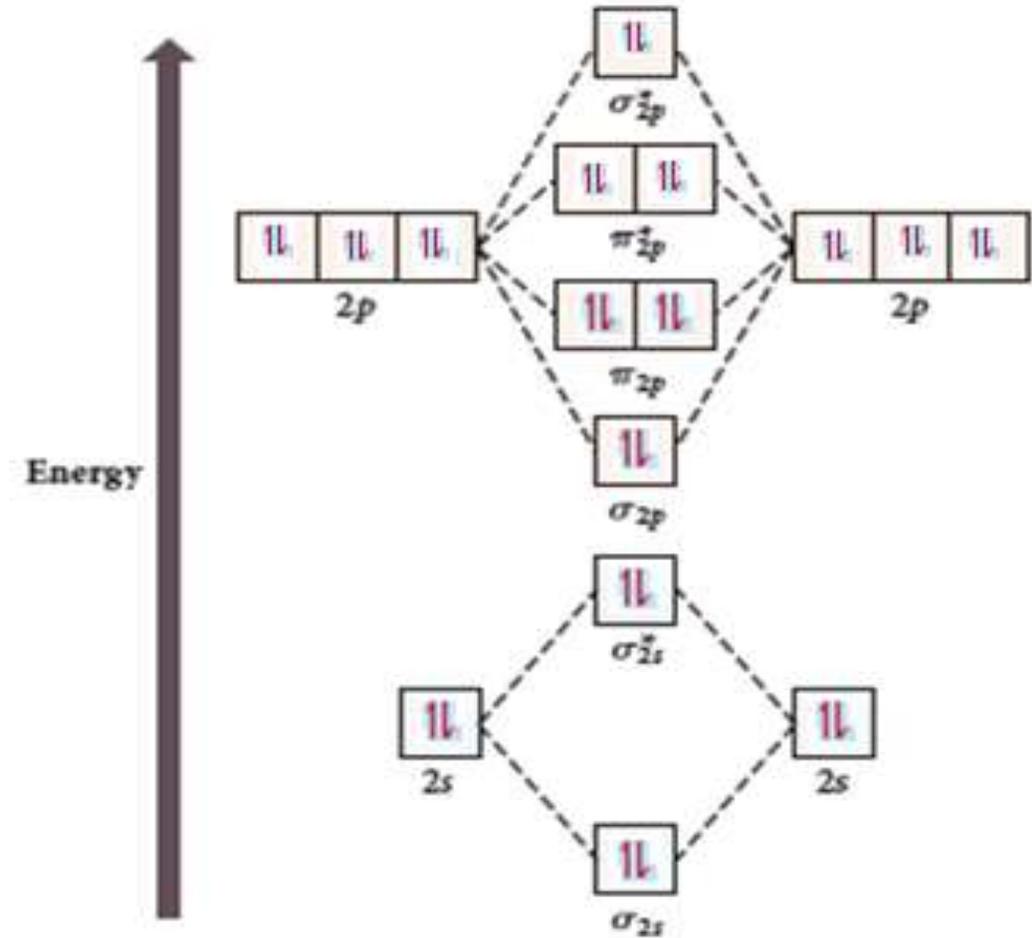
The ground electronic configuration of Ne<sub>2</sub> molecule, therefore, is -

$\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^2$   
 $\pi^*(2p_y)^2 \sigma^*(2p_z)^2$

From the electronic configuration of Ne<sub>2</sub> molecule, it is clear that **ten electrons are present in bonding** and **antibonding molecular orbitals**.

Its bond order, therefore, is  $= \frac{1}{2} (10 - 10) = 0$ .

So the neon molecule is unstable and not exists. It **diamagnetic** in nature



# Molecular Orbital Theory

## B<sub>2</sub> molecule

The electronic configuration of boron is  $1s^2 2s^2 2p^1$ .

One electron of each B atom present in 2P orbital (**P<sub>z</sub> orbital** that **lie along the internuclear axis** from each atom undergoes overlapping) which are **able to form sigma bond** (linear combination) along with 2s.

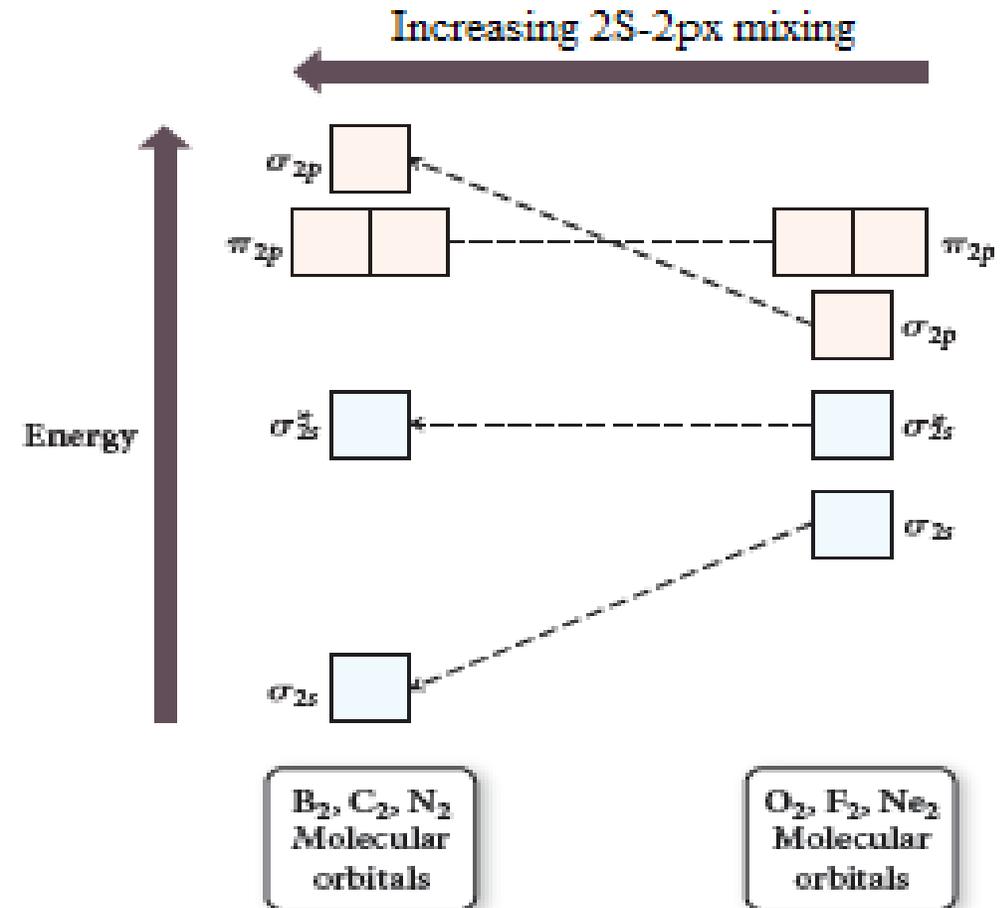
The **bonding MO increased electron density in the internuclear region** due to constructive interference between the two 2p atomic orbitals.

2p<sub>x</sub> and the 2p<sub>y</sub> atomic orbitals are added together in a **side-by-side orientation** result the formation of π(2p) orbital have same energy.

The two 2s orbitals and the two 2p<sub>z</sub> orbitals should all be combined to form a total of **four molecular orbitals**. The type of mixing affect the energy levels of the corresponding MOs.

**Mixing of the 2s and 2p<sub>z</sub> orbitals** is therefore **greater** in B<sub>2</sub>, C<sub>2</sub>, and N<sub>2</sub> than in O<sub>2</sub>, F<sub>2</sub>, and Ne<sub>2</sub> because in B, C, and N **the energy levels of the atomic orbitals are more closely spaced** than in O, F, and Ne.

Change in **energy ordering** for the **π(2p) and σ(2p)** molecular orbitals. After mixing of **2s and 2p<sub>z</sub> orbitals**, the **energy difference of σ(2s) and σ(2p)** in B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub> **increases** due to gain and loss of energy.

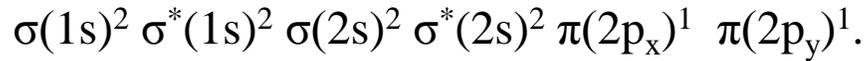


# Molecular Orbital Theory

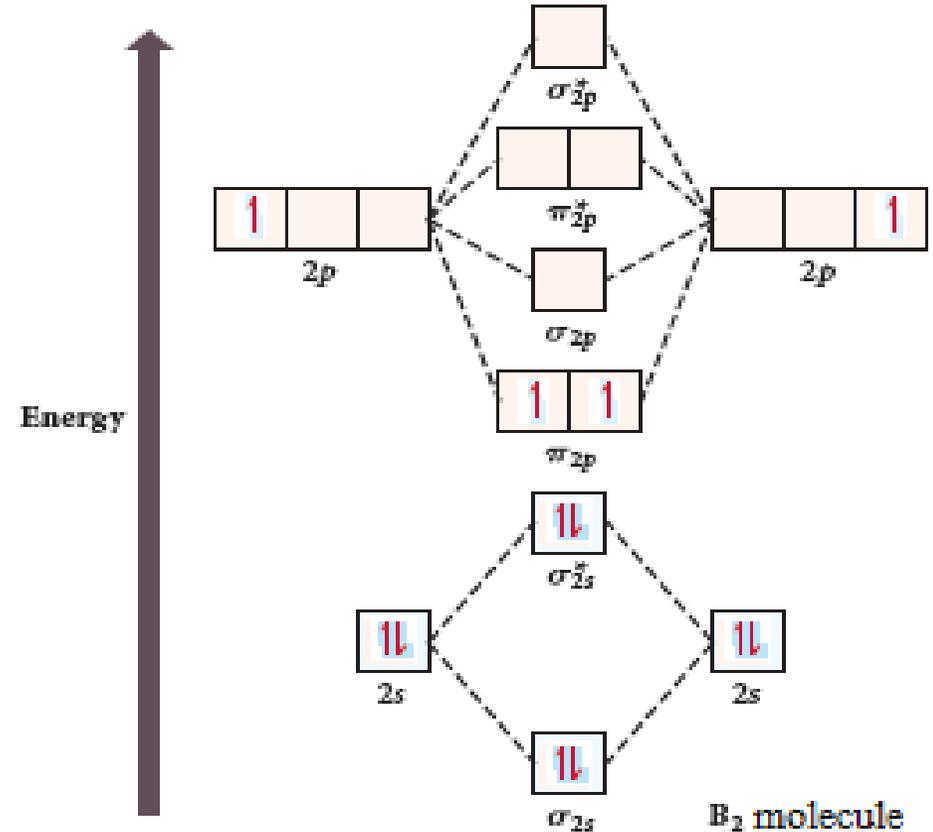
## B<sub>2</sub> molecule

The electronic configuration of boron is  $1s^2 2s^2 2p^1$ .

There are ten electrons in B<sub>2</sub>. The ground electronic configuration of B<sub>2</sub> molecule, therefore, is -



Bond order of B<sub>2</sub> =  $\frac{1}{2} (6 - 4) = 1$ .



It may be noted that it contains two unpaired electrons in  $\pi(2p_x)$  and  $\pi(2p_y)$  molecular orbitals, therefore, B<sub>2</sub> molecule should be paramagnetic.

# Molecular Orbital Theory

## C<sub>2</sub> molecule

The electronic configuration of carbon is  $1s^2 2s^2 2p^2$ .

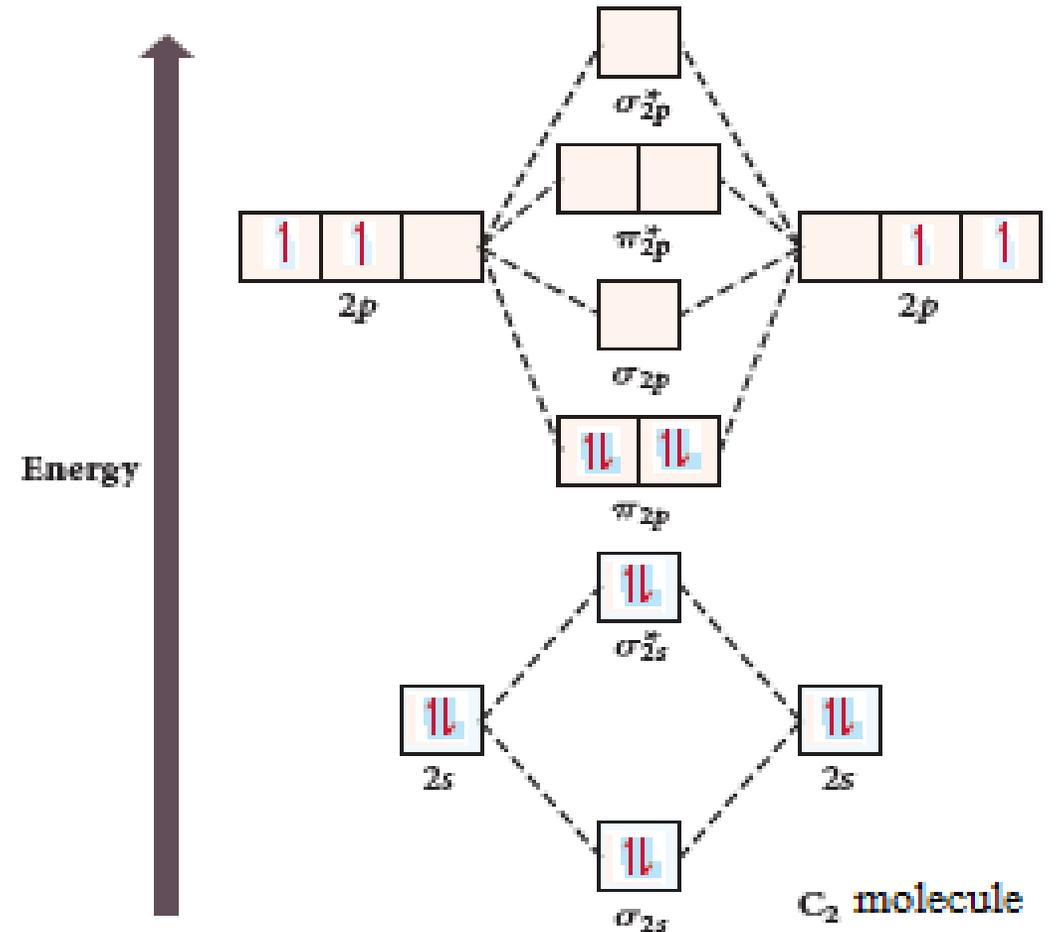
There are twelve electrons in C<sub>2</sub>. The ground electronic configuration of C<sub>2</sub> molecule, therefore, is –

$$\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2.$$

$$\text{Bond order of C}_2 = \frac{1}{2} (8 - 4) = 2.$$

It is important to note that double bond in C<sub>2</sub> consists of *both pi bonds* because of the presence of four electrons in two pi molecular orbitals.

All electrons present in molecular orbitals are paired so C<sub>2</sub> is diamagnetic in nature.

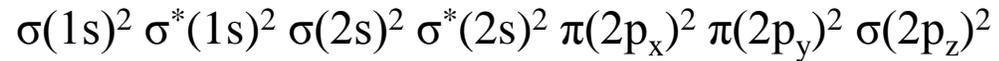


# Molecular Orbital Theory

## N<sub>2</sub> molecule

The electronic configuration of nitrogen is  $1s^2 2s^2 2p^3$ .

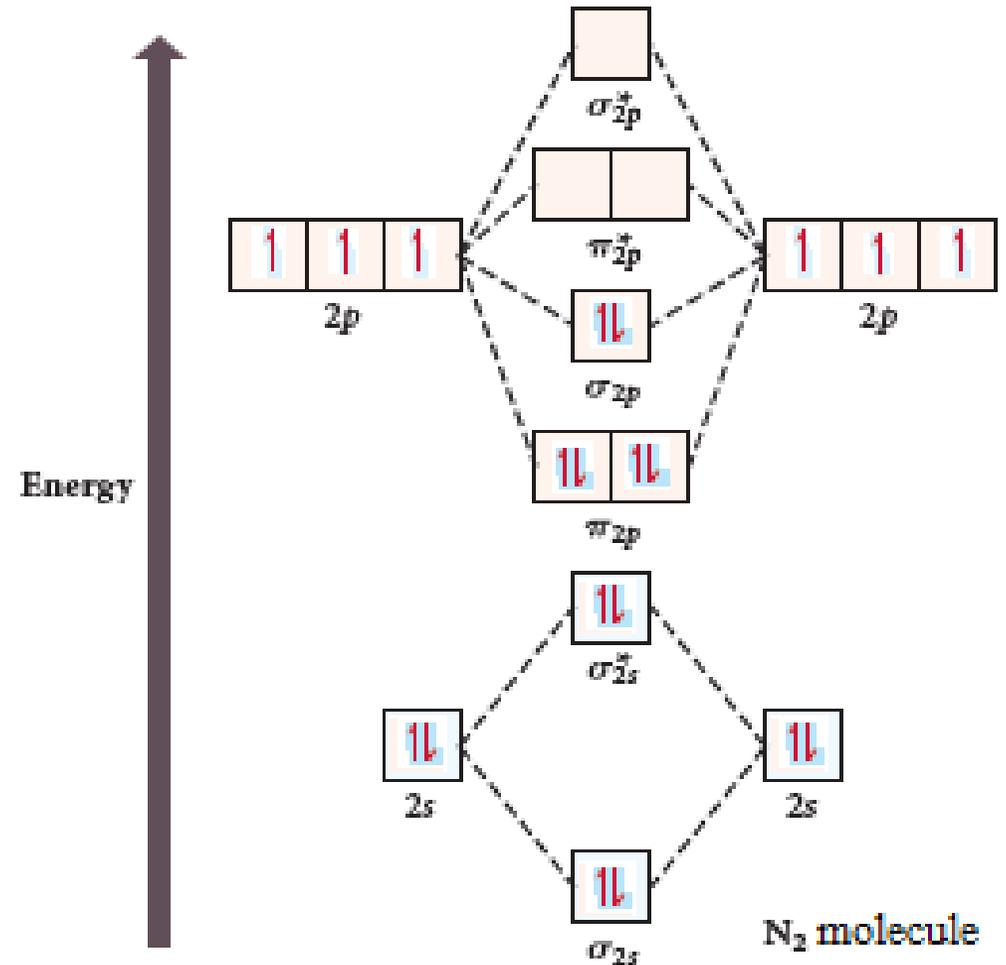
There are fourteen electrons in N<sub>2</sub>. The ground electronic configuration of N<sub>2</sub> molecule, therefore, is –



Bond order of N<sub>2</sub> =  $\frac{1}{2} (10 - 4) = 3$ .

It is important to note that triple bond in N<sub>2</sub> consists of one sigma and *two pi bonds* because of the presence of two electrons in sigma-orbital and four electrons in two pi molecular orbitals.

N<sub>2</sub> is diamagnetic in nature.



# Molecular Orbital Theory



The electronic configuration

The ground electronic configuration of molecule -

Bond order =

magnetic property = \_\_\_\_\_ nature

