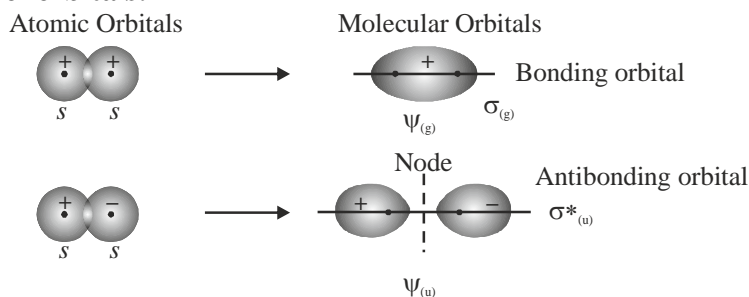


TYPES OF SYMMETRIES OF MO'S

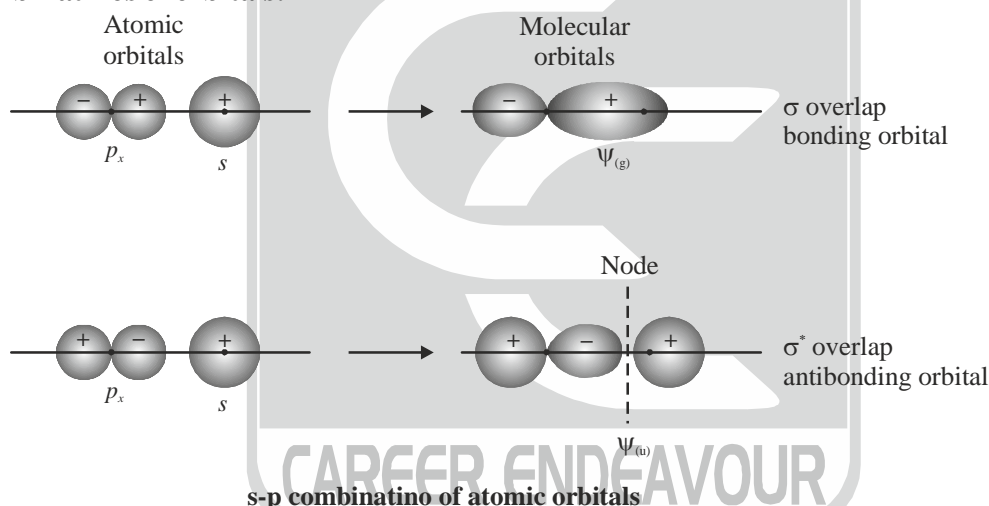
s-s combinations of orbitals:



s-s combinations of atomic orbitals

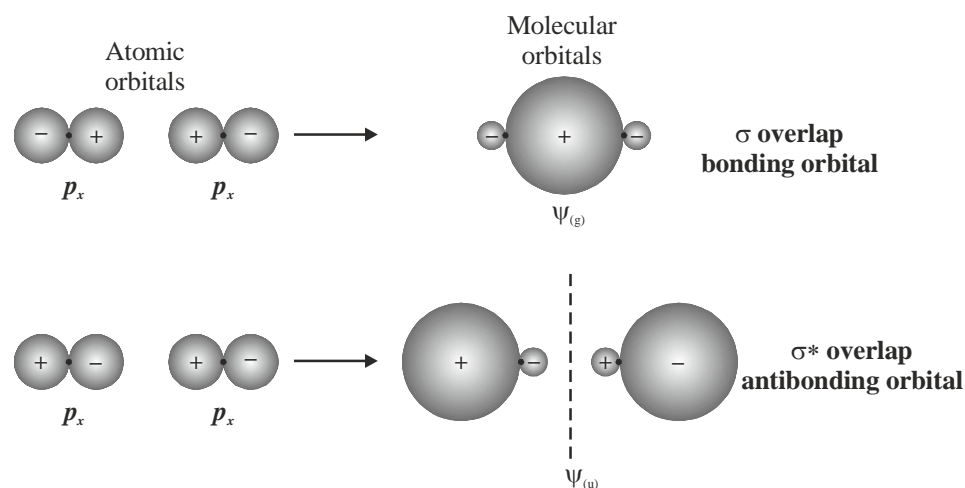
In the bonding MO there is increased electron density between the nuclei whereas in the anti-bonding MO the electron density between the nuclei is zero (since the two lobes of opposite sign cancel the function). Both in the atomic orbital pair before interaction and the MO's formed after interaction, 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, σ , if they are bonding and σ^* , if they are antibonding.

s-p combinations of orbitals:

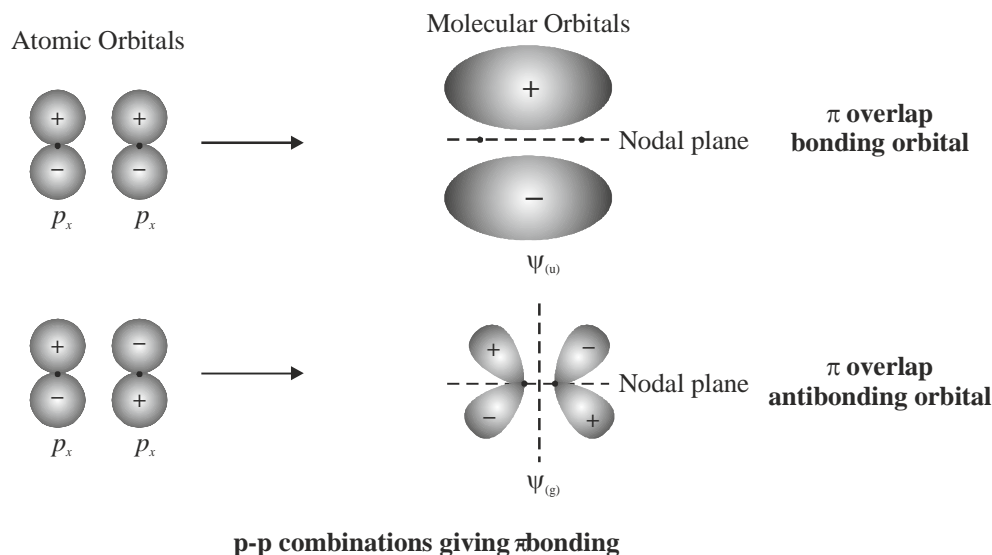


s-p combination of atomic orbitals

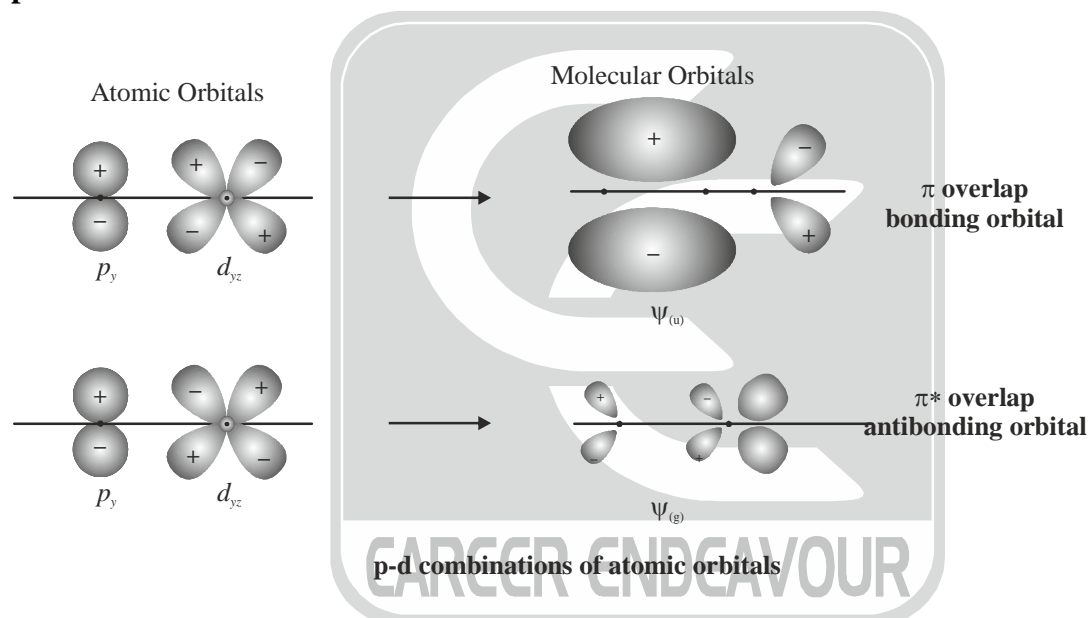
p-p combinations of orbitals:



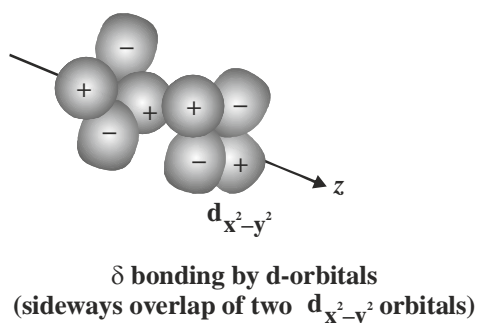
p-p combinations of atomic orbitals



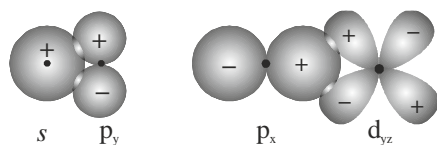
p-d combinations of orbitals:



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

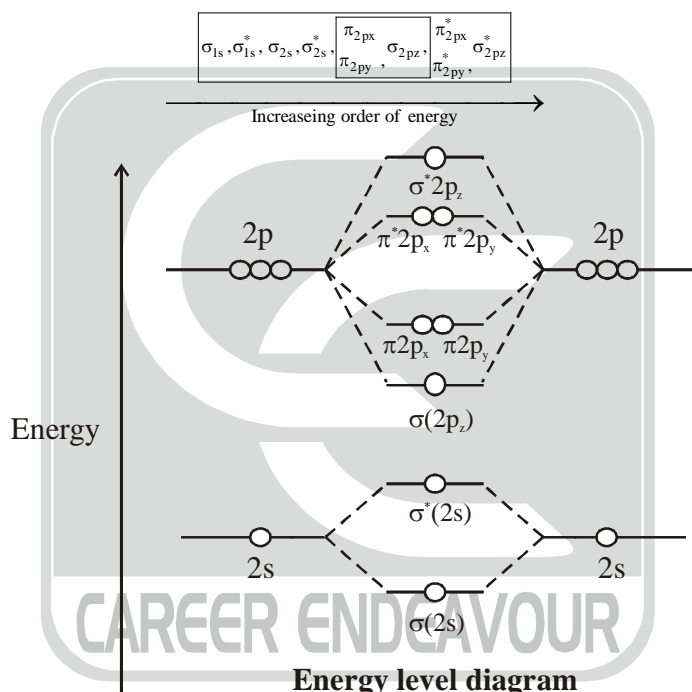
ABMO's : $\sigma^*(2s)$ $\sigma^*(2p_z)$ $\pi^*(2p_x)$ $\pi^*(2p_y)$

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 ≤ 14 , the energy level of MO's follow this sequence.

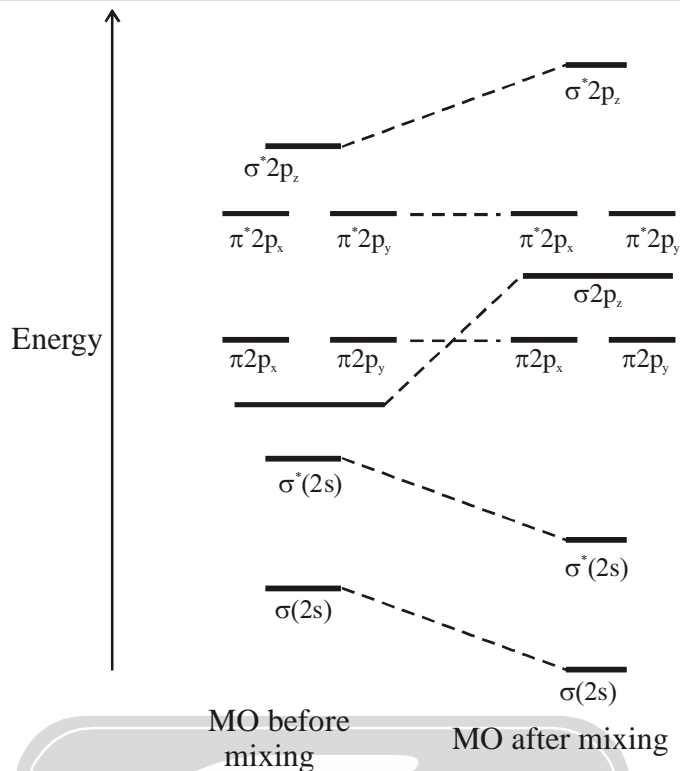


Mixing of Orbitals: However spectroscopic studies have reverse sequence of energy levels of MO's is not correct for all molecules.

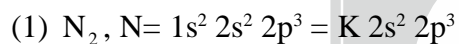
It has been observed that in case of homonuclear diatomic molecules of second row elements, $2p_z$ MO is higher in energy than the π_{2px} and π_{2py} MO's. Therefore the sequence of energy levels of MO's is due to the possibility of mixing of $2s$ and $2p_z$ atomic orbitals.

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.

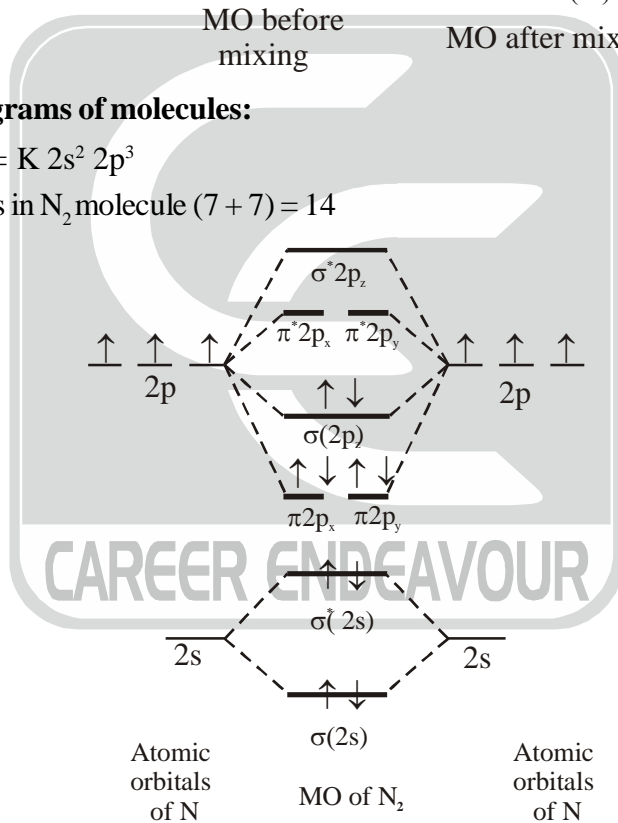
MO's as σ_{2s} and σ_{2s}^* obtained from mixed atomic orbitals would be lower in energy while σ_{2pz} and σ_{2pz}^* MO's would be higher in energy than the corresponding MO's obtained from mixed atomic orbitals.



Molecular orbital diagrams of molecules:

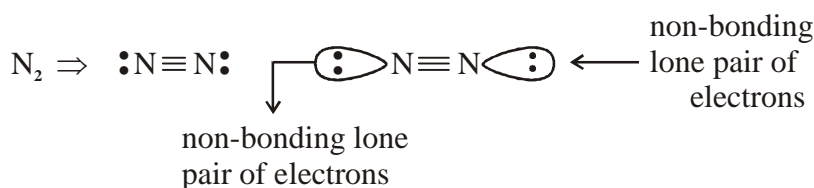


Total number of electrons in N_2 molecule $(7 + 7) = 14$



• 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:

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

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.

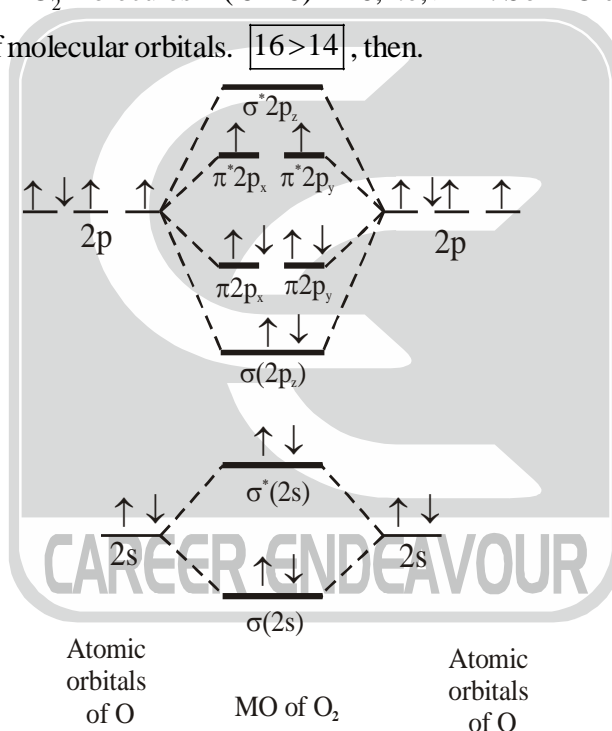
Note: If total number of electrons in molecule > 14 , then the energy sequence of energy of molecular orbitals in MO diagram will be

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

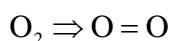
MO diagram of O_2 :

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

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 π_{2px}^* and π_{2py}^* antibonding molecular orbitals.

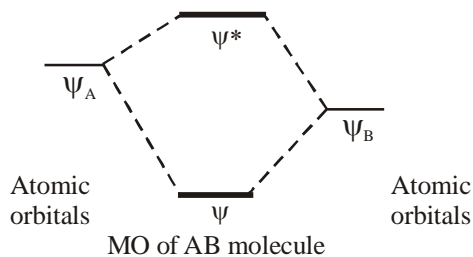
Electronic configuration:

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

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

MO diagram for hetero diatomic molecules:

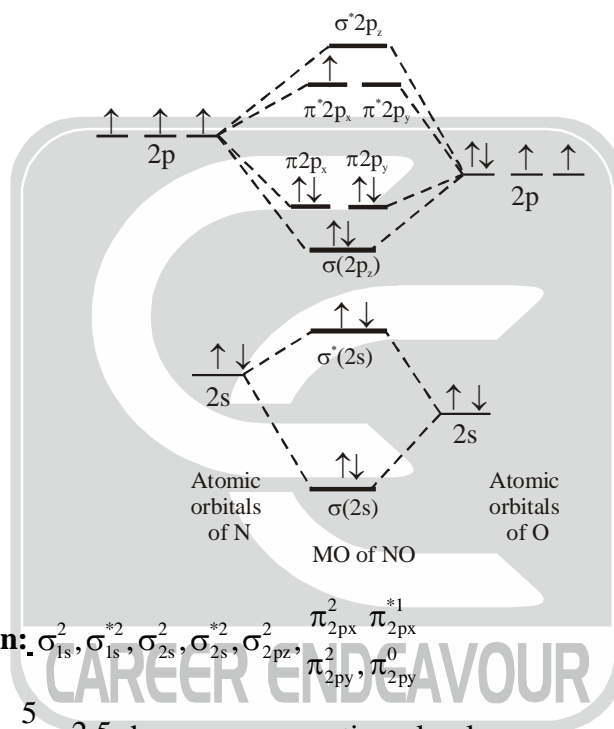
AB molecule



$\chi_B > \chi_A$, where χ = 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.

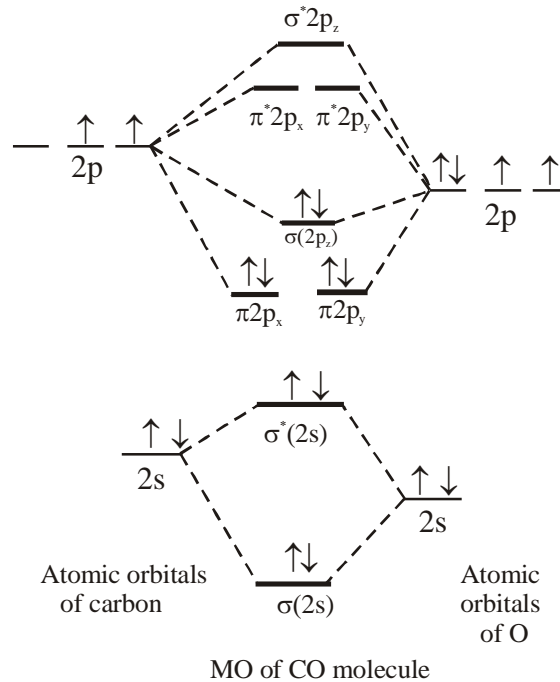
Note: MO of NO and NO⁺ are same.

NO⁺ Total e_s⁻ = 14

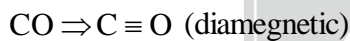
Diamagnetic molecule

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

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



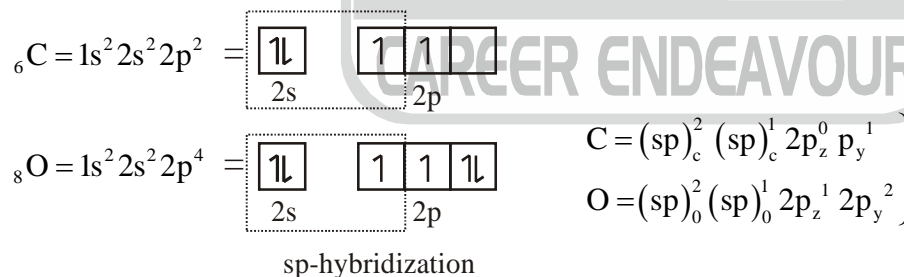
$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}[10 - 4] = \frac{6}{2} = 3 \text{ (Triple bond between carbon and oxygen atom)}$$



(1) Coulson's Treatment of CO molecules:

CO is ionised to give CO^+ by removing of one electron from the σ_{2p_z} orbital then the bond order should be reduced to $2\frac{1}{2}$ and the bond length increased. Infact the bond length of CO^+ decreases and the bond order increases. This cannot be explained by simple CO, MO diagram.

Coulson modified the MO diagram of CO by using concept of hybridization.



Note: Elcetron pairs in $(\text{sp})_c$ and $(\text{sp})_o$ hybrid orbitals are not involved in bonding and hence are called σ

Non-bonding electron pairs (σ_{nb} - pairs). $(\text{sp})_c$ hybrid orbital containing a lone pair of electron has higher energy and higher degree of p-character, is very reactive and hence accounts for the properties of CO.

• $(\text{sp})_o$ hybrid orbital containing a lone pair of electrons, lower in energy than $(\text{sp})_o$ hybrid orbital containing a single electron, has high degree of s-orbital character and hence is very stable (i.e. unreactive) hybrid-orbital.

Now we are left with two singly filled $(\text{sp})_c$ and $(\text{sp})_o$ hybrid orbitals and two 2p-atomic orbitals ($2p_x$ and $2p_y$) on both the atoms which overlap together in pair to give the following molecular orbitals.

• $(\text{sp})_c + (\text{sp})_o$ give σ_{sp} and σ_{sp}^* molecular orbitals

- $2p_x$ atomic orbital on C-atom + $2p_x$ - atomic orbital on O-atom give π_x and π_x^* MO's
- $2p_y$ atomic orbital on C-atom + $2p_y$ atomic orbital on O-atom give π_{2p_y} and π_y^* MO's.

The relative order of energy of different MO's in CO:

$$\boxed{(\text{sp})_O < \sigma_{\text{sp}^b} < \pi_x^b = \pi_y^b < (\text{sp})_C < \pi_x^* = \pi_y^* < \sigma_{\text{sp}^*}}$$

and hence molecular orbital configuration of CO is -

$$(\text{sp})_O^2, (\sigma_{\text{sp}^b})^2, (\pi_x^b)^2 = (\pi_y^b)^2, (\text{sp})_C^2, (\pi_x^*) = \pi_y^* < \sigma_{\text{sp}^*}$$

Bond order = $\frac{1}{2}(6-0) = 3$, showing that C and O in CO molecule are linked together by a triple bond

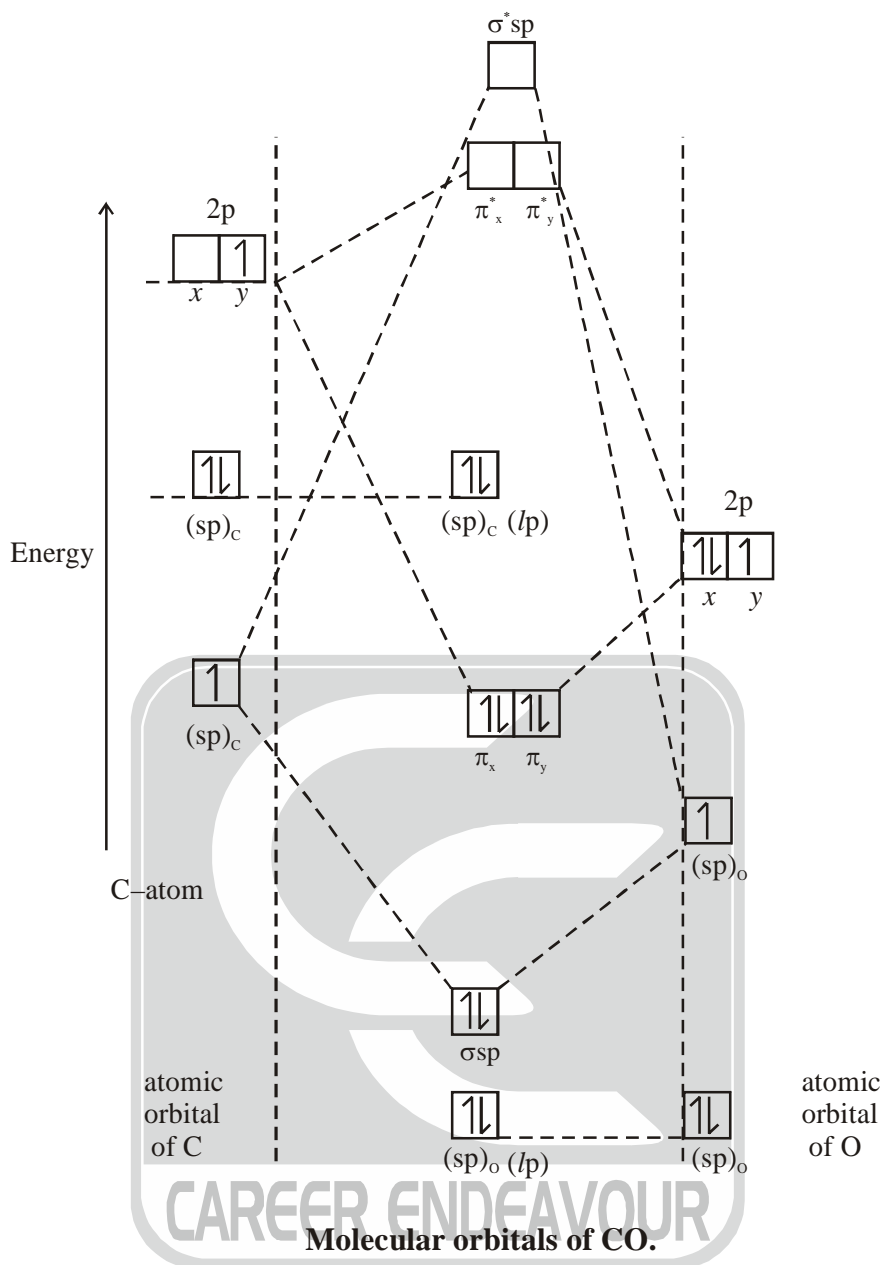
($1\sigma + 2\pi$ bonds)

- σ_{sp^b} molecular orbitals is mostly on oxygen atom π_x^b and π_y^b molecular orbitals are mostly on O-atom. Since O-atoms contributes more to the formation of these MO's than does C-atom.

These MO's are leaning some what toward oxygen atom are shown in figure. The other π -MO's are at right angles i.e, in front and behind the paper to the one shown below.

In the formation of π_x^* and π_y^* molecular orbitals (degenerate MO's) carbon atom makes a larger contribution than O-atom. Both of these degerate π^* MO's are also at right sides to each other. The π^* MO's are much closer to C-atom and are, therefore concentrated mostly on C-atom.

Note: Both these π^* MO's are empty and can therefore, accept electron pairs by interacting with appropriate, filled orbitals of transitional elements. These π^* MO's are therefore, called acceptor MO's. This acceptor property of these MO's is very important in considering the $M \rightarrow L$ bond in metal carbon and hence M is the metal an L indicates π - ligand such as CO.

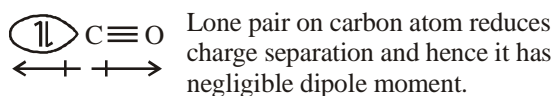


Problem: Why CO molecule, co-ordinated through carbon ?

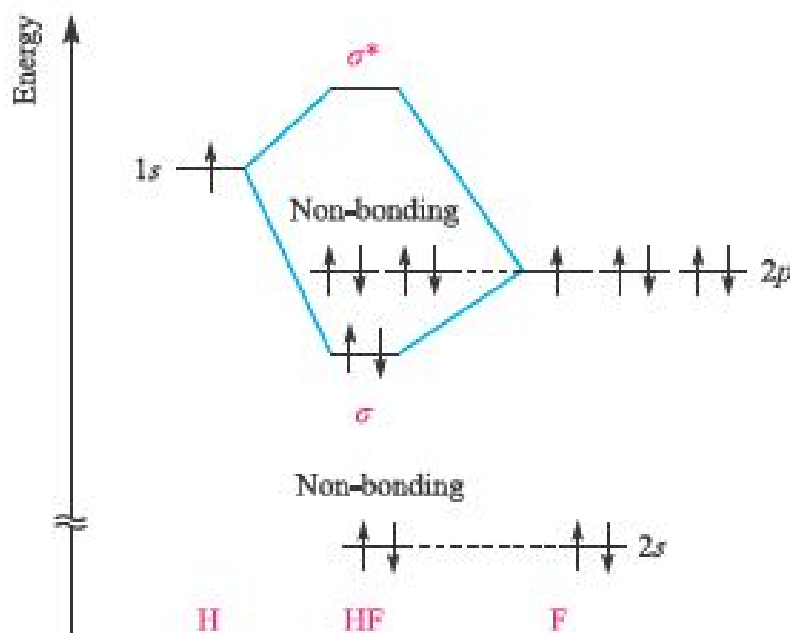
Soln. Electron pairs in $(sp)_c$ and $(sp)_o$ hybrid orbitals in Coulson's CO diagram, are not involved in bonding, hence called non-bonding electron pairs. Lone pair of electrons in non-bonding $(sp)_c$ hybrid orbital, has highest energy i.e. HOMO. It is concentrated on carbon atoms and easily available for bonding with other atoms/metals. This is the reason CO coordinate with other atoms through carbon atom.

Problem: Why CO has negligible dipole moment ?

Soln. Lone pair of electrons on carbon atom in CO molecule points away from O-atom (i.e. extends away from C—O bond). This reduces the effective electronic charge between carbon and oxygen atoms. This accounts for the low dipole moment of CO.



Molecular orbital diagram of HF:



An orbital interaction diagram for the formation of HF .
Only the valence atomic orbitals and electrons are shown.

Comparison between valence bond theory and molecular orbital theory:

Common features: valence bond and molecular orbital theories have following features in common.

- (i) Both the theories are the interpretation of covalent bonds.
- (ii) According to both theories the Atomic orbitals of the two atoms must overlap to form a covalent bond. The Atomic orbitals overlapping each other must have the same symmetry and must be of same energy.
- (iii) According to both, the electronic charge reside in the region between the atomic nuclei.
- (iv) The basic principles involved in the distribution of electrons are similar. Thus an orbital, whether atomic or molecular cannot have more than two electrons. They are filled in order of increasing energy.
- (v) Both the theory postulate that a covalent bonds possesses directional properties.

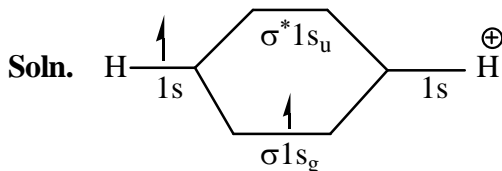
Differences:

MOT **VBT**

(1)	Molecular orbitals are formed by LCAO approximation method. The atomic orbitals involved in the formation of these molecules orbitals are from valence shell of two atoms.	(1)	Two atomic orbitals give an interatomic orbital obtained by the combination of the space function of two unpaired electrons; one being in each of the two AO's
(2)	Atomic orbitals of the resulting molecule lose their individual identity.	(2)	The resulting molecule consists of atoms which although interacting retain a large measure of their individual character.
(3)	Molecular orbitals are polycentric.	(3)	Atomic orbitals are mono-centric.
(4)	MOT explains the paramagnetic character of oxygen	(4)	VBT fails to explain paramagnetic character of O ₂ .
(5)	Resonance play no role in MOT	(5)	Resonance play an important role in VBT
(6)	The MOT inherently gives an equal weightage to the covalent and ionic structures	(6)	However in the initial stage of development the VBT ignored the ionic contribution to chemical bond

SOLVED PROBLEMS

1. Which one of the following statements concerning H_2^+ is incorrect? [BHU 2011,15]
- (a) The non-degenerate LCAO-MOs (without spin) must be either symmetric or anti-symmetric for inversion
 (b) The lowest energy MO (without spin) of the molecule is anti-symmetric for inversion
 (c) The ground state has a multiplicity of two
 (d) The MOs transform into AOs of the helium ion as the two nuclei are fused together



Ground state : $1\sigma_g^1 \Rightarrow$ spin multiplicity $\rightarrow 2s+1 \Rightarrow 2 \times \frac{1}{2} + 1 = 2$

The lowest energy MO (without spin) of the molecule is symmetric for inversion.

Correct option is (b)

2. Which of the following combination of atoms of A and B forms bonding molecular orbitals?

(a) $(\psi_A - \psi_B)$ (b) $(\psi_A + \psi_B)$ (c) $(\psi_A \times \psi_B)$ (d) $\frac{\psi_A}{\psi_B}$ [BHU 2012]

Soln. The additive linearly combination of wave function of atom A (ψ_A) and B (ψ_B) is responsible formation of bonding molecular orbital

$$\psi_{AB} = N(C_1\psi_A + C_2\psi_B)$$

Correct option is (b)

3. Which of the following processes involves increasing in bond order? [BHU 2012]

(a) $N_2 \rightarrow N_2^+ + e^-$ (b) $CO + e^- \rightarrow CO^-$ (c) $NO \rightarrow NO^+ + e^-$ (d) $O_2 + e^- \rightarrow O_2^-$

Soln. According to Molecular Orbital Theory

$$NO^+ \rightarrow \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^* < \pi_{2py}^* < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

Correct option is (c)

4. Which molecule has zero bond order? [BHU 2012]

(a) H_2^+ (b) H_2 (c) HeH (d) He_2

Soln. $He_2 \Rightarrow \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2}$

$$\text{Bond order} = \frac{2 - 2}{2} = 0$$

5. What is the bond order in NO molecule? [BHU 2012,13]

(a) 2.5 (b) 2 (c) 1.5 (d) 1

Soln. $NO \rightarrow \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^{*1} = \pi_{2py}^* < \sigma_{2pz}^*$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

Correct option is (a)

6. Which molecule has zero bond order?

[BHU 2014]

- (a) H_2^+ (b) H_2 (c) HeH (d) He_2

Soln. $\text{He}_2 \Rightarrow \sigma_{1s}^2 < \sigma_{1s}^{*2}$

$$\text{Bond order} = \frac{2-2}{2} = 0$$

Correct option is (d)

7. What is the bond order in NO molecule?

[BHU-2014]

- (a) 2.5 (b) 2 (c) 1.5 (d) 1

Soln. Electronic configuration of

$$\text{NO} = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^{*1} = \pi_{2py}^* < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 5) = \frac{5}{2} = 2.5$$

Correct answer is (a)

8. Arrange the following oxygen molecular ions and the molecule in order of increasing bond energy or in decreasing order of (O-O) bond length. The molecular ions and the molecule are : O_2^{2+} , O_2^+ , O_2 , O_2^- and O_2^{2-} . The possible orders are given below. Choose the correct one:

[BHU 2016]

- (a) $\text{O}_2 < \text{O}_2^+ < \text{O}_2^- < \text{O}_2^{2+} < \text{O}_2^{2-}$ (b) $\text{O}_2^{2-} < \text{O}_2^- < \text{O}_2 < \text{O}_2^+ < \text{O}_2^{2+}$
 (c) $\text{O}_2 < \text{O}_2^- < \text{O}_2^{2-} < \text{O}_2^+ < \text{O}_2^{2+}$ (d) $\text{O}_2^- < \text{O}_2^{2-} < \text{O}_2 < \text{O}_2^{2+} < \text{O}_2^+$

Soln. Bond order \propto bond energy $\propto \frac{1}{\text{bond length}}$

$$\text{O}_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*1} = \pi_{2py}^* < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{1}{2}(10 - 6) = \frac{4}{2} = 2$$

$$\text{O}_2^+ = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*1} = \pi_{2py}^* < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{1}{2}(10 - 5) = \frac{5}{2} = 2.5$$

$$\text{O}_2^{2+} = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{1}{2} \left(\frac{10-4}{2} \right) = 3$$

$$\text{O}_2^- = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*2} = \pi_{2py}^{*1} < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{1}{2}(10 - 7) = \frac{3}{2} = 1.5$$

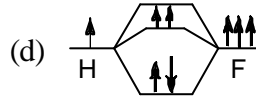
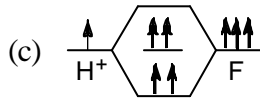
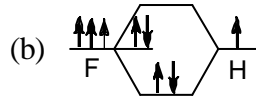
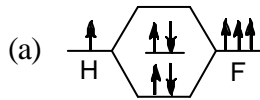
$$\text{O}_2^{2-} = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*2} = \pi_{2py}^{*2} < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{1}{2}(10 - 8) = \frac{2}{2} = 1$$

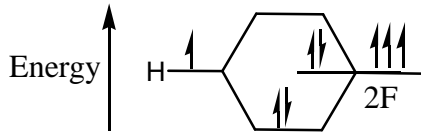
Correct option is (b)

9. Which one of the following M, O.'s of $(\text{HF}_2)^-$ is correct?

[BHU 2016]



Soln. Molecular orbital diagram for $[\text{HF}_2]^-$



Correct option is (b)

10. Out of the following diatomic molecules, the paramagnetic ones are

- (A) Be_2 (B) B_2 (C) C_2 (D) N_2
 (E) O_2 (F) F_2 (G) C_2^+ (H) C_2^-
 (a) Be_2, B_2 and C_2, N_2 (c) $\text{B}_2, \text{C}_2, \text{N}_2$ and C_2^- [BHU 2016]
 (b) $\text{C}_2, \text{N}_2, \text{O}_2$ and C_2^+ (d) $\text{B}_2, \text{O}_2, \text{C}_2^+, \text{C}_2^-$

Pick the correct choice out the above four choices.

Soln. $\text{B}_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^1 = \pi_{2py}^1$

Number of unpaired electrons = 2

$\text{C}_2^+ = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^1$

Number of unpaired electron = 1

$\text{C}_2^- = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^1$

Number of unpaired electron = 1

$\text{N}_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2$

Number of unpaired electron = 0

$\text{Be}_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2}$

Number of unpaired electron = 0

$\text{O}_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*1} = \pi_{2py}^{*1} < \sigma_{2pz}^*$

Number of unpaired electron = 2

$\text{F}_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*2} = \pi_{2py}^{*2} < \sigma_{2pz}^*$

Number of paired electron = 0

Correct option is (d)

11. Which of the following has a bond order 2.5:

- (a) HCl (b) CO (c) NO (d) N_2

Soln. $\text{NO} = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^{*1} = \pi_{2py}^*$

$$\text{Bond order} = \frac{10 - 5}{2} = 2.5$$

$\text{N}_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

N_2 and CO both are isoelectronic hence same bond order.

Correct option is (c)

12. According to M.O. theory, the ground state of H_2 is σ_{1s}^2 . In addition to the ground state, there are following excited states of H_2 : [BHU 2017]



The highest and lowest energy states of H_2 will respectively be :

- (a) (2) and (1) (b) (3) and (1) (c) (1) and (2) (d) (2) and (3)

Soln. Highest and lowest energy excited states are



Highest energy state

Lowest energy state

Correct option is (b)

13. Which of the following is a paramagnetic molecule? [HCU-2013]

- (a) H_2 (b) B_2 (c) C_2 (d) N_2

Soln. $B_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^1 = \pi_{2py}^1$

Number of unpaired = 2

Hence, paramagnetic

H_2 , C_2 and N_2 has no unpaired electron hence diamagnetic.

Correct option is (b)

14. Consider four diatomic molecules M_1 , M_2 , M_3 and M_4 of same atoms with bond orders 2.5, 3, 4 and 2 respectively. Which of the following arrangements describes them with decreasing bond energy?

- (a) $\text{M}_3 > \text{M}_4 > \text{M}_1 > \text{M}_2$ (b) $\text{M}_1 > \text{M}_2 > \text{M}_3 > \text{M}_4$ [HCU-2013]
(c) $\text{M}_3 > \text{M}_2 > \text{M}_4 > \text{M}_1$ (d) $\text{M}_3 > \text{M}_2 > \text{M}_1 > \text{M}_4$

Soln. Bond order \propto bond energy

Hence, order of bond energy will be $\text{M}_3 > \text{M}_2 > \text{M}_1 > \text{M}_4$

Thus, correct option is (d)

15. The bond order and bond type in the C_2 molecule are, respectively [HCU-2014]

- (a) 2; one sigma bond and one pi bond (b) 3; one sigma bond and two pi bonds
(c) 2; two pi bonds (d) 2; two sigma bonds

Soln. $C_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2$

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

as both the bonds are formed by π -bonding orbitals hence both the bonds are π -type.

Correct option is (c)

16. Identify the species with the lowest bond order among the following [HCU-2015]

- (a) C_2 (b) NO (c) Cl_2^+ (d) O_2^+

Soln. $\text{Cl}_2^+ = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*2} = \pi_{2py}^{*2}$

$$< \sigma_{2pz}^{*2} < \sigma_{3s}^2 < \sigma_{3s}^{*2} < \sigma_{3pz}^2 < \pi_{3px}^2 = \pi_{3py}^2 < \pi_{3px}^{*2} = \pi_{3py}^{*1}$$

$$\text{Bond order} = \frac{1}{2}[18 - 15] = 1.5$$

$$C_2 = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2, \text{ Bond order} = \frac{1}{2}(8-4) = 2$$

$$NO = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^{*1} = \pi_{2py}^{*2}$$

$$\text{Bond order} = \frac{1}{2}(10-5) = 2.5$$

$$O_2^+ = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^2 = \pi_{2py}^2 < \pi_{2px}^{*1} = \pi_{2py}^* < \sigma_{2pz}^*$$

$$\text{Bond order} = \frac{1}{2}(10-5) = 2.5$$

Correct option is (c)

17. The species having the shortest bond length among the following is :

[HCU 2017]

- (a) NO (b) NO⁺ (c) NO²⁺ (d) NO⁻

Soln. $NO = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^{*1} = \pi_{2py}^*$

$$\text{Bond order} = \frac{1}{2}(10-5) = 2.5$$

$$NO^+ = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2$$

$$\text{Bond order} = \frac{1}{2}(10-4) = 3$$

$$NO^- = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^2 < \pi_{2px}^{*1} = \pi_{2py}^{*1}$$

$$\text{Bond order} = \frac{1}{2}(10-6) = 2$$

$$NO^{2+} = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 = \pi_{2py}^2 < \sigma_{2pz}^1$$

$$\text{Bond order} = \frac{1}{2}(10-4) = \frac{5}{2} = 2.5$$

Correct option is (c)

18. Among the following, the most unstable molecule is

- (a) Li₂ (b) Be₂ (c) B₂ (d) C₂ [HCU-2012]

Soln. Electronic configuration of

$$Li_2(6) \rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*0} \Rightarrow \text{Bond order} = \frac{1}{2}(4-2) = 1$$

$$Be_2(8) \rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*0} \Rightarrow \text{Bond order} = \frac{1}{2}(4-4) = 0$$

$$B_2(10) \rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^1 \pi_{2p_y}^1 \Rightarrow \text{Bond order} = \frac{1}{2}(6-4) = 1$$

$$C_2(12) \rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^2 \pi_{2p_y}^2 \Rightarrow \text{Bond order} = \frac{1}{2}(10-4) = 3$$

Be₂ is most unstable because the bond order is zero.

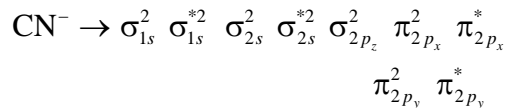
Correct answer is (b)

19. The common features among the species CN^- , CO and NO^+ are [DU-2014]
- (a) Bond order three and isoelectronic (b) Bond order three and weak field ligands
(c) Bond order two and stronger field ligands (d) Iso-electronic and weak field ligand

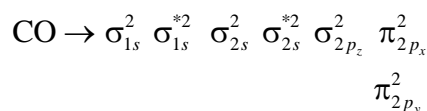
Soln. $\text{CN}^- \rightarrow 14$ electrons

$\text{CO} \rightarrow 14$ electrons

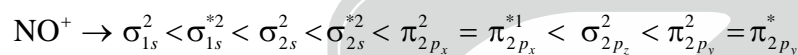
$\text{NO}^+ \rightarrow 14$ electrons, they are iso-electronic



$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = \frac{6}{2} = 3$$



$$\text{Bond order} = \frac{1}{2}(10 - 4) = 3$$



$$\text{Bond order} = \frac{1}{2}(10 - 4) = \frac{6}{2} = 3$$

Correct answer is (a)

20. The HOMO in CO is? [ISM-2015]
- (a) π -bonding (b) σ -bonding (c) π -antibonding (d) σ -antibonding

Soln. Correct answer is (d)

21. Among the following molecules, the shortest bond length is to be found in
- (a) C_2 (b) N_2 (c) O_2 (d) F_2

Soln. Bond order is reciprocal to bond length, so, the molecule with higher bond order will have shorter bond length.

$$\text{Bond order of } \text{C}_2 = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(6 - 2) = 2$$

$$\text{Bond order of } \text{N}_2 = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 2) = 3$$

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

$$\text{Bond order of } \text{F}_2 = \frac{1}{2}(8 - 6) = 1$$

N_2 has highest value of bond order, so it will have shortest bond length.

Correct answer is (b)

22. The bond order for N_2 , O_2 , N_2^- , O_2^- varies as
- (a) $\text{N}_2 > \text{N}_2^- > \text{O}_2 > \text{O}_2^-$ (b) $\text{N}_2 > \text{O}_2 > \text{N}_2^- > \text{O}_2^-$
(c) $\text{O}_2 > \text{N}_2 > \text{O}_2^- > \text{N}_2^-$ (d) $\text{N}_2^- > \text{N}_2 > \text{O}_2^- > \text{O}_2$

Soln. Bond order of $\text{N}_2 = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3$

$$\text{Bond order of } O_2 = \frac{1}{2}(10 - 6) = 2$$

$$\text{Bond order of } N_2^- = \frac{1}{2}(10 - 5) = 2.5$$

$$\text{Bond order of } O_2^- = \frac{1}{2}(10 - 7) = 1.5$$

Thus, the bond order is $N_2 > N_2^- > O_2 > O_2^-$

Correct answer is (a)

23. According to MO theory for the atomic species C_2

(a) bond order is zero and paramagnetic

(b) bond order is zero and diamagnetic

(c) bond order is two and paramagnetic

(d) bond order is two and diamagnetic

Soln. Electronic configuration of C_2 is

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

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{8 - 4}{2} = 2$$

No unpaired electrons, So, C_2 is diamagnetic

Correct answer is (d)

24. On the basis of LCAO-MO theory, the magnetic characteristics of N_2 and N_2^+ are

(a) both diamagnetic

(b) both paramagnetic

(c) N_2 diamagnetic and N_2^+ paramagnetic

(d) N_2 paramagnetic and N_2^+ diamagnetic

Soln. $N_2(14) = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 \approx \pi_{2py}^2 < \sigma_{2pz}^2$

$$N_2^+(13) = \sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^2 \approx \pi_{2py}^2 < \sigma_{2pz}^1$$

Nitrogen has no unpaired electron, so it is diamagnetic while N_2^+ has one unpaired electron, so it is paramagnetic in nature.

Correct answer is (c)

25. The highest occupied molecular orbital of HF is

(a) bonding

(b) anti-bonding

(c) ionic

(d) non-bonding

Soln. **Correct answer is (d)**

26. Which of the following have identical bond order

(a) CN^-

(b) O_2^-

(c) NO^+

(d) CN^+

Soln. CN^- and NO^+ are isoelectronic, have the same bond order of 3.

Correct answers are (a) and (c)

27. Given the species N_2 , CO , CN^- and NO^+

which of the following statements are true for these

(a) All species are paramagnetic

(b) All species are isoelectronic

(c) All the species have dipole moment

(d) All the species are linear

Soln. All the species are isoelectronic (total electron is 14)

$$N_2 \rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \sigma_{2pz}^2 \pi_{2py}^2 \quad (\text{diamagnetic})$$

All species are diamagnetic (i.e., N_2 is diamagnetic) and linear.

Correct answers are (b) and (d)