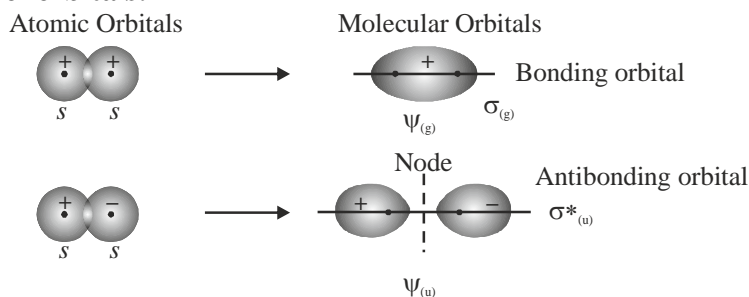


## TYPES OF SYMMETRIES OF MO'S

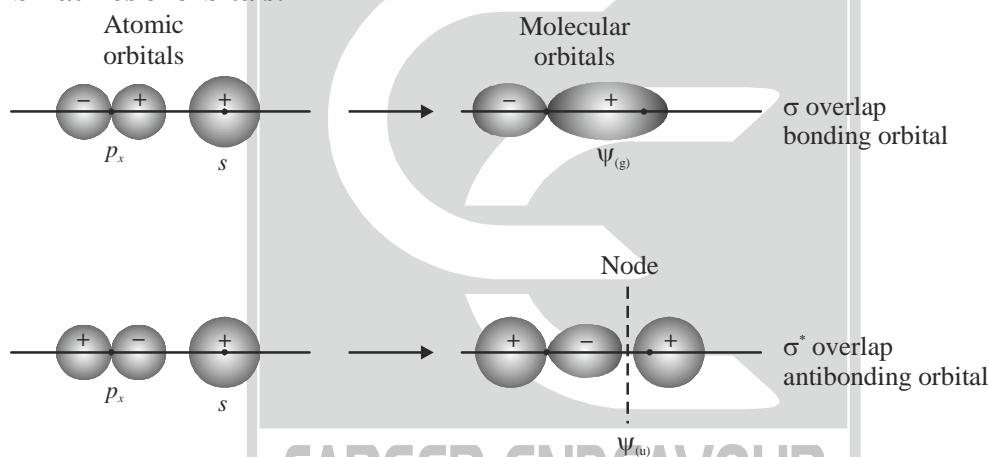
## s-s combinations of orbitals:



s-s combinations of atomic orbitals

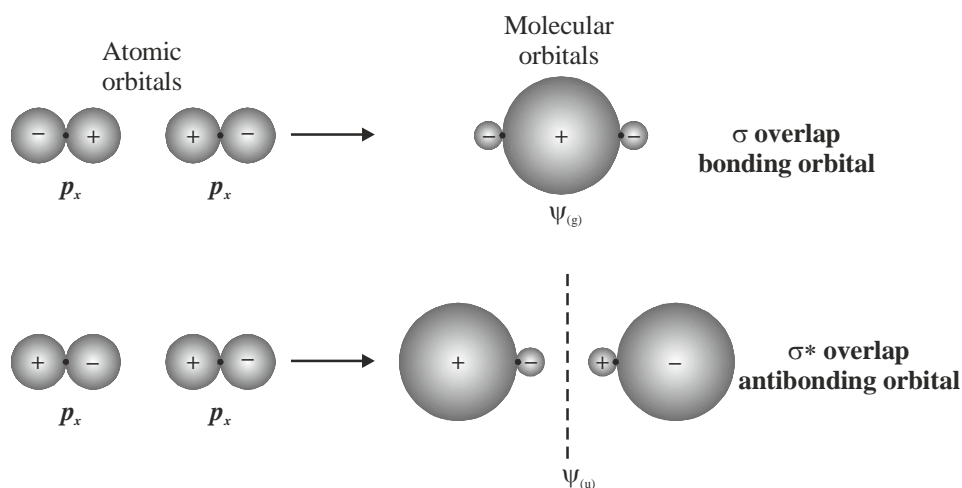
In the bonding MO there is increased electron density between the nuclei whereas in the anti-bonding MO the electron density between the nuclei is zero (since the two lobes of opposite sign cancel the function). Both in the atomic orbital pair before interaction and the MO's formed after interaction, there is cylindrical symmetry around the bond axis i.e., any point on the orbital surface describes a circle as the MO is rotated around the bond axis. This circle is a plane perpendicular to the bond axis. All the points on such a circle have either a positive sign or negative orbital sign. There is no change of sign i.e., no node as we move over the circle. This is termed cylindrical symmetry and orbitals with cylindrical symmetry are designated,  $\sigma$ , if they are bonding and  $\sigma^*$ , if they are antibonding.

## s-p combinations of orbitals:

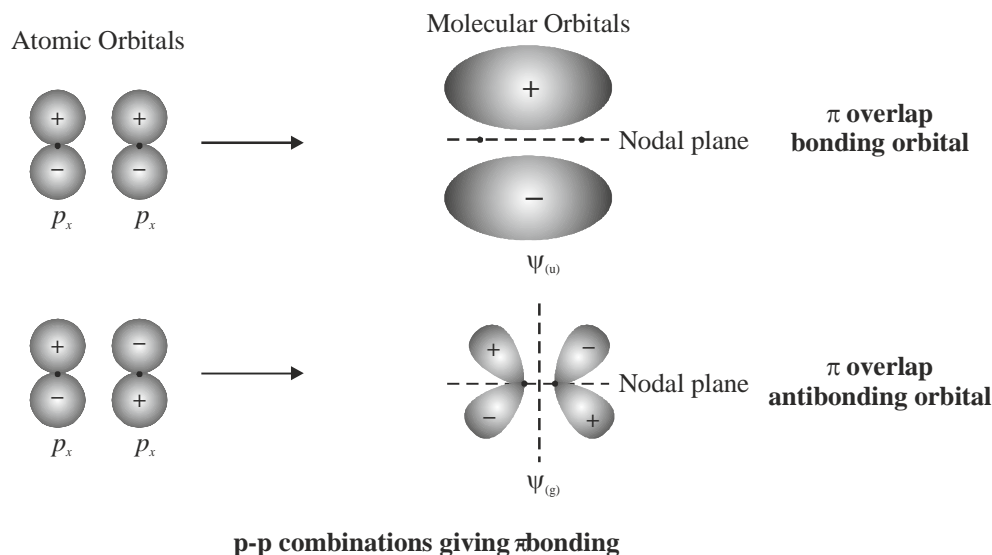


s-p combination of atomic orbitals

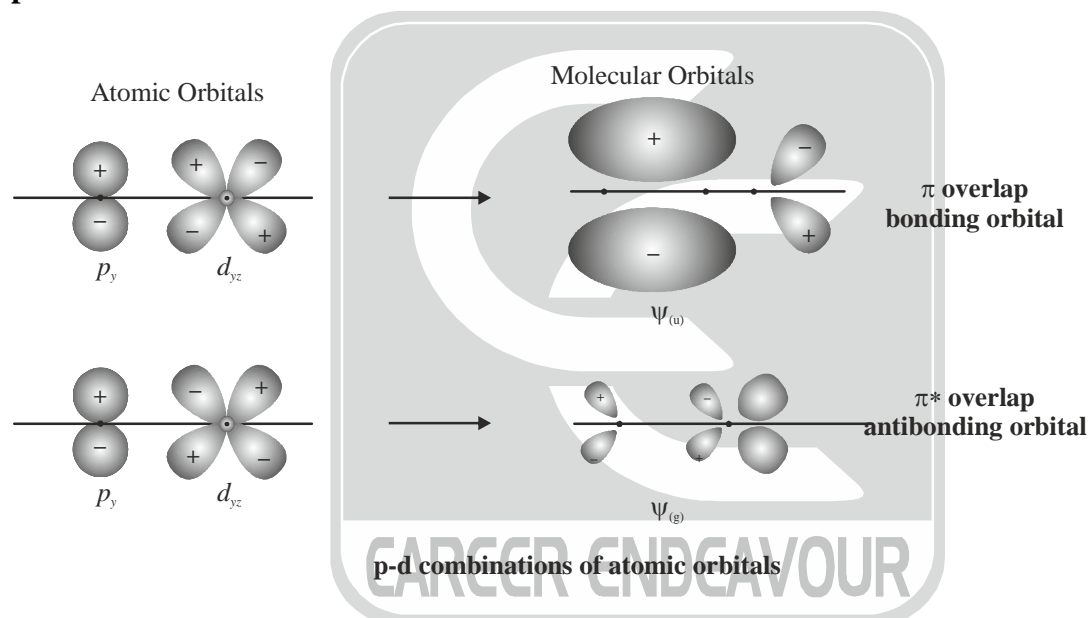
## p-p combinations of orbitals:



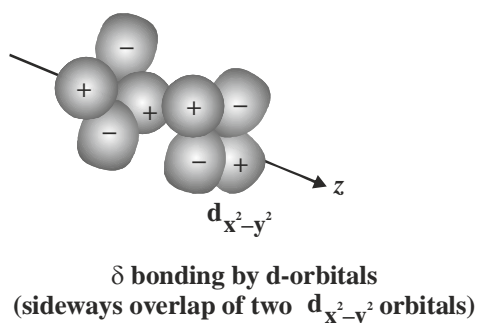
p-p combinations of atomic orbitals



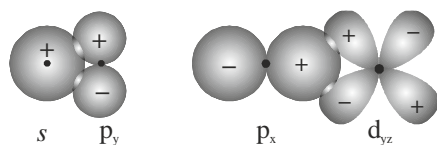
**p-d combinations of orbitals:**



**d-d combinations of orbitals:**



**Non-bonding combinations of orbitals:** In the combinations shown in the figure below any stabilization which occurs from overlapping + with + is destabilized by an equal amount of overlap of + with -. There is no overall change in energy, and this situation is termed non-bonding. It should be noted that in all these non-bonding cases the symmetry of the two atomic orbitals is different, i.e. rotation about the axis changes the sign of one.



Some non-bonding combinations of atomic orbitals

### Energy level diagram for molecular orbitals:

**BMO's** :  $\sigma(2s)$   $\sigma(2p_z)$   $\pi(2p_x)$   $\pi(2p_y)$

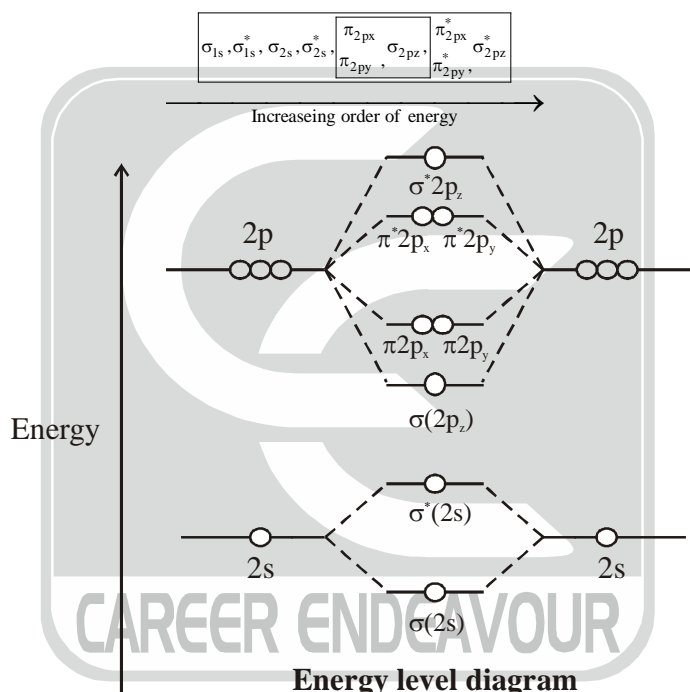
**ABMO's** :  $\sigma^*(2s)$   $\sigma^*(2p_z)$   $\pi^*(2p_x)$   $\pi^*(2p_y)$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data.

$$\boxed{\text{Total bonding MO's} = \text{Total antibonding MO's}}$$

### NOTE:

(1) If total number of electrons in a molecular  $\leq 14$ , the energy level of MO's follow this sequence.

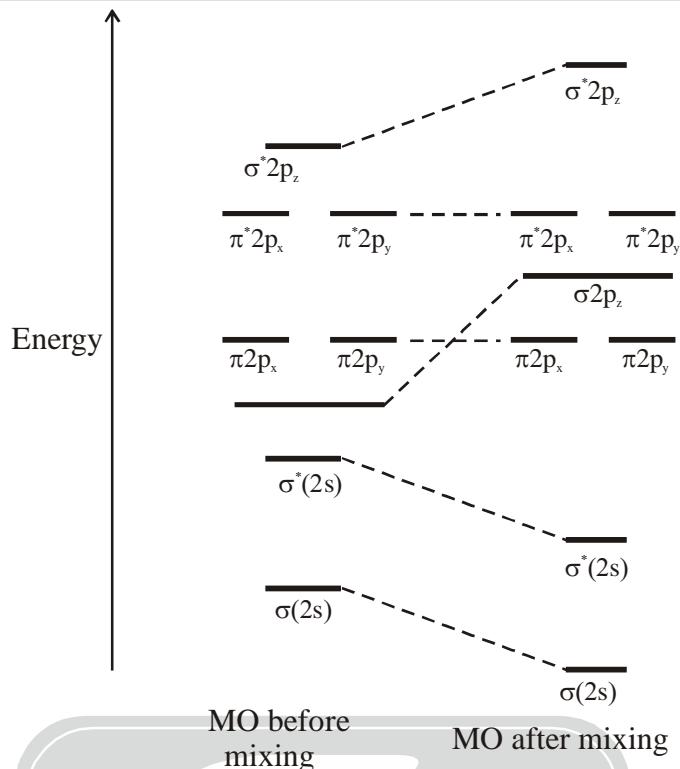


**Mixing of Orbitals:** However spectroscopic studies have reverse sequence of energy levels of MO's is not correct for all molecules.

It has been observed that in case of homonuclear diatomic molecules of second row elements,  $2p_z$  MO is higher in energy than the  $\pi_{2px}$  and  $\pi_{2py}$  MO's. Therefore the sequence of energy levels of MO's is due to the possibility of mixing of  $2s$  and  $2p_z$  atomic orbitals.

**Note:** If the difference between  $2s$  and  $2p$  atomic orbital are small, there is a possibility of the mixing of these orbitals to form mixed atomic orbitals. Which would be comparatively more stable.

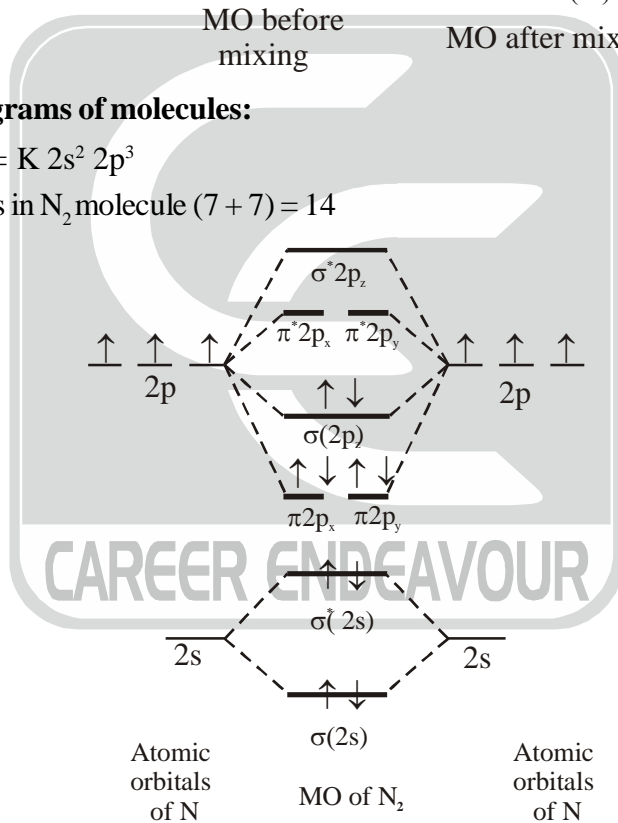
MO's as  $\sigma_{2s}$  and  $\sigma_{2s}^*$  obtained from mixed atomic orbitals would be lower in energy while  $\sigma_{2pz}$  and  $\sigma_{2pz}^*$  MO's would be higher in energy than the corresponding MO's obtained from mixed atomic orbitals.



**Molecular orbital diagrams of molecules:**

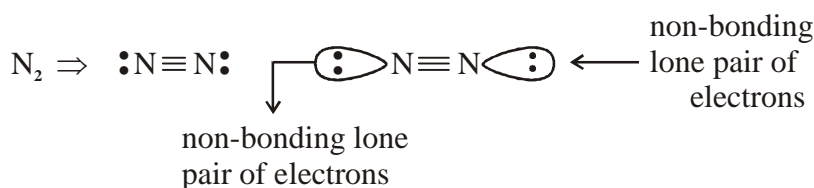
(1)  $N_2$ ,  $N = 1s^2 2s^2 2p^3 = K 2s^2 2p^3$

Total number of electrons in  $N_2$  molecule  $(7 + 7) = 14$



• Bond order =  $\frac{1}{2} [N_b - N_a] = \frac{1}{2} [10 - 4] = \frac{1}{2} \times 6 = 3$  (triple bond between two N atoms)

So,



There is no unpaired electron in  $N_2$  molecule and hence **diamagnetic**.

**Electronic configuration:**

$$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2px}^2, \pi_{2py}^2, \sigma_{2pz}^2, \sigma_{2pz}^{*0}, \pi_{2px}^{*0}, \pi_{2py}^{*0}, \sigma_{2pz}^0 \text{ OR } \sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2px}^2, \pi_{2py}^2, \sigma_{pz}^2$$

**Note:** MO diagrams follow the same sequence of energy levels (same as  $N_2$ ) of molecular orbitals for  $H_2, H_2^+, He_2, Li_2^+, Be_2, B_2, C_2, N_2$ , etc. i.e, for those homodiatomic molecules in which the total number of electrons are equal to 14 or less than 14.

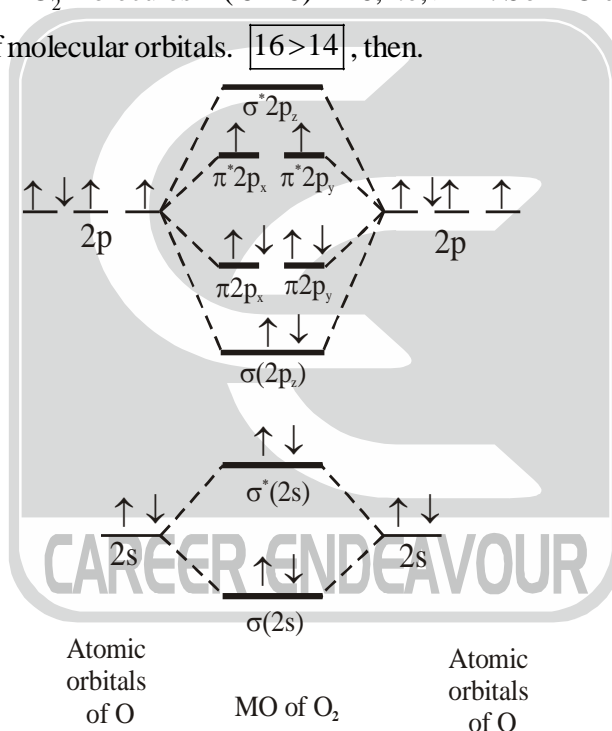
**Note:** If total number of electrons in molecule  $> 14$ , then the energy sequence of energy of molecular orbitals in MO diagram will be

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \left[ \sigma_{2pz} < \begin{matrix} \pi_{2px} \\ \pi_{2py} \end{matrix} \right] < \begin{matrix} \pi_{2px}^* \\ \pi_{2py}^* \end{matrix} < \sigma_{2pz}^*$$

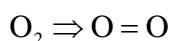
**MO diagram of  $O_2$ :**

$$O = 1s^2 2s^2 2p^4 = 2s^2 2p^4$$

Total number of electrons in  $O_2$  molecules =  $(8 + 8) = 16$ , i.e,  $> 14$ . So MO diagram follows the following sequence of energy level of molecular orbitals.  $[16 > 14]$ , then.



$$\text{Bond order} = \frac{1}{2} [N_B - N_A] = \frac{1}{2} [8 - 4] = \frac{4}{2} = 2 \text{ (two bonds between oxygen atoms)}$$



- Paramagnetic due to presence of two unpaired electrons in  $\pi_{2px}^*$  and  $\pi_{2py}^*$  antibonding molecular orbitals.

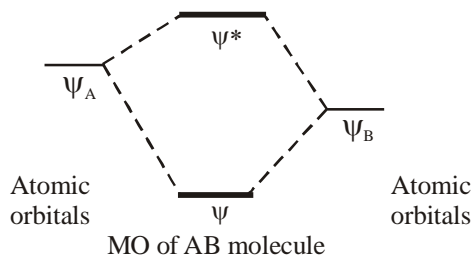
**Electronic configuration:**

$$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2pz}^2, \pi_{2px}^2, \pi_{2py}^2, \pi_{2px}^{*1}, \pi_{2py}^{*1}$$

**Note:** Same MO diagram for  $O_2^-, O_2^{2-}, F_2$ , etc.

**MO diagram for hetero diatomic molecules:**

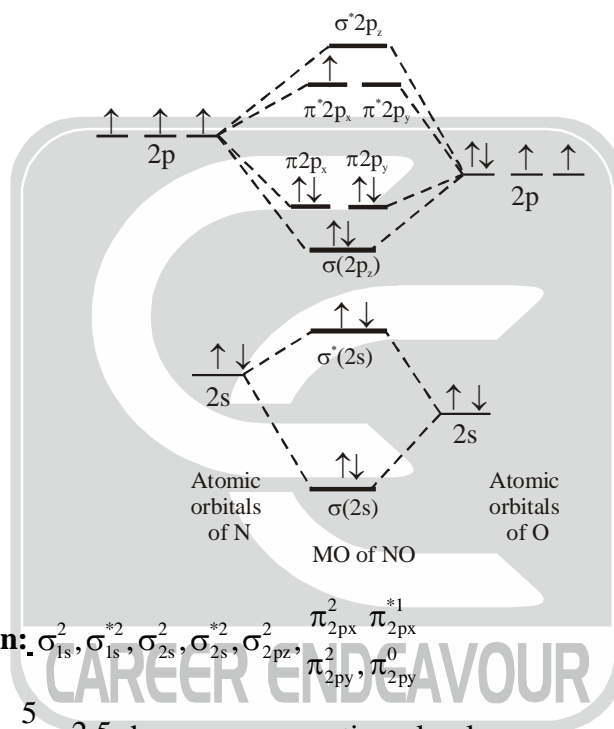
**AB molecule**



$\chi_B > \chi_A$ , where  $\chi$  = electronegativity

eg. NO

$$\left. \begin{aligned} {}_7\text{N} &= 1s^2 2s^2 2p^3 = 7e_s^- \\ {}_8\text{O} &= 1s^2 2s^2 2p^4 = 8e_s^- \end{aligned} \right\} \rightarrow 15e_s^- > 14$$



**Electronic Configuration:**

$$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2pz}^2, \pi_{2px}^2, \pi_{2py}^2, \pi_{2px}^{*1}, \pi_{2py}^{*0}$$

Bond order =  $\frac{1}{2}(10 - 5) = \frac{5}{2} = 2.5$ , hence paramagnetic molecule.

**Note:** MO of NO and NO<sup>+</sup> are same.

NO<sup>+</sup> Total e<sub>s</sub><sup>-</sup> = 14

Diamagnetic molecule

Bond order =  $\frac{1}{3}[10 - 4] = \frac{6}{3} = 3$ ; [N ≡ O]<sup>+</sup>

**MO diagram for CO:**  $\left. \begin{aligned} \text{O} &= 1s^2 2s^2 2p^4 \\ \text{C} &= 1s^2 2s^2 2p^2 \end{aligned} \right\} \rightarrow 14e^-$