

# **MOLECULAR ORBITAL THEORY**

- 1. ATOMIC ORBITALS (s,p,d,f) orbitals**
- 2. ELECTRONIC CONFIGURATION**
- 3. MOLECULAR ORBITAL THEORY  
(BONDING & ANTIBONDING ORBITALS)**
- 4. MOT DIAGRAMS OF HOMONUCLEAR &  
HETERONUCLEAR DIATOMIC MOLECULES**

**Be<sub>2</sub>, O<sub>2</sub>, CO, NO their bond order & magnetic properties**

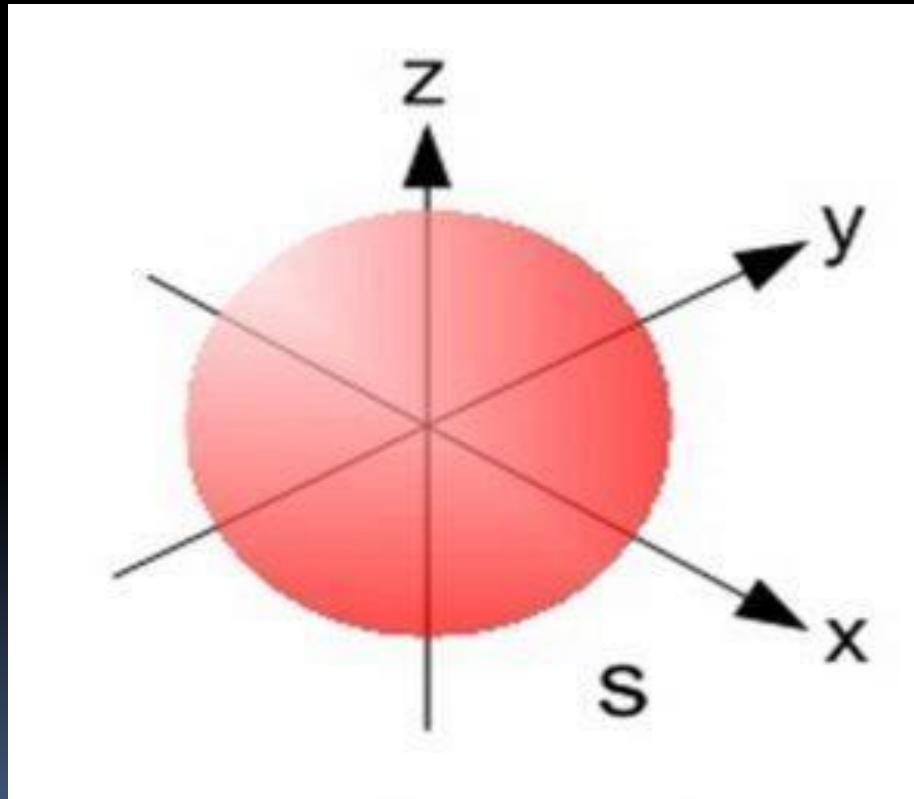
- Molecular Orbital Theory is primarily used to explain the bonding in molecules that cannot be explained by Valence Bond Theory. These are molecules that generally involve some form of resonance. Resonance implies that a bond is neither single nor double but some hybrid of the two. **Valence bond theory only describes the bonding of single or double or triple bonds. It does not provide an explanation for resonance bonding.**
- Molecular orbital theory does describe resonance.

# ATOMIC ORBITAL

- An **orbital** is the region of space around the nucleus within which the probability of finding an **electron** of given energy is maximum .

# Atomic Orbitals

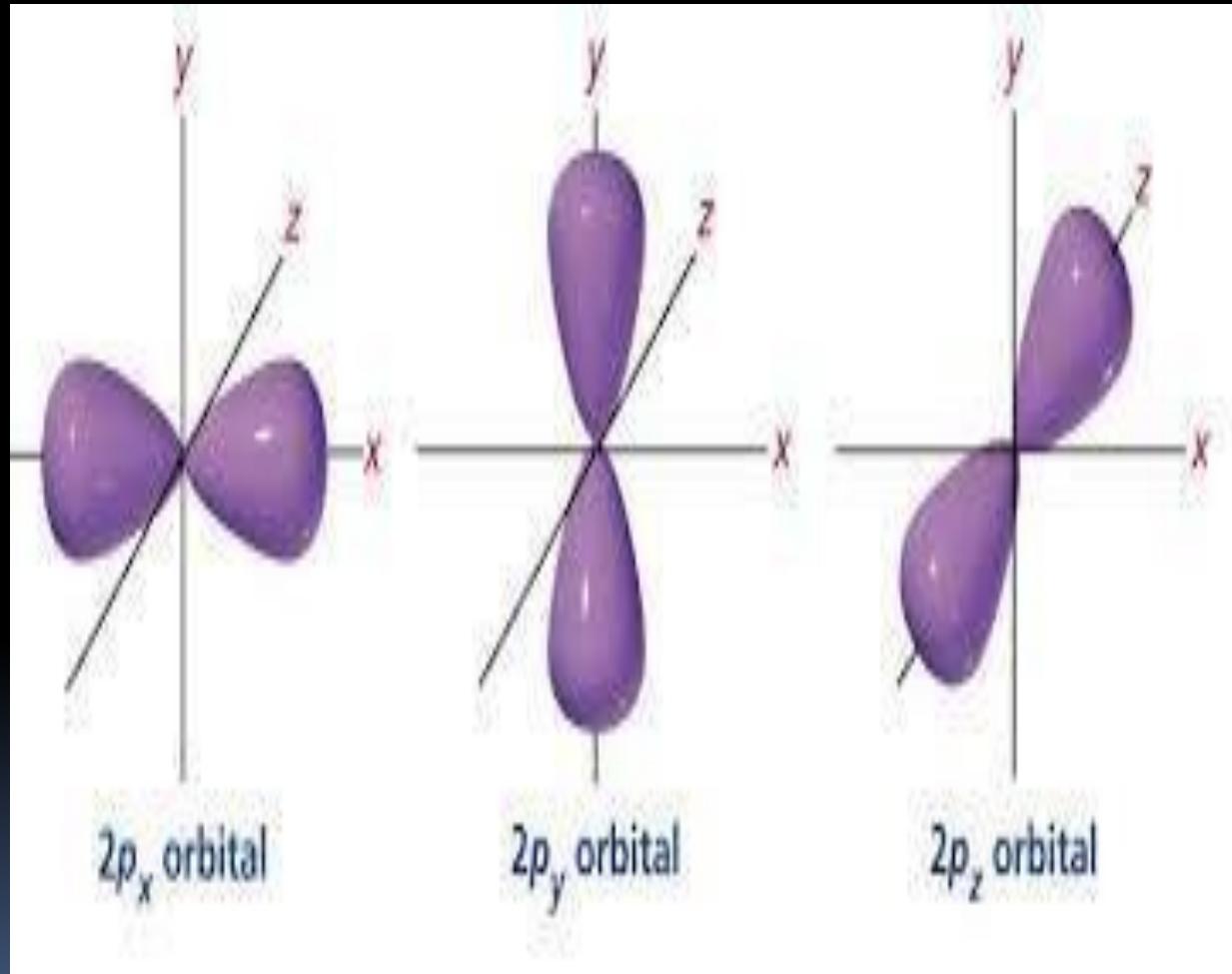
- S orbitals



- For s-orbitals, when  $l = 0$ , the value of  $m$  is 0 i.e., there is only one possible orientation. This means that the probability of finding an electron is the same in all directions at a given distance from the nucleus. It should, therefore, be spherical in shape. Hence all s- orbitals are non-directional and spherically symmetrical about the nucleus.

- The size of an s-orbital depends upon value of the principal quantum number n. Greater the value of 'n' larger is the size of the orbital.

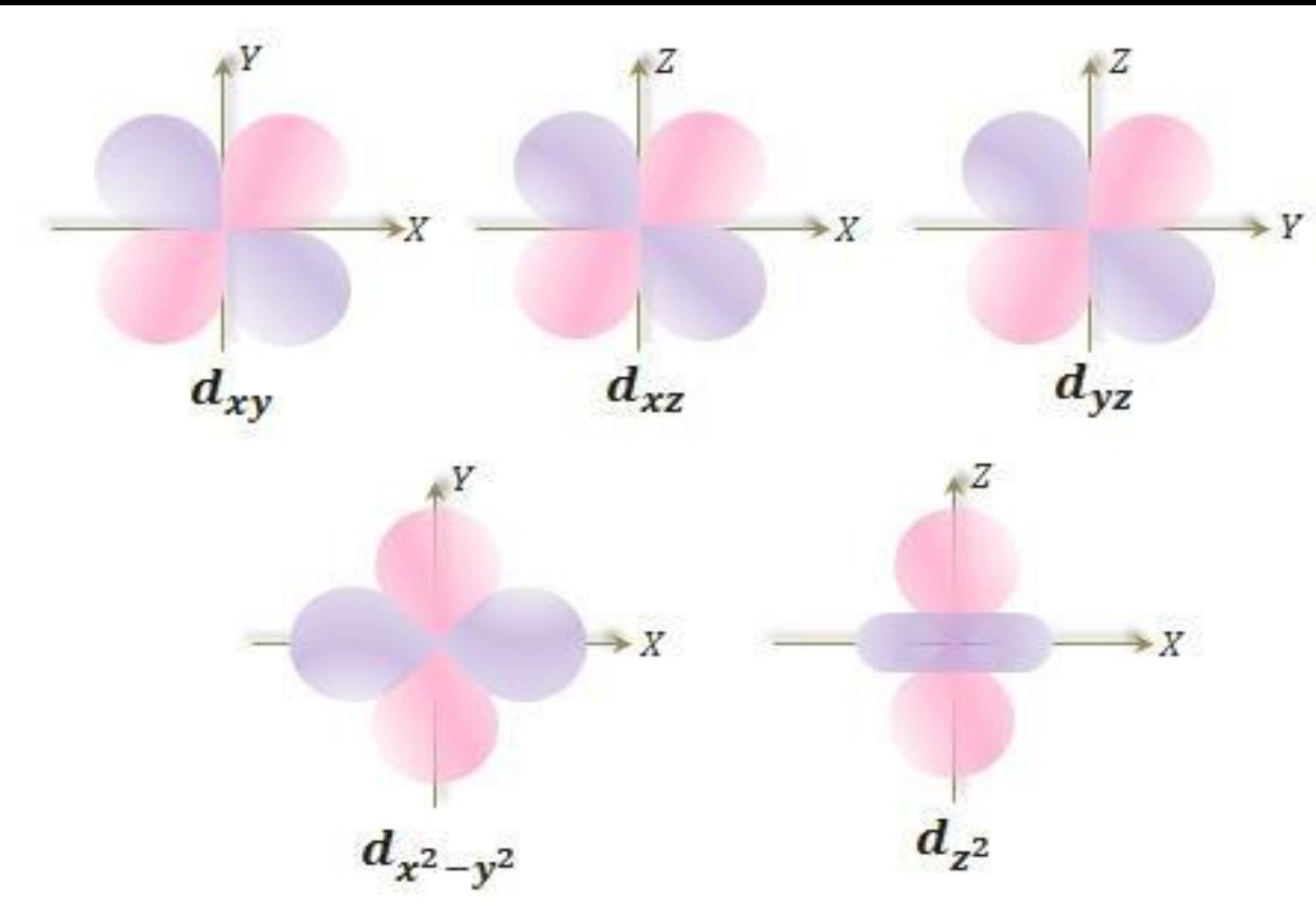
# P orbitals



- For p-subshell  $l = 1$ , there are three values of  $m$  namely -1, 0, +1. It means that p orbitals can have three possible orientations.
- These three p-orbitals are equal in energy (degenerate state) but differ in their orientations. respectively.

- Each p-orbital consists of two lobes symmetrical about a particular axis. Depending upon the orientation of the lobes, these are denoted as  $2p_x$ ,  $2p_y$  and  $2p_z$  accordingly as they are symmetrical about X, Y and Z-axis

# d orbitals



- Magnetic orbital quantum number for d orbitals is given as (-2, -1, 0, 1, 2).
- It means d- orbitals can have five orientations. These are represented by  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals have same shape i.e., clover leaf shape but they lie in XY, YZ and ZX-planes respectively.

- The  $d_z^2$  orbital is symmetrical about Z-axis and has a dumb - bell shape with a doughnut shaped electron cloud in the centre. The leaf  $d_x^2$  orbital is also clover shaped but its leaves are directed along the X and Y- axis.

# QUIZ 1

- WRITE DIFFERENCE  
BETWEEN ORBIT &  
ORBITAL

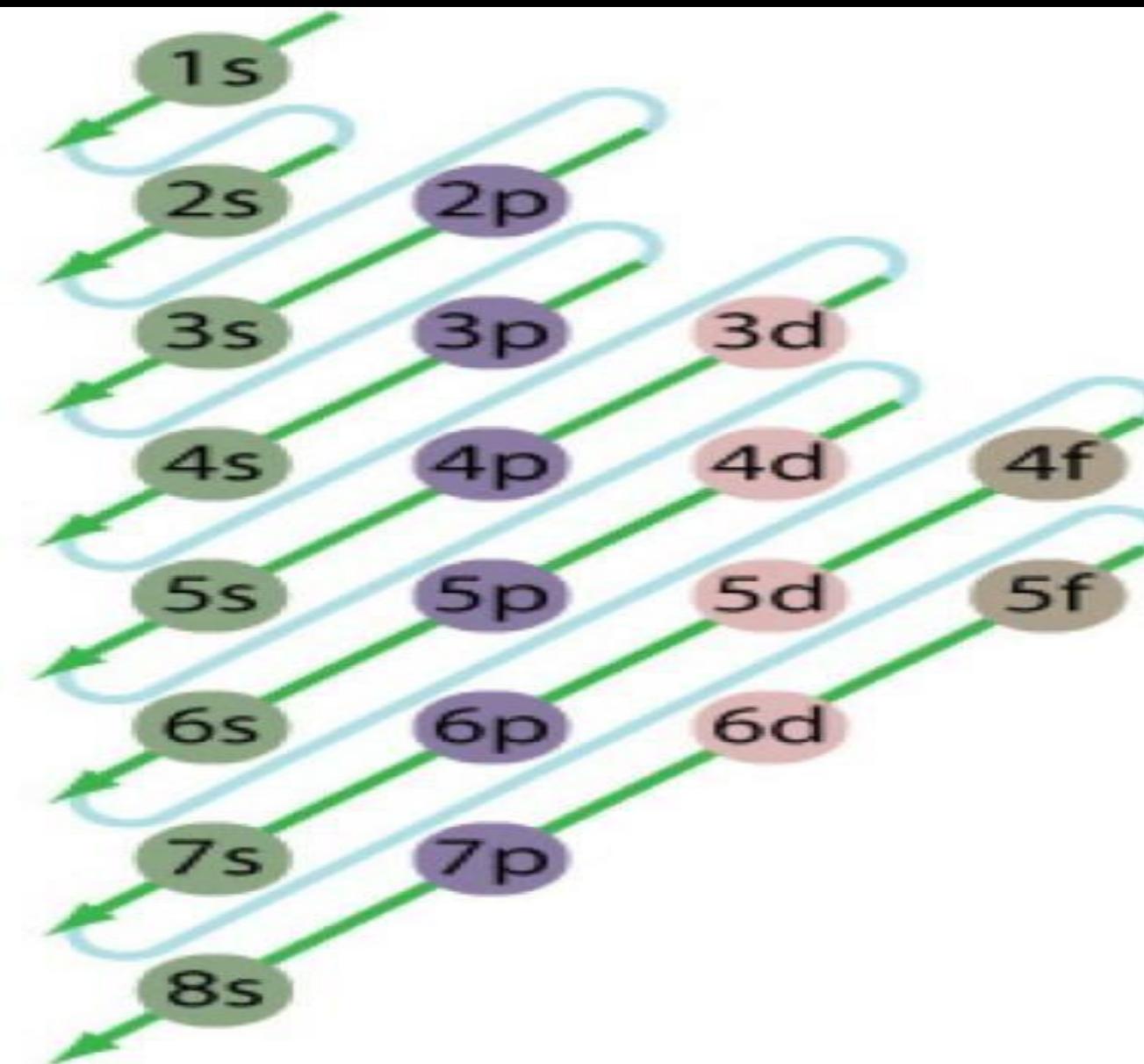
# ELECTRONIC CONFIGURATION

- The distribution of electrons in various orbitals is known as electronic configuration.

- The filling of electrons in orbitals is determined by following rules.
- 1) Aufbau Principle
- 2) Pauli's exclusion principle
- 3) Hund's Rule of maximum multiplicity

# Aufbau Principle

- **The Building-Up (Aufbau) Principle**
  - According to the principle, electrons fill orbitals starting at the lowest available energy states before filling higher states (e.g., 1s before 2s).

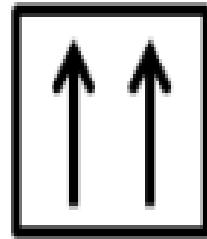


- Following steps detail how to draw an Aufbau diagram:
  - Determine the number of electrons that the atom has.
  - Fill the s orbital in the first energy level (the 1s orbital) with the first two electrons.
  - Fill the s orbital in the second energy level (the 2s orbital) with the second two electrons.

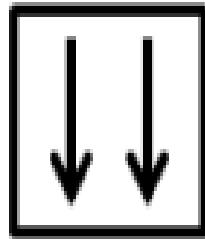
- Put one electron in each of the three p orbitals in the second energy level (the 2p orbitals) and then if there are still electrons remaining, go back and place a second electron in each of the 2p orbitals to complete the electron pairs.
- Continue in this way through each of the successive energy levels until all the electrons have been drawn.

# PAULI'S EXCLUSION PRINCIPLE

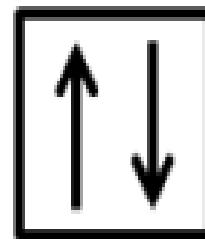
HELIUM 1s ORBITAL ELECTRON SPIN



X



X



✓

- **Pauli's Exclusion Principle**
- According to it: “no two electrons can have the same set of all four quantum numbers.”

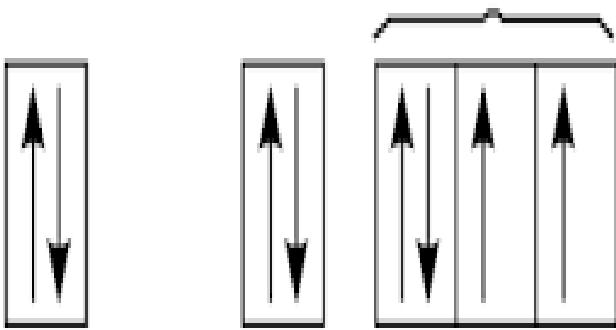
- Or, it states that an orbital can have maximum of two electrons and that must be of opposite spin. Due to this, it was concluded that an orbital can have maximum of two electrons which can have all 3-quantum number same but the spin will be definitely different.

# Hund' s Rule of Maximum

## Multiplicity

- When two or more orbitals of equal energy (or very close energy) are available, electrons will fill the orbitals singly before filling doubly. All the electrons in the orbitals will have the same spin to maximize the multiplicity.

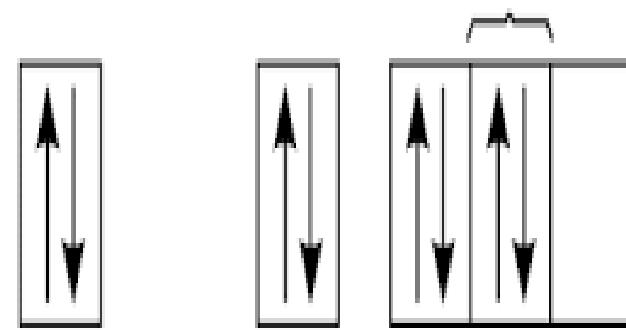
no electron-electron repulsion  
equals lower energy



1s    2s    2p

correct

electron-electron repulsion  
equals higher energy



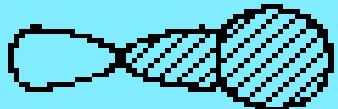
1s    2s    2p

incorrect

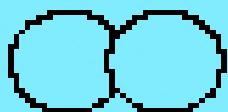
# Orbital Overlapping



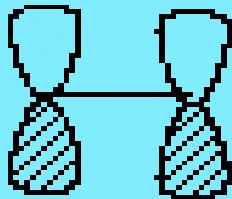
sigma(  $\sigma$  ) bond maximum overlap



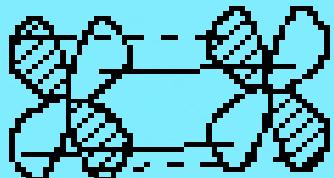
sigma(  $\sigma$  ) bond medium overlap



sigma(  $\sigma$  ) bond small overlap



pi(  $\pi$  ) bond small overlap



delta(  $\delta$  ) bond very small overlap

# Linear Combination of Atomic Orbitals

- The Linear combination of atomic orbitals which is also known as LCAO is an approximate method for representing molecular orbitals. It's more of a superimposition method where constructive interference of two atomic wave function produces a bonding molecular orbital whereas destructive interference produces non-bonding molecular orbital.

- **Conditions to be satisfied for LCAO:**
- **Same Energy of combining orbitals -**

The combining atomic orbitals must have same or nearly same energy. This means that 2p orbital of an atom can combine with another 2p orbital of another atom but 1s and 2p cannot combine as they have appreciable energy difference.

- **Same symmetry about the molecular axis** - The combining atoms should have same symmetry around the molecular axis for proper combination, otherwise, the electron density will be sparse.

For e.g. all the sub-orbitals of 2p have the same energy but still, the  $2p_z$  orbital of an atom can only combine with a  $2p_z$  orbital of another atom but cannot combine with  $2p_x$  and  $2p_y$  orbital as they have a different axis of symmetry.

In general, the z-axis is considered as the molecular axis of symmetry.

- Proper Overlap between the atomic orbitals -
- The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the electron density between the nuclei of the two atoms.

# Orbital as wave function

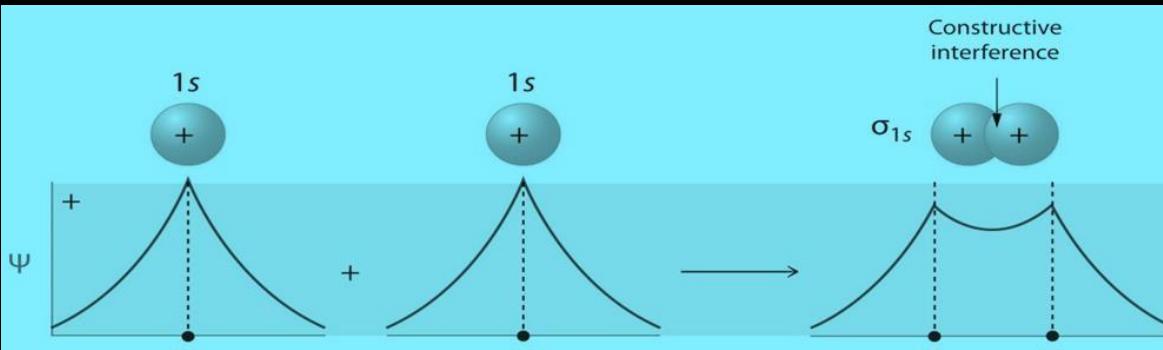
In atomic theory and quantum mechanics, an atomic **orbital** is a mathematical **function** describing the location and **wave-like** behavior of an electron in an atom. This **function** can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus.

- Consider two atoms A & B which have atomic orbitals described by the wave functions  $\Psi_A$  &  $\Psi_B$  then the wave function of molecular orbital AB can be obtained by a linear combination of atomic orbitals  $\Psi_A$  &  $\Psi_B$ .
- $\Psi = N(C_1 \Psi_A \pm C_2 \Psi_B)$
- Where  $\Psi$  is the wave function of MO,  $C_1$  &  $C_2$  are constant chosen to give minimum energy for  $\Psi$ .
- $N$  is normalizing constant chosen to insure that the probability of finding an electron in the whole of the space is unity.

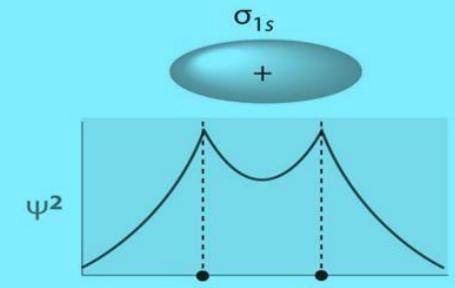
- $\Psi = N(C_1 \Psi_A \pm C_2 \Psi_B)$
- This equation clearly shows that linear combination gives rise to formation of two Mos. (Bonding MO & Antibonding MO)
- Bonding MO is obtained by taking the sum of two AO wave functions which result in an increased electron density.
- $\Psi_b = N(C_1 \Psi_A + C_2 \Psi_B)$

- Antibonding MO is obtained by taking the difference between two wave functions.
- $\Psi_a = N(C_1 \Psi_A - C_2 \Psi_B)$
- It has node with zero electron density between the nuclei due to cancellation of two wave functions.
- Antibonding MO have higher energy than the combining AOs

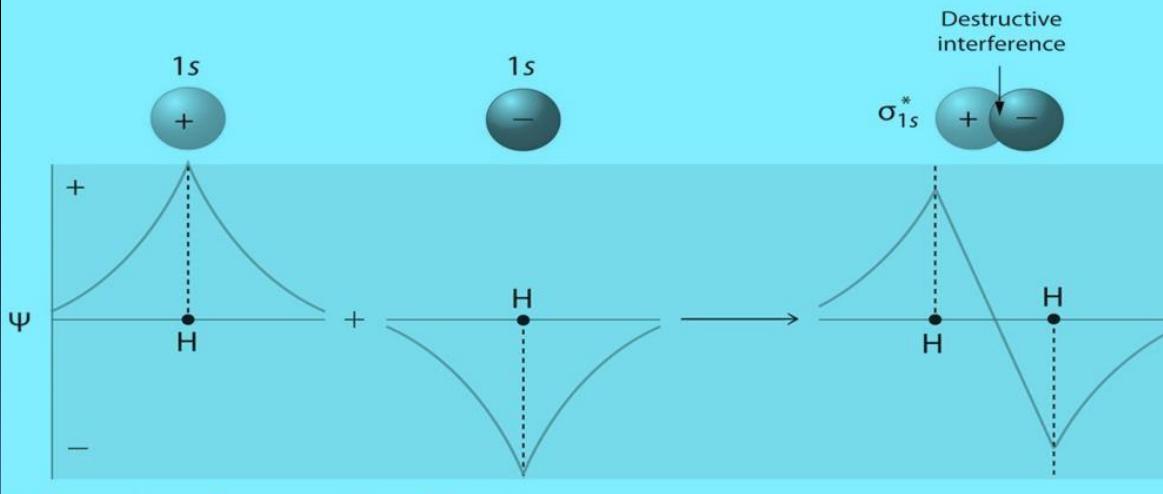
# Constructive interaction: The two 1s orbitals are in phase and have the same sign.



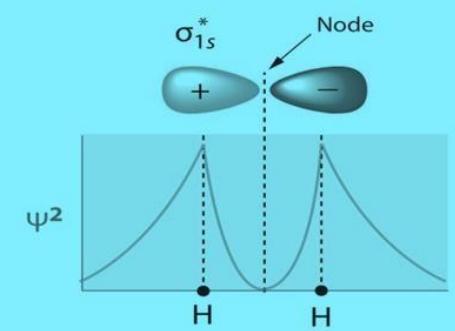
(a) Wave functions combined for  $\sigma_{1s}$



(b) Bonding probability density



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



(d) Antibonding probability density

# Destructive interaction The two 1s Orbitals are out

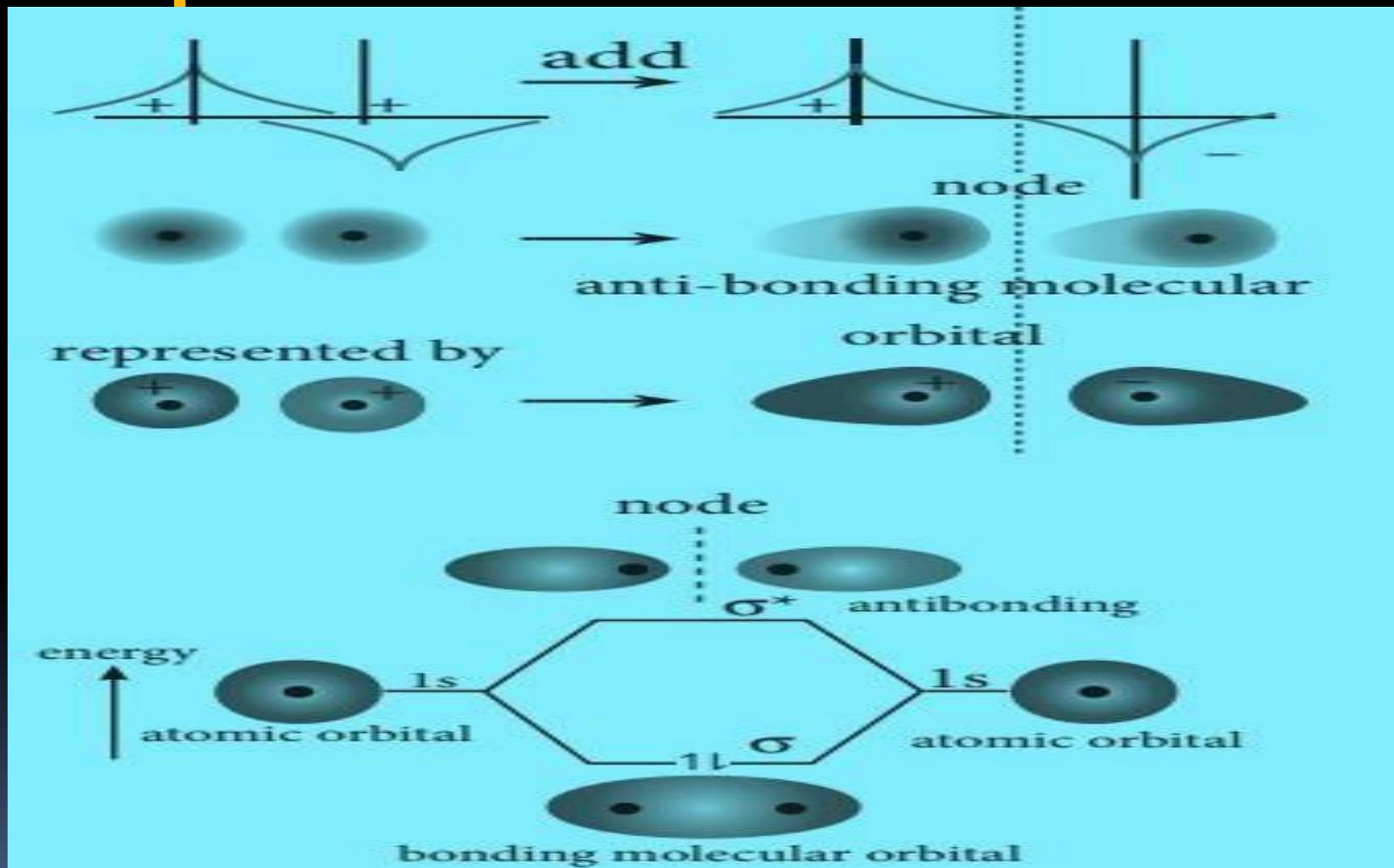


Fig 10.29 Linear Combination of atomic orbitals

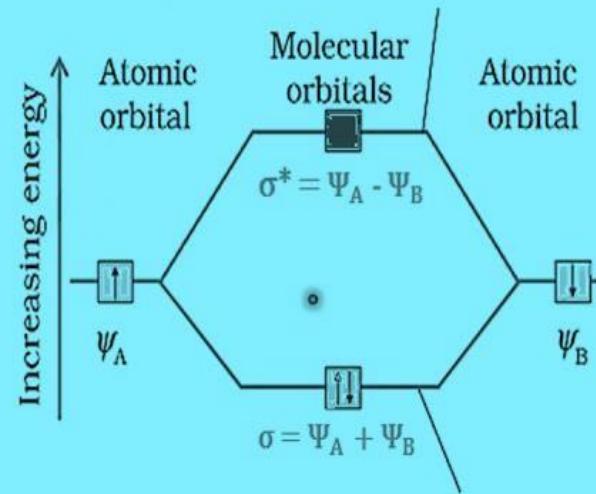
# Chemical Bonding

## CHEMICAL BONDING

### ✓ Linear Combination of Atomic Orbitals

Two AOs (A & B) combine to form an MO, the wave functions ( $\Psi_A$  &  $\Psi_B$ ) are combined both 'in phase' ( $\Psi_A + \Psi_B$ ) & 'out of phase' ( $\Psi_A - \Psi_B$ ); creating one bonding molecular orbital or gerade/symmetrical molecular orbital ( $\sigma$  or  $\Psi$  or  $\Psi_g$ ) & one anti-bonding molecular orbital ( $\sigma^*$  or  $\Psi^*$  or  $\Psi_u$ ) respectively. Such that

Antibonding Molecular Orbital;  
Higher energy than that of  
atomic orbitals



Bonding Molecular Orbital  
Lower energy than that of  
atomic orbitals

# The Rules (Postulates) of Molecular Orbital Theory:

- **First principle:** The number of molecular orbitals produced is always equal to the number of atomic orbitals brought by the atoms that have combined.

**Second principle:** Bonding molecular orbitals are lower in energy than the parent orbitals, and the antibonding orbitals are higher in energy.

- **Third principle:** Electrons of the molecule are assigned to orbitals from lowest to successively higher energy
- 
- Fourth principle:** Atomic orbitals combine to form molecular orbitals most effectively when the atomic orbitals are of similar energy.

- **Principle 1:** Example - Hydrogen ( $H_2$ ) Each hydrogen atom has a single valence orbital, this being the  $1s$  orbital. Two molecular orbitals may be formed by the constructive and destructive overlap of these two atomic orbitals. So if you have two  $1s$  atomic orbitals you can only make two molecular orbitals from them. This is the First Principle.

$1s \pm 1s$

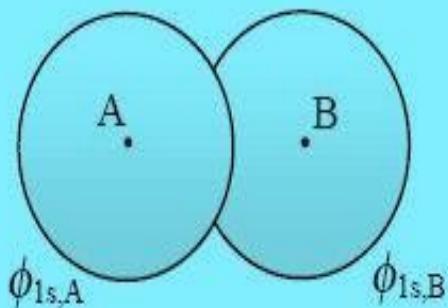
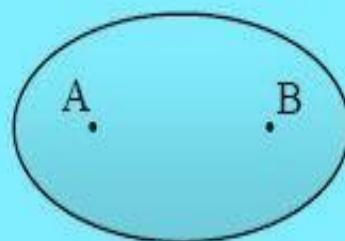


Diagram showing the superposition of the two 1s atomic orbitals



$1s \sigma$   
( $1\sigma_g$ )

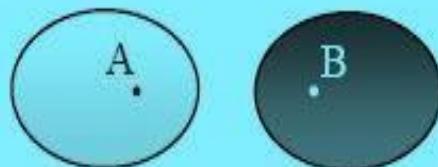


Bonding molecular orbital

$$\psi_+ = c_+ \phi_{1s,A} + c_+ \phi_{1s,B} = c_+ (\phi_{1s,A} + \phi_{1s,B})$$

or

$1s \sigma^*$   
( $1\sigma_u$ )



Antibonding molecular orbital

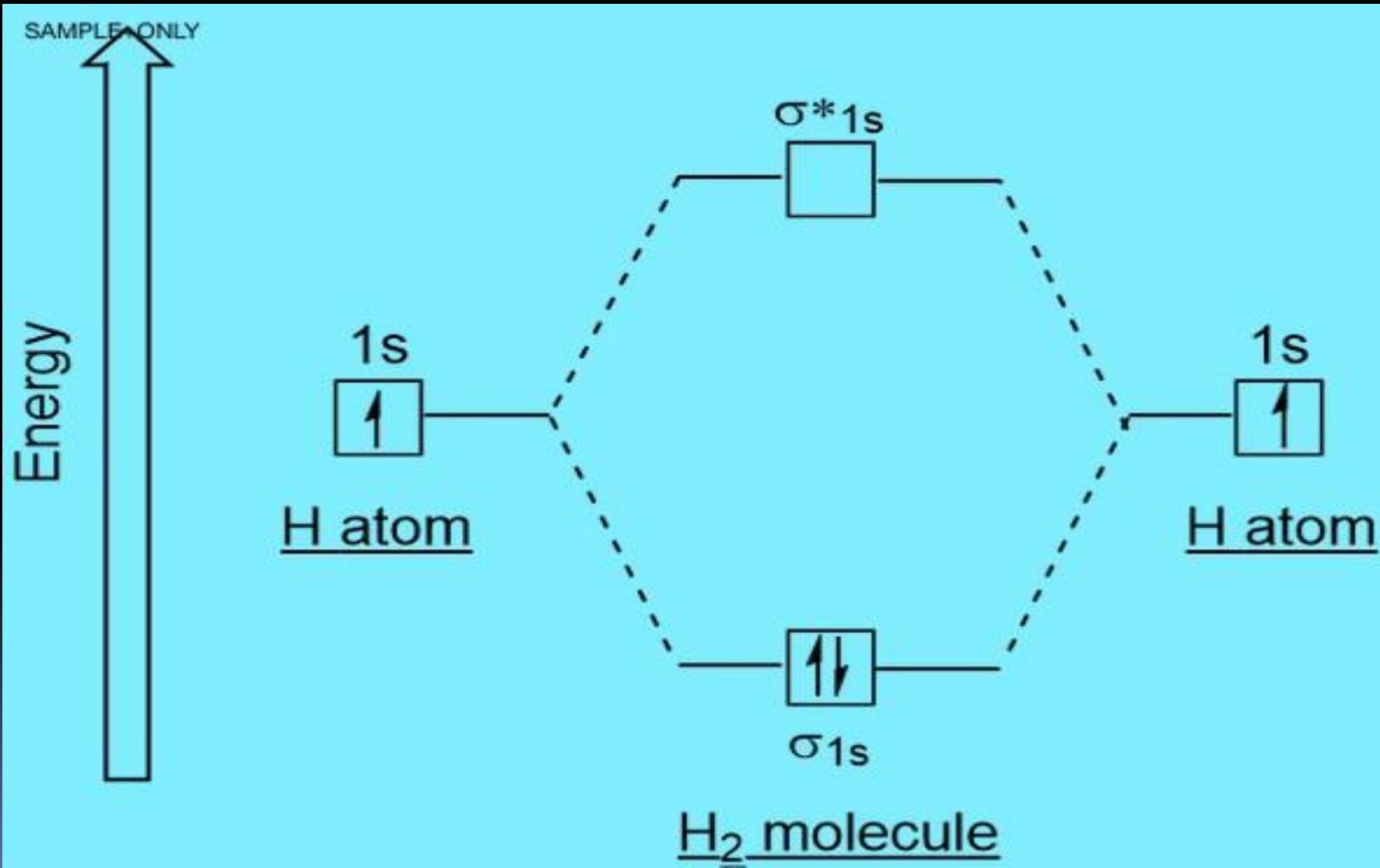
$$\psi_- = c_- \phi_{1s,A} - c_- \phi_{1s,B} = c_- (\phi_{1s,A} - \phi_{1s,B})$$

- According to MO Theory, the two molecular orbitals that form are called s (sigma = bonding) and s\* (sigma star = antibonding). In the case of H<sub>2</sub> both of the valence electrons that form the bond between the hydrogens fill the bonding or sorbital

## Principle 2 & 3:

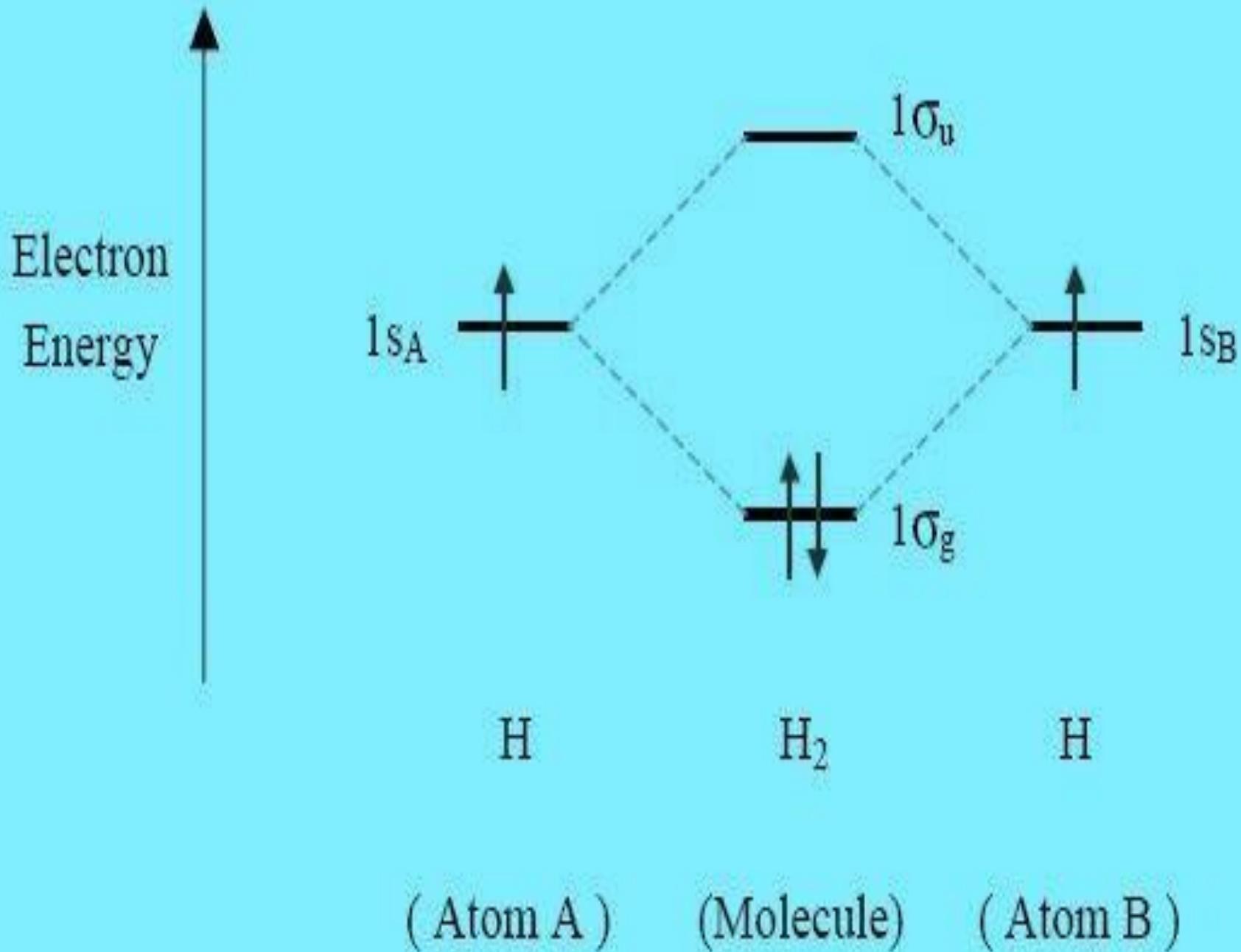
- In the specific case of hydrogen each of the isolated atoms has one electron in its  $1s$  orbital and when the atoms combine to form  $H_2$  the two electrons may be accommodated (with opposite spins) in the bonding molecular orbital, as illustrated below.

# MO diagram of H<sub>2</sub>



- The second principle explains why electrons would want to fill molecular orbitals in the first place. As you should know by now, stability comes from lowering energy needs.

This interaction of atomic orbitals, which gives rise to the molecular orbitals, may also be represented in the form of an orbital (electron) energy diagram which shows the relative energies of the orbitals.



# Principle 4

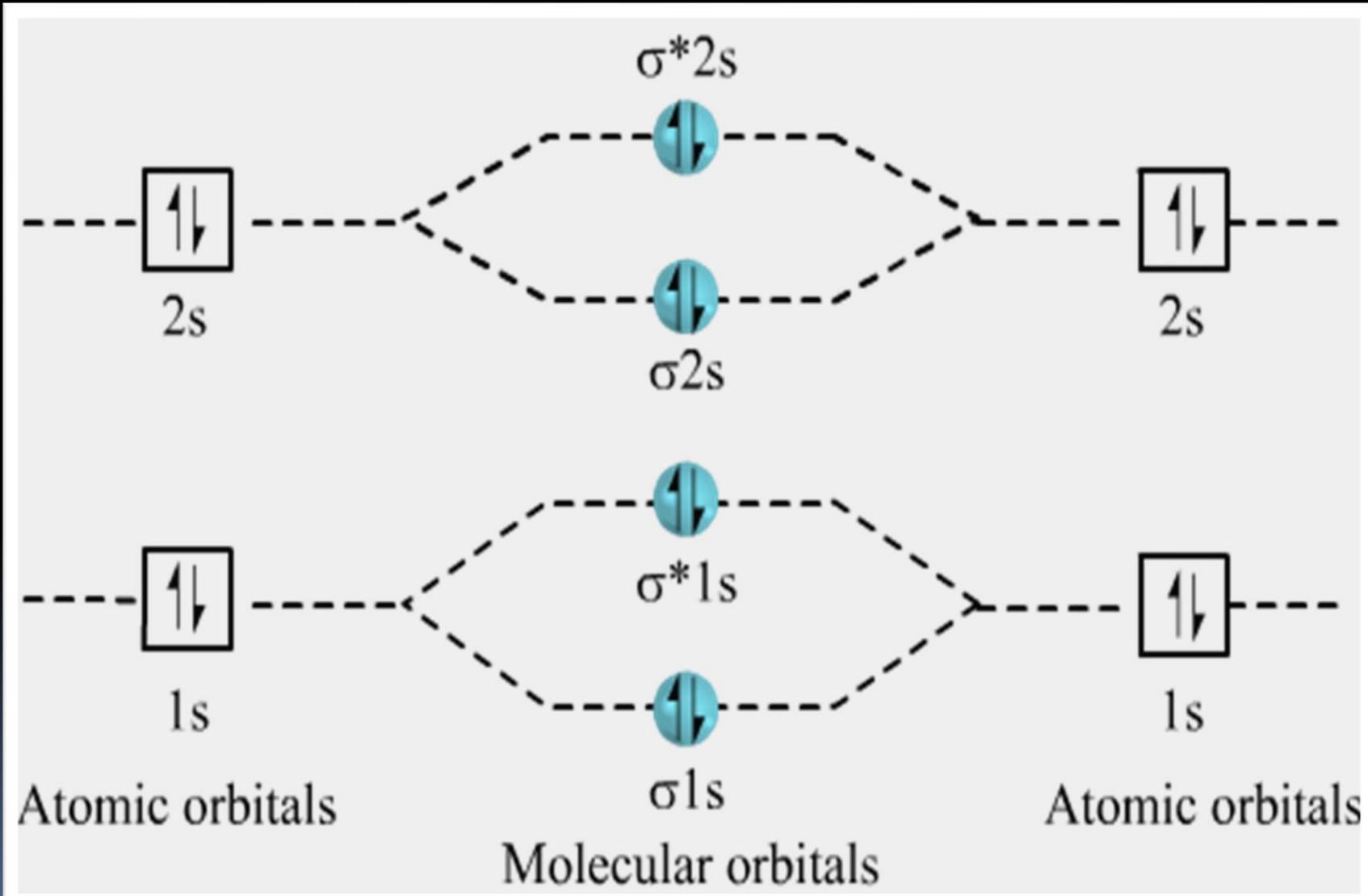
- If you note in  $H_2$  we combined two 1s orbitals to form a single lower energy s molecular orbital. The fourth principle states that stable molecular orbitals are easiest to form when constructed out of atomic orbitals of similar energies. This means that 1s orbitals should combine with 1s orbitals and 2p orbitals should combine with 2p orbitals etc. to form the most stable molecular orbitals.

# Bond Order

- The bond order for a molecule can be determined as follows:
- $\text{bond order} = \frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons})$ .
-

- Therefore, the  $\text{H}_2$  molecule has a bond order of  $\frac{1}{2} (2 - 0) = 1$ . In other words, there is a single bond connecting the two H atoms in the
- In the case of  $\text{He}_2$ , on the other hand, the bond order is  $\frac{1}{2} (2 - 2) = 0$ . This means that  $\text{He}_2$  is not a stable molecule.

# Energy Diagram of $\text{Be}_2$ (Be At. No.4, $1s^2 2s^2$ )



# Bond Order of Be<sub>2</sub>

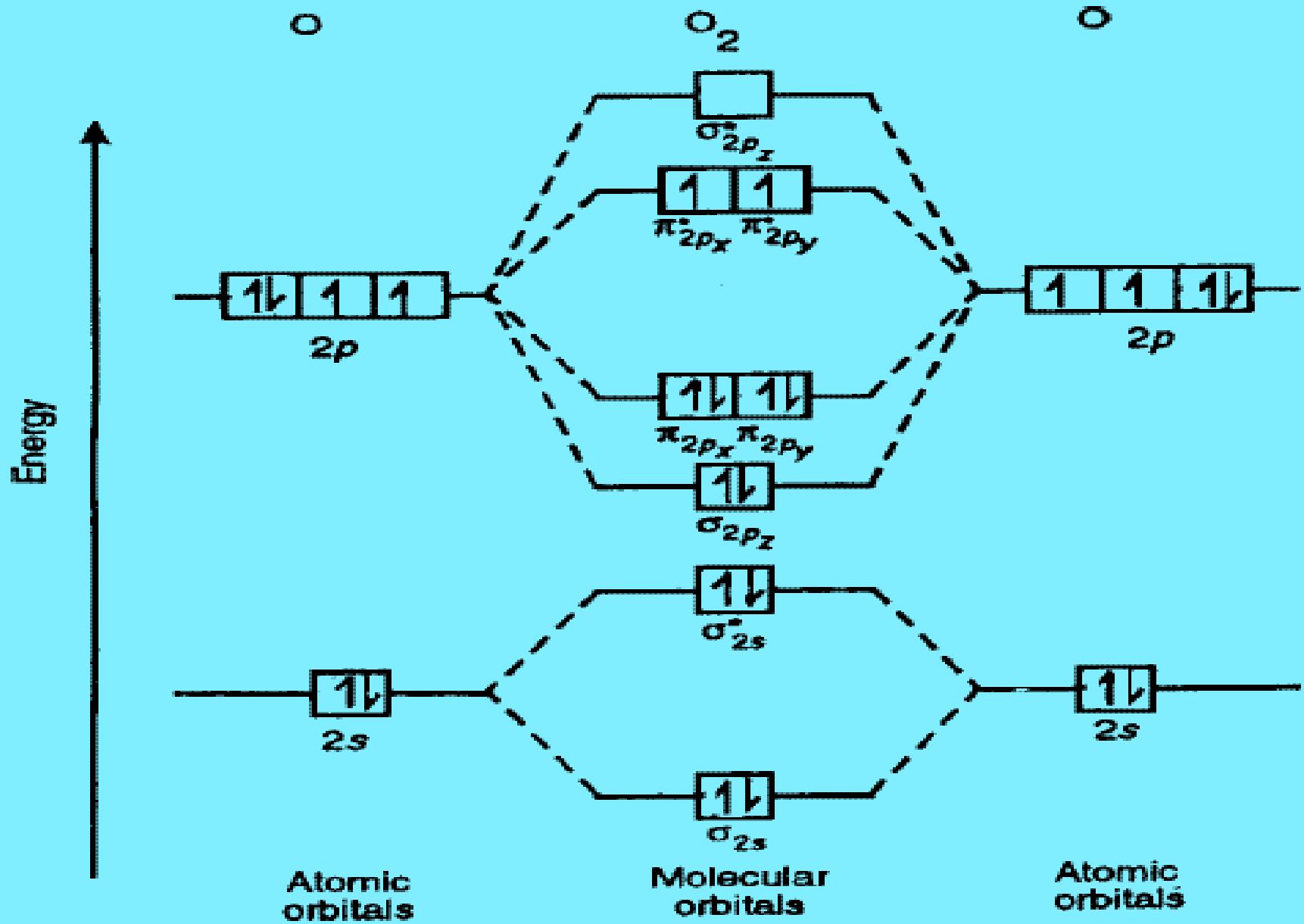
- Bond order =  $\frac{1}{2}$  (No. of electrons in bonding MO – No. of electrons in anti bonding MO)

$$= \frac{1}{2} (4-4)$$

$$= 0$$

Since bond order is zero, Be<sub>2</sub> is imaginary non-existent molecule.

# MO diagram of O<sub>2</sub>

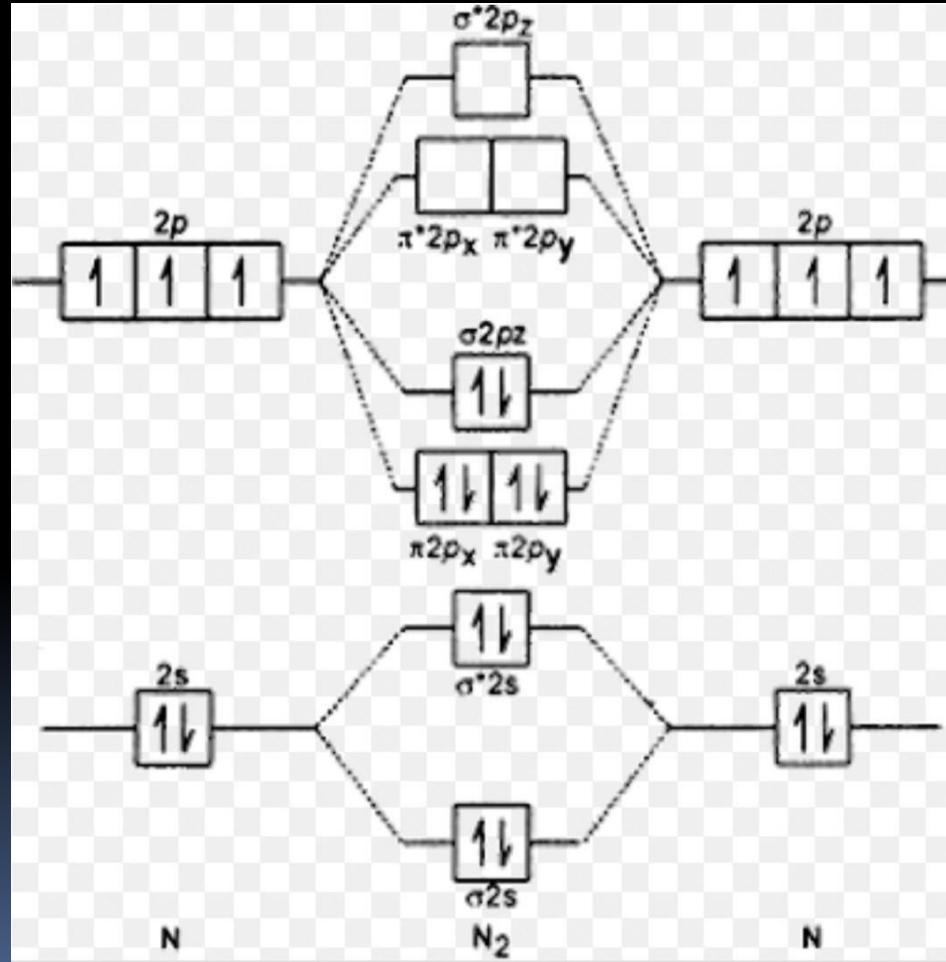


# Bond Order & Magnetic Properties

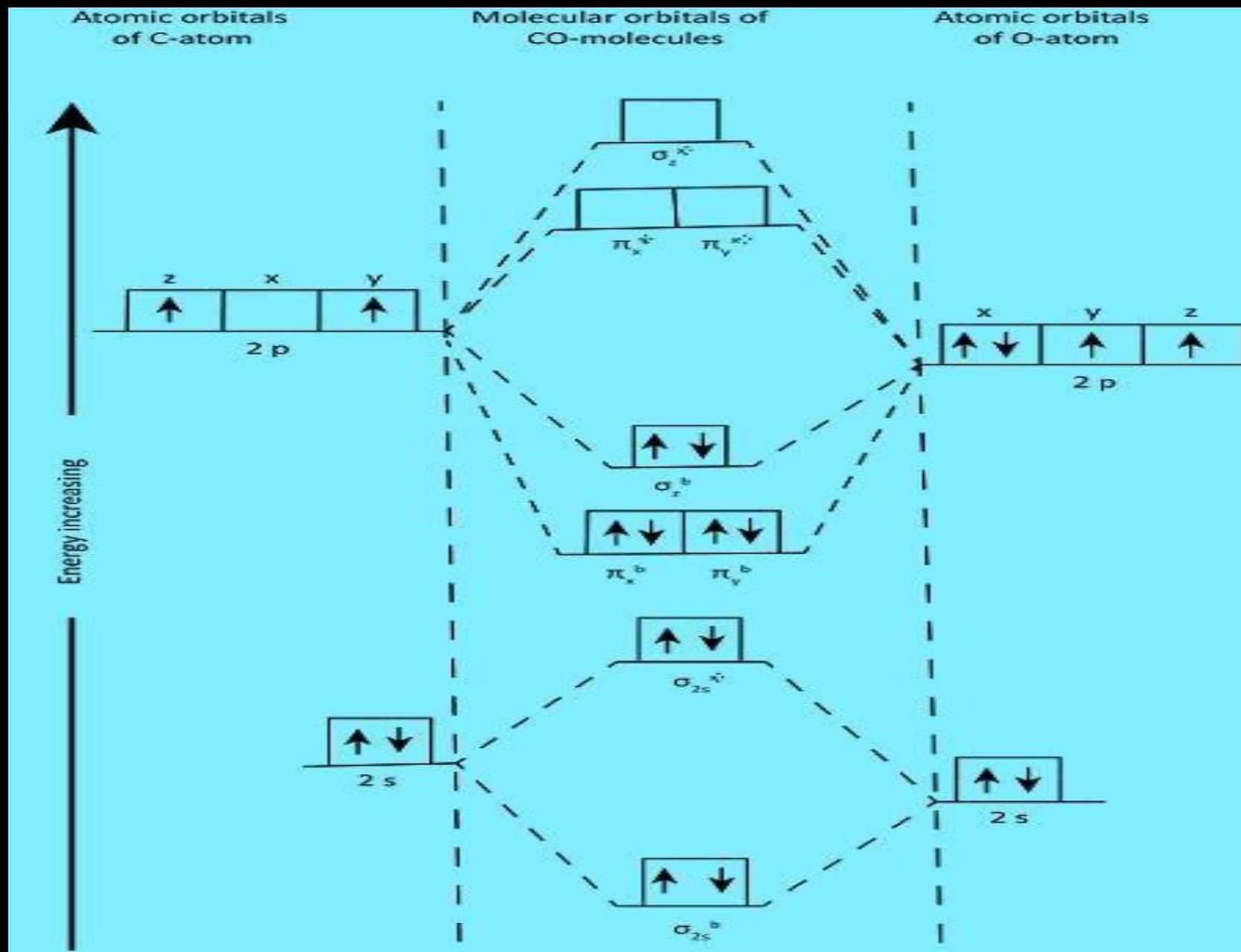
- Bond Order of O<sub>2</sub> =  $\frac{1}{2}$  (Nb-Na)  
=  $\frac{1}{2}$  (8-4)  
= 2
- O<sub>2</sub> has double bond in its structure.

It is paramagnetic in nature due to presence of unpaired electrons

# Assignment: Draw MO diagram of N<sub>2</sub> (not in the syllabus)



# MO diagram of CO

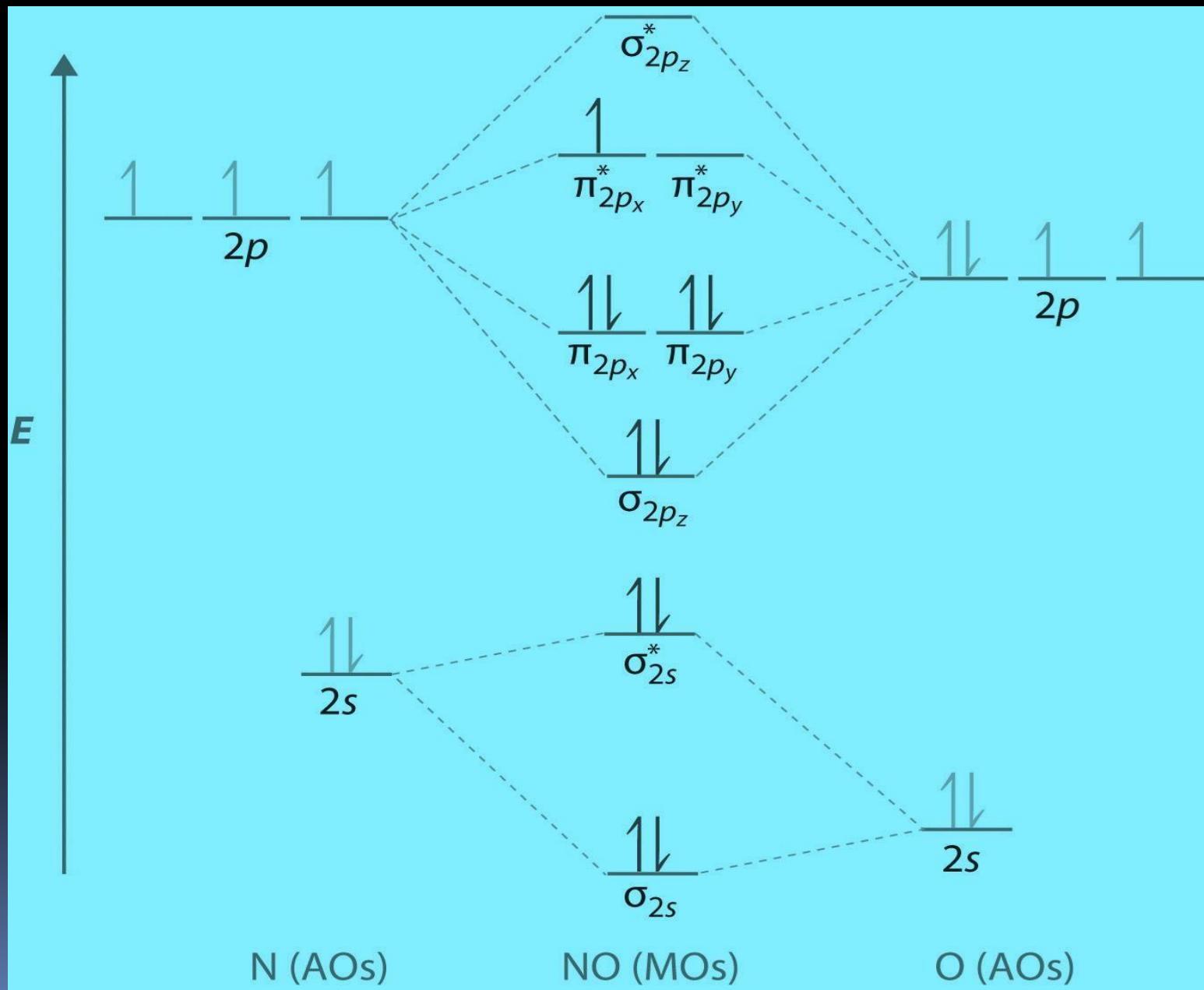


- In case of CO, due to sp mixing of orbitals of carbon atom the energy of  $\sigma_z$  orbital ( which is formed by overlap of sp orbital of carbon & Pz orbital of oxygen ) increases. Hence  $\sigma_z$ s observed at higher energy level than  $\pi_{Px}$  &  $\pi_{Py}$ .
- SP mixing occurs generally in molecule with total atomic number 14 or less than 14 as the energy gap between 2s & 2p orbital is less in case of these atoms

## Bond order & magnetic properties of CO

- Bond Order =  $\frac{1}{2}(\text{Nb} - \text{Na})$
- $= \frac{1}{2} (8-2)$
- $= 3$
- Hence CO has triple bond.
- It is dimagnetic as no unpaired electrons are present.

# MO diagram of NO



# Bond order & Magnetic Properties

- Bond order =  $\frac{1}{2}$  (Nb- Na)  
▪ =  $\frac{1}{2}$  ( 8-3)  
▪ = 2.5
- Since bond order is 2.5 bond is between double & triple bond. Or the molecule has double bond with unpaired electron.
- It is paramagnetic due to presence of unpaired electrons