

BRUSH UP YOUR CONCEPTS

Class XI

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

CHEMICAL BONDING AND MOLECULAR STRUCTURE

MOLECULAR ORBITAL THEORY

Valence bond theory fails to explain the paramagnetic nature of O_2 and S_2 molecules, higher bond dissociation energy of CO^+ than CO molecules etc. It fails to explain the stability of odd electron species like H_2^+ , NO , etc. A new idea was put forward by Hund and Mulliken in 1932 and was further improved by Lenard and Jones and is known as Molecular Orbital Theory (MOT).

Main features of MOT

- All electrons of an atom take part in bonding.
- Atomic orbitals lose their identity.
- Two atomic orbitals produce two molecular orbitals. Linear combination gives bonding sigma molecular orbitals and antibonding sigma molecular orbitals while sideways combination gives bonding pi molecular orbitals and antibonding pi molecular orbitals by linear combination of atomic orbitals.
- Bonding molecular orbitals have lower energy than combining atomic orbitals, higher electron density between the nuclei to stabilise the bond.
- Antibonding molecular orbitals have higher energy than combining atomic orbitals, lower electron density between the nuclei to destabilise the bond.
- Sequence of increasing energies for filling of molecular orbitals by electrons are :
 - upto 15 electrons, set-I (mixing of $2s$ and $2p$ is operative), $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \pi 2p_x = \pi 2p_y, \sigma 2p_z, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$
 - For other cases, set-II (mixing of $2s$ and $2p$ is not operative), $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$
 - For CO, CO^+ and CO^- , set-III, $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \pi 2p_x = \pi 2p_y, \sigma 2p_z, \sigma^* 2s, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$ shifting

Conditions for formation of molecular orbitals

- Atomic orbitals must have comparable energies.
- Overlapping should be maximum.
- Atomic orbitals must have same axial symmetry.

Probability of finding electron in molecular orbital

- Addition overlap of atomic orbitals produces bonding molecular orbitals where probability of finding electron (ψ_{BMO}^2) is higher by $2\psi_A \psi_B$ than in atomic orbitals ($\psi_A^2 + \psi_B^2$).

$$\psi_{BMO} = \psi_A + \psi_B$$

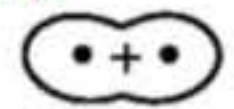
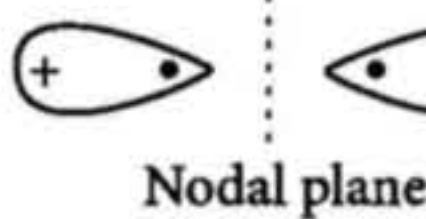
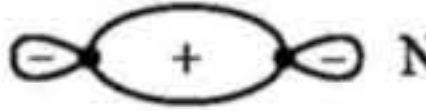
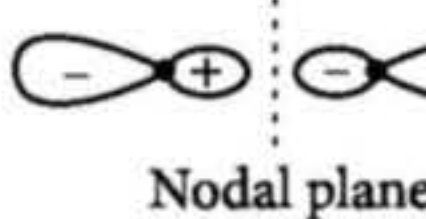
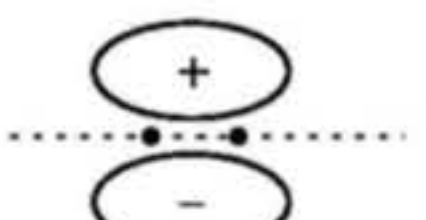
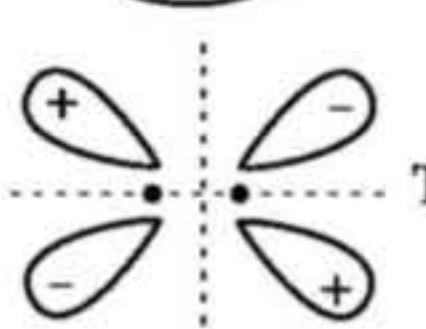
$$\psi_{BMO}^2 = (\psi_A^2 + \psi_B^2) + (2\psi_A \psi_B)$$

- Subtraction overlap of atomic orbitals produces antibonding molecular orbitals where probability of finding electron (ψ_{ABMO}^2) is lower by $2\psi_A \psi_B$ than in atomic orbitals ($\psi_A^2 + \psi_B^2$).

$$\psi_{ABMO} = \psi_A - \psi_B$$

$$\psi_{ABMO}^2 = (\psi_A^2 + \psi_B^2) - (2\psi_A \psi_B)$$

Shapes of molecular orbitals

- $\sigma 1s$ and $\sigma 2s$  No nodal plane
- $\sigma^* 1s$ and $\sigma^* 2s$  One nodal plane
- $\sigma 2p_z$  No nodal plane
- $\sigma^* 2p_z$  One nodal plane
- $\pi 2p_x$ or $\pi 2p_y$  One nodal plane
- $\pi^* 2p_x$ or $\pi^* 2p_y$  Two nodal planes

*By R.C. Grover, having 45+ years of experience in teaching chemistry.

BOND ORDER (B.O.)

It represents number of covalent bonds between bonded atoms. Mathematically, $B.O. = \frac{1}{2}[N_b - N_a]$. N_b and N_a are electrons in bonding and antibonding molecular orbitals respectively.

For bond formation, $B.O. > 0$

$B.O. = 1/2$, unstable but exists.

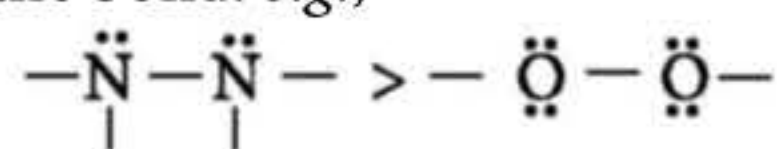
$B.O.$ of 1, 2, or 3 means single, double or triple bond respectively.

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

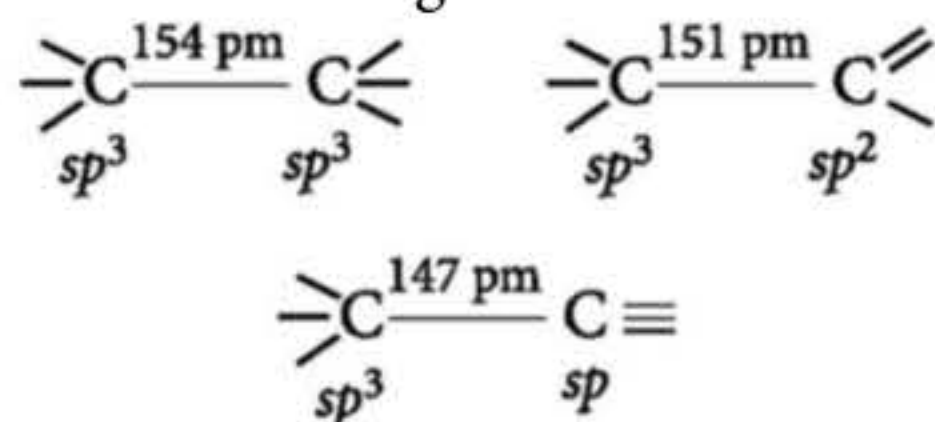
$$\text{Bond strength} \propto \text{bond order}$$

Unpaired electron(s) means species is paramagnetic.

- If two diatomic species have equal number of electrons, they have equal bond orders with exception of CO^+ . e.g., N_2 and CO have 14 electrons and bond order = 3. N_2^+ , $13e^-$, has bond order = 2.5 while CO^+ , Be^- has bond order = 3.5.
- Two species may have same bond order even when they do not have equal number of electrons. e.g., H_2 ($2e^-$) and F_2 ($18e^-$) have same bond order of one.
- More the number of lone pairs on the bonded atom, weaker is the bond. e.g.,



- Higher the percentage of s -character in hybridisation, smaller is the bond length.



MULTIPLE CHOICE QUESTIONS

- Which of the following is correct according to valence bond theory?
(a) H_2^+ can exist.
(b) Bond dissociation energy of CO^+ is higher than that of CO molecule.
(c) O_2 molecule is paramagnetic.
(d) None of these.
- Molecular orbital theory was initially given by
(a) Mulliken (b) Lenard
(c) Pauling (d) Lewis and Kossel.
- Which of the following is not correct according to MOT?
(a) Electrons of valence shell of an atom form major bonds than other electrons.

- (b) During the formation of molecular orbitals, atomic orbitals lose their identity.
(c) Two atomic orbitals combine to form two molecular orbitals.
(d) Bonding molecular orbitals have lower energy than antibonding molecular orbitals.

4. Select the correct statement of the following for Aufbau principle for MOT :

- (a) For 1 to 15 electrons the position of $\sigma 2p_z$ is, $\pi 2p_x = \pi 2p_y$, $\pi^* 2p_x = \pi^* 2p_y$, $\sigma 2p_z$, $\sigma^* 2p_z$
(b) For O_2 , N_2 and F_2 the correct position of $\sigma 2p_z$ is, $\pi 2p_x = \pi 2p_y$, $\sigma 2p_z$, $\pi^* 2p_x = \pi^* 2p_y$, ...
(c) For CO related cases $\sigma^* 2s$ is correctly placed as, $\pi 2p_x = \pi 2p_y$, $\sigma 2p_z$, $\sigma^* 2s$, ...
(d) All of these are correct.

5. The electron probability between nuclei of two bonded atoms is higher than the sum of probabilities for individual atoms by

- (a) $\psi_A \psi_B$ (b) $\frac{\psi_A}{\psi_B}$
(c) $2\psi_A \psi_B$ (d) $\psi_A^2 - \psi_B^2$

6. Which of the following molecular orbital has only one nodal plane?

- (a) $\sigma 2s$ (b) $\sigma 2p_z$ (c) $\pi 2p_y$ (d) $\pi^* 2p_x$

7. Which of the following has two nodal planes?

- (a) $\sigma 1s$ (b) $\sigma^* 2p_z$ (c) $\pi 2p_x$ (d) $\pi^* 2p_y$

8. Which of the following molecular orbital has three lobes?

- (a) $\sigma 2s$ (b) $\sigma 2p_z$ (c) $\pi 2p_x$ (d) $\pi^* 2p_y$

9. Mathematically, bond order is equal to

- (a) $2[N_b - N_a]$ (b) $\frac{1}{2}[N_b - N_a]$
(c) $\frac{2N_b}{N_a}$ (d) $\frac{1}{2}[N_b^2 - N_a^2]$

10. Which of the following is correct for bond order (B.O.)?

- (a) For the formation of bond, B.O. must be a whole number.
(b) Fractional bond order means that the species does not exist.
(c) For $B.O. = \frac{A, B, C}{1 \ 2 \ 3}$, the decreasing order of bond length is $A > B > C$.
(d) For $B.O. = \frac{A, B, C}{1 \ 2 \ 3}$ the decreasing order of bond strength is $A > B > C$.